β-Phosphinoethylboranes as Ambiphilic Ligands in Nickel−Methyl Complexes

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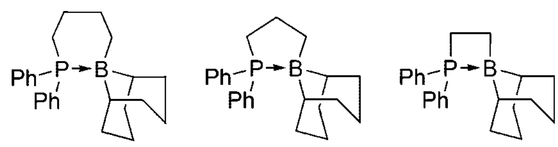
The ambiphilic *β*-phosphinoethylboranes $Ph_2PCH_2CH_2BR_2$ ($BR_2 = BCy_2$ (**1a**), BBN (**1b**)), which feature the ethano spacer CH_2CH_2 between the Lewis acidic boryl and Lewis basic phosphino groups, were synthesized in nearly quantitative yields via the hydroboration of vinyldiphenylphosphine. Compounds **1a**,**b** were fully characterized by elemental analysis and by NMR and IR spectroscopy. X-ray crystallographic studies of compound **1b** revealed infinite helical chains of the molecules connected through P···B donor–acceptor interactions. The ability of these ambiphilic ligands to concurrently act as donors and acceptors was highlighted by their reactions with (dmpe)$NiMe_2$. The zwitterionic complexes (dmpe)NiMe($Ph_2PCH_2CH_2BCy_2Me$) (**2a**) and (dmpe)NiMe($Ph_2PCH_2CH_2$[BBN]Me) (**2b**) were generated via the abstraction of one of the methyl groups, forming a borate, and intramolecular coordination of the phosphine moiety to the resulting cationic metal center. Compound **2b** was characterized by X-ray crystallography. Furthermore, $B(C_6F_5)_3$ abstracts the methyl group of a coordinated borate ligand to generate a free, three-coordinate borane center in $[(dmpe)NiMe(\mathbf{1a})]^+[MeB(C_6F_5)_3]^-$ (**3**).

Introduction

The elucidation of the mechanisms by which many enzymes operate has revealed nature's use of multifunctional catalysis as a strategy for the optimization of chemical conversions.[1] The exploitation of the synergistic interaction of two or more reactive centers can lead to cooperative catalytic effects on a variety of chemical processes. In homogeneous catalysis, use of ambiphilic ligands of the type LA−spacer−LB, with both Lewis acidic (LA) and Lewis basic (LB) functionalities, offers the interesting possibility of activating both the metal center and the substrate molecule in a cooperative fashion. For example, the use of such ambiphilic ligands was reported by Labinger and Miller in 1982 to facilitate the formation of CO insertion products.[2,3] Although relatively scarce, there have been subsequent reports on the use of ambiphilic ligands in catalysis. The bifunctional ligand $Me_2PCH_2AlMe_2$, first synthesized by Karsch et al.,[4]was employed as a cocatalyst in the nickel(II)-catalyzed dehydrogenative oligomerization of $PhSiH_3$,[5a] and has recently been studied as a ligand in rhodium complexes.[5b] Phosphino/boryl compounds, featuring a variety of different spacer groups, have also been reported as bifunctional ligands in transition-metal chemistry.[6–8]

Ambiphilic ligands can interact with metal complexes in a variety of ways. After coordination of the phosphino group to the metal center, the Lewis acidic group can interact with an anionic ligand in the metal's coordination sphere, abstract an anionic ligand from the metal, or interact directly with the metal center. Indeed, a number of such interactions have been observed,[6–10] and this supports the notion that ambiphilic ligands can have a profound effect on the chemistry at the metal center. We now report an efficient synthetic method for the preparation of *β*-phosphinoethylboranes and their use as ambiphilic ligands that interact with both the metal center and a second ligand (a methyl group) in the metal's coordination sphere.

Chart 1



A B C

Results and Discussion

In 1997 Schmidbaur and co-workers reported the synthesis and structural characterization of *cyclo*-[(9-borabicyclo[3.3.1]-nonanyl)**butano**(diphenyl)phosphine], $Ph_2P(CH_2)_4BC_8H_{14}$, and *cyclo*-[(9-borabicyclo[3.3.1]nonanyl)**propano**(diphenyl)phosphine], $Ph_2P(CH_2)_3BC_8H_{14}$, (**A** and **B**, respectively; Chart 1).[11,12] The possibility that these phosphino/boryl compounds possess

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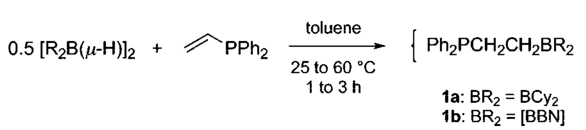
relatively strong P−B interactions might be expected to greatly reduce their ability to interact with organometallic species. Therefore, the synthesis of related compounds possessing shorter spacer groups was undertaken. Although compounds **A** and **B** were both prepared by the rapid and quantitative hydroboration of allyldiphenylphosphine ($Ph_2PCH_2CH{=}CH_2$) and butenyldiphenylphosphine ($Ph_2PCH_2CH_2CH{=}CH_2$) with 9-borabicyclononane (9-BBN), attempts to prepare the ethano-bridged *cyclo*-[(9-borabicyclo[3.3.1]nonanyl)**ethano**(diphenyl)phosphine] derivative $Ph_2P(CH_2)_2BC_8H_{14}$ (**C**; Chart 1) by reaction of 9-BBN with diphenylvinylphosphine ($Ph_2PCH{=}CH_2$) did not produce the desired product. Instead, the reaction gave mixtures of products thought to contain P−B-bonded compounds generated through a boraphosphetane intermediate (with loss of ethylene).[11]

A simple modification of the published hydroboration conditions,[11] involving aromatic solvents instead of THF, allowed the preparation of β-phosphinoethylboranes with an ethano spacer group separating the Lewis acidic boryl and the Lewis basic phosphino groups. Two equivalents of diphenylvinylphosphine was allowed to react with freshly recrystallized, dimeric dicyclohexylborane $[Cy_2B(\mu\text{-}H)]_2$ and 9-BBN, respectively, to produce compounds **1a**,**b** (eq 1). The [(dicyclohexyl)boryl]ethyl(diphenyl)phosphine (**1a**) formed in a fast and quantitative reaction (isolated yield 89%) within less than 1 h at ambient temperature. However, slightly elevated temperatures were required for synthesis of (9-borabicyclo[3.3.1]nonanyl)ethyl-(diphenyl)phosphine (**1b**) (isolated yield 56%). Both reactions proceed in a nearly quantitative fashion on the basis of NMR-scale reactions; however, the high solubility of the compounds led to lower isolated yields. Phosphine−borane adducts, which are possible intermediates in the reaction, were not observed in reactions using the highly reactive $[Cy_2B(\mu\text{-}H)]_2$. However, when using 9-BBN, a broad signal in the $^{31}P\{^1H\}$ NMR spectrum at 5.4 ppm, observable in an NMR-scale reaction at ambient temperature after 15 min, most likely corresponds to the intermediate $[Ph_2(H_2C{=}CH)P](BBN)$. The formation of this adduct is consistent with the elevated temperatures required for the reaction to proceed. Note that the related compound $Mes_2PCH_2CH_2B(C_6F_5)_2$ (Mes = 2,4,6-$Me_3C_6H_2$) was recently reported.[13]



(1)

Compounds **1a**,**b** were isolated and purified as white solids via crystallization from saturated hexane (**1a**) or toluene solutions (**1b**) at –30 °C. They were fully characterized by means of elemental analysis and NMR[14] and IR spectroscopy. Singlets in the $^{31}P\{^1H\}$ NMR spectra at –8.5 (**1a**) and –11.5 ppm (**1b**) and broad signals in the borane region of the $^{11}B\{^1H\}$ NMR spectra at 83.0 (**1a**) and 86.4 ppm (**1b**) are indicative of three-coordinate phosphorus and boron centers with no P−B donor–acceptor interactions in solution. However, low-temperature NMR experiments, performed in toluene-d_8 at –80 °C, resulted in a distinct broadening of both signals, suggesting the possibility of some interaction between the phosphorus and boron centers. Recrystallization of compound **1b** from a toluene/THF mixture (4:1) at –30 °C yielded colorless single crystals suitable for an X-ray crystallographic study. Compound **1b** crystallizes in the tetragonal space group $I4_1/a$. Table 1 gives crystal data and data collection parameters for **1b**. The molecular structure of **1b** does indeed reveal the presence of P−B interactions in the solid state. However, unlike the C_3- and C_4-bridged phosphinoboranes **A** and **B**, which possess cyclic structures, compound **1b** forms a polymeric framework of infinite helical chains of **1b** connected through P···B donor–acceptor interactions. The asymmetric unit is illustrated in Figure 1, and a short section of one of the helices is shown in Figure 2.

Much of the metrical data for compound **1b** is in agreement with that of the corresponding C_3- (**B**) and C_4-bridged cyclic derivatives (**A**).[11] The P–C1 and C2–B distances of 1.834(2) and 1.640(3) Å, respectively, show only minor differences compared to values for the previously reported analogues (**A**, 1.824(1), 1.643(2) Å; **B**, 1.828(2), 1.628(4) Å)[11] or structurally related phosphine−borane adducts (e.g., $[BH_2–CH_2–PPh_2]_2$, 1.800(2), 1.645(3) Å[15]). The P–B bond length of 2.056(2) Å lies between the corresponding values for **B** (2.029(2) Å) and **A** (2.072(3) Å).[11] The helical arrangement of the infinite

Table 1. Crystal Data and Data Collection Parameters of Compounds 1b and 2a

	1b	2a
chem formula	$C_{22}H_{28}BP$	$C_{34}H_{58}BNiP_3$
fw	334.22	629.23
color/shape	colorless/fragment	yellow/fragment
cryst size (mm)	0.5 × 0.5 × 0.3	0.16 × 0.13 × 0.09
cryst syst	tetragonal	triclinic
space group	$I4_1/a$	$P\bar{1}$
a (Å)	21.039(2)	10.400(2)
b (Å)	21.039(2)	11.840(2)
c (Å)	17.050(2)	15.520(3)
α (deg)	90	76.509(3)
β (deg)	90	88.116(3)
γ (deg)	90	68.598(3)
V (Å^3)	7547.0(13)	1727.3 (5)
Z	16	2
T (K)	108	133
ρ_{calcd} (g cm^{-3})	1.177	1.210
μ (mm^{-1})	0.146	0.722
F_{000}	2880	680
θ range (deg)	1.54–23.26	3.26–24.77
data collected	$-18 \le h \le 23$, $-23 \le k \le 23$, $-18 \le l \le 16$	$-9 \le h \le 12$, $-10 \le k \le 13$, $-17 \le l \le 18$
no. of rflns collected	16867	8973
no. of indep rflns/R_{int}	2701 (all)/0.0357	5700 (all)/0.0722
no. of params refined	217	352
R1 (obsd/all)	0.0339/0.0422	0.0386/0.0859
wR2 (obsd/all)	0.0788/0.0834	0.1571/0.1716
GOF	1.037	1.018
max/min $\Delta\rho$ (e Å^{-3})	+0.277/−0.201	+0.94/−0.89

(12) A variety of phosphinoboranes without a spacer group between the boron and phosphorus ($R_2P{-}BR'_2$), and corresponding transition-metal complexes, have previously been reported. For example, see: (a) Paine, R. T.; Nöth, H. *Chem. Rev.* **1995**, *95*, 343 and references therein. (b) Dorn, H.; Singh, R. A.; Massey, J. A.; Nelson, J. M.; Jaska, C. A.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 6669. (c) Jaska, C. A.; Dorn, H.; Lough, A. J.; Manners, I. *Chem. Eur. J.* **2003**, *9*, 271. (d) Dorn, H.; Rodezno, J. M.;Brunnhöfer, B.; Rivard, E.; Massey, J. A.; Manners, I. Macromolecules 2003, *36*, 291. In addition, Stephan and co-workers have reported interesting properties for free phosphinoboranes with rigid spacer groups: (e) Welch, G. C.; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P. R.; Stephan, D. W. *Dalton Trans.* **2007**, 3407. (f) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 5802.

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(14) HMQC-NMR techniques were necessary to assign all of the proton and carbon signals.

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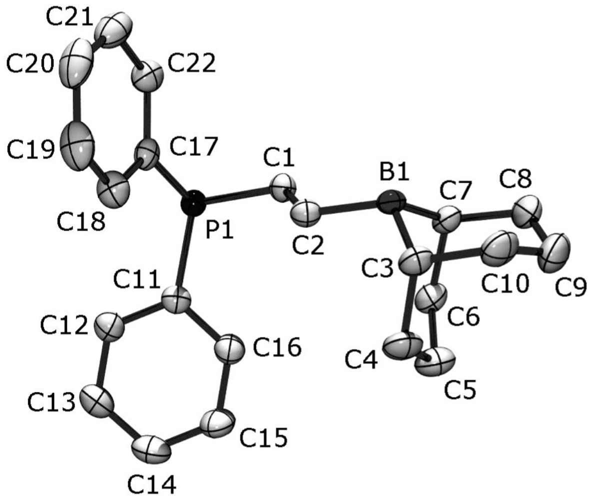


Figure 1. Molecular structure of compound **1b** with atomic numbering (ORTEP; 50% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): P1···B1′, 2.056(2); P1–C1, 1.834(2); C1–C2, 1.530(2); C2–B1, 1.640(3); P1–C11, 1.827(2); P1–C17, 1.836(2); B1–C3, 1.634(3); B1–C7, 1.630(3); C1–P1–B1′, 120.0(1); C1–P1–C11, 106.7(1); C1–P1–C17, 99.5(1); C11–P1–C17, 106.1(1); P1–C1–C2, 116.5(1); C1–C2–B1, 118.5(2); C2–B1–P1′, 103.6(2); C2–B1–C3, 110.2(2); C2–B1–C7, 117.0(2); C3–B1–C7, 105.0(2).

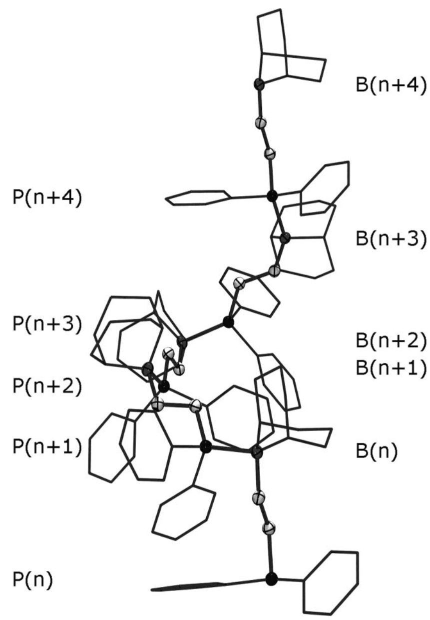
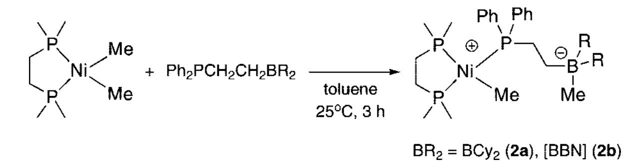


Figure 2. Molecular structure of compound **1b**: short section of one of the P···B connected helices.

phosphine–borane adduct chain results in a quasi-C_4 symmetry for the $\{PC_2B\}_x$ core, with a $P_n \cdots P_{n+4}$ distance of 1.7 nm.

To probe the ambiphilic character of the β-phosphinoethylboranes **1**, reactions of these compounds with an organometallic complex were investigated. The nickel dimethyl compound (dmpe)$NiMe_2$ (dmpe = bis(dimethylphosphino)ethane) was treated with both **1a** and **1b** in equimolar quantities at ambient temperature. This led to formation of the zwitterionic nickel–methyl complexes **2a**,**b**, respectively (eq 2). The ambiphilic nature of the β-phosphinoethylboranes is manifested in their behavior as phosphine donors, and as Lewis acids, in the abstraction of a methyl group from the nickel center.

The identities of complexes **2a**,**b** were established by elemental analysis and by NMR and IR spectroscopy. The

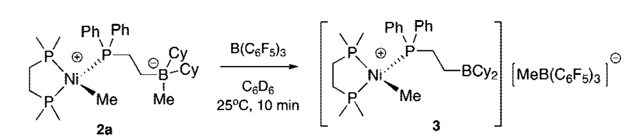


(2)

$^{31}P\{^1H\}$ NMR spectra of both compounds display three doublets of doublets due to the presence of three inequivalent phosphorus atoms coordinated to the nickel center. Another characteristic feature of both compounds is that they display signals for two distinct methyl groups in their ^1H and $^{13}C\{^1H\}$ NMR spectra.[14] Specifically, the hydrogen atoms of the abstracted methyl groups, now bound to B, appear as broad resonances at 0.10 (**2a**) and –0.42 ppm (**2b**), due to the quadrupole moment of the boron center. The ^1H NMR shifts for the remaining Ni–CH_3 groups appear as singlets at 0.23 (**2a**) and −0.05 ppm (**2b**) and are shifted upfield with respect to those for the starting complex (dmpe)$NiMe_2$ (–0.31 ppm).[16] In addition, sharp signals in the $^{11}B\{^1H\}$ spectra, at –14.9 (**2a**) and –16.3 ppm (**2b**), support the proposed alkyl abstraction and the formation of borate groups.

Further confirmation of the assignments of compounds **2a**,**b** as zwitterionic compounds was obtained from structural studies. Crystallization of complex **2a** from a toluene/THF mixture (1:2) at –30 °C gave yellow single crystals suitable for an X-ray diffraction structure determination. Table 1 gives crystal data and data collection parameters for **1b**. The solid-state structure of complex **2a** and the atom-numbering scheme are given in Figure 3. Complex **2a** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the formula unit. The nickel atom exhibits a distorted-square-planar geometry (sum of angles about Ni: 360.6°).

The ability of the β-phosphinoethylborane ligands to react further with nickel zwitterions **2a**,**b** was explored. Addition of another 1 equiv of compound **1** to **2a**,**b** did not result in a second methyl group transfer reaction or displacement of the coordinated phosphine. The signals for both the Ni–CH_3 and B–CH_3 groups remained clearly visible in the NMR spectra of the reactions. Interestingly, addition of the highly Lewis acidic compound $B(C_6F_5)_3$ to **2a** resulted in a methyl group transfer from the cyclohexylborate moiety to the $B(C_6F_5)_3$ molecule (eq 3). The newly formed complex (**3**) was identified in an NMR-scale reaction as the only product after 10 min at ambient temperature. The $^{11}B\{^1H\}$ NMR spectra contained two distinct signals at 82.1 (broad) and –14.4 ppm (sharp), which were assigned to the three-coordinate –BCy_2 group (without any type of B···Me interaction) and the four-coordinate, anionic borate counteranion $[MeB(C_6F_5)_3]^-$, respectively.



(3)

Experimental Section

General Considerations. All operations were performed with rigorous exclusion of air and water, using standard Schlenk and drybox techniques (Vacuum Atmospheres NEXUS; <1 ppm O_2, <1 ppm H_2O). Dry, oxygen-free solvents were employed through-

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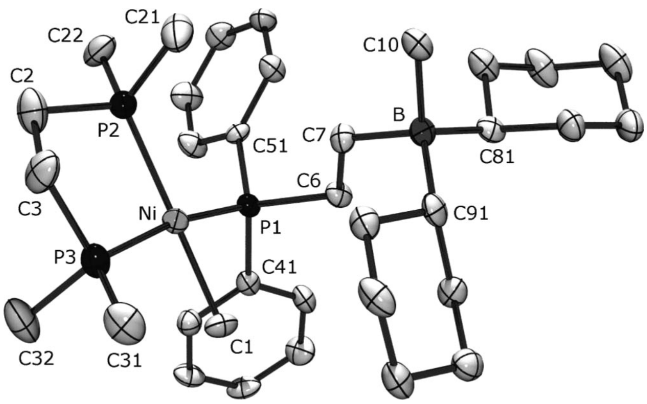

Figure 3. Molecular structure of **2a** with atomic numbering (ORTEP; 50% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni–P1, 2.195(2); Ni–P2, 2.199(1); Ni–P3, 2.17(2); Ni–C1, 1.970(4); P1–C6, 1.827(5); C6–C7, 1.550(6); C7–B, 1.662(7); B–C10, 1.659(7); B–C81, 1.662(7); B–C91, 1.684(7); P1–Ni–P2, 102.32(5); P2–Ni–P3, 86.72(5); P3–Ni–C1, 85.8(2); C1–Ni–P1, 85.7(2); Ni–P1–C6, 107.2(2); P1–C6–C7, 110.8(3); C6–C7–B, 118.9(4); C7–B–C10, 105.2(4).

out. Removal of thiophenes from benzene and toluene was accomplished by washing each with H_2SO_4 and saturated $NaHCO_3$ followed by drying over $MgSO_4$. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, saturated $NaHCO_3$, and then the drying agent $MgSO_4$. All solvents were distilled from sodium benzophenone ketyl and stored under nitrogen. Benzene-d_6 (Cambridge Isotope Laboratories Inc.) was purified by vacuum distillation from Na/K alloy. Dichloromethane-d_2 (Cambridge Isotope Laboratories Inc.) was purified by vacuum distillation from CaH_2. All other chemicals were obtained from Aldrich and used without further purification.

All NMR spectra were recorded at room temperature in benzene-d_6 or dichloromethane-d_2 unless otherwise noted, using a Bruker AM-400 spectrometer (FT, 400.1 MHz ^1H; 128.4 MHz ^{11}B; 100.6 MHz ^{13}C; 162.0 MHz ^{31}P), a Bruker AMX-400 spectrometer (FT, 400.1 MHz ^1H; 376.5 MHz ^{19}F) or a Bruker DRX-500 spectrometer (FT, 500.1 MHz ^1H, 160.5 MHz ^{11}B; 125.8 MHz ^{13}C; 202.5 MHz ^{31}P). Spectra were referenced to the residual nondeuterated solvent for ^1H and ^{13}C or to external standard samples ($BF_3 \cdot OEt_2$ for ^{11}B, 85% H_3PO_4 for ^{31}P, C_6F_6 for ^{19}F). Infrared spectra were recorded as Nujol mulls using a Mattson FT-IR spectrometer at a resolution of 4 cm^{-1}. Elemental analyses (CHN) were performed by the microanalytical laboratory at the University of California, Berkeley.

$Ph_2PCH_2CH_2BCy_2$ (1a). At ambient temperature a solution of 2.506 g of vinyldiphenylphosphine (11.81 mmol) in 5 mL of toluene was added to a suspension of 2.103 g of dicyclohexylborane (11.81 mmol) in 10 mL of toluene with stirring. A colorless solution formed within 1 min. After the mixture was stirred for 2 h at ambient temperature, the solvent was removed in vacuo. The sticky crude product was redissolved in 15 mL of hexanes and crystallized during ca. 14 h at –30 °C to give **1a** as a colorless solid (3.922 g, 10.05 mmol, 85%). A second crop of crystals (195 mg, 0.50 mmol, 4.2%) was obtained from the concentrated mother liquid. IR (Nujol, KBr): 1946 w, 1880 w, 1806 w, 1587 w, 1304 s, 1262 m, 1227 m, 1142 m, 1094 m, 1027 m, 976 m, 957 m, 890 w, 841 w, 737 s, 696 s, 505 w cm^{-1}. ^1H NMR (benzene-d_6): δ 7.52 (t, $^3J_{HH}$ = 7.6 Hz, 4 H, *o*-Ph), 7.13–7.03 (m, 6 H, *m*-/*p*-Ph), 2.12 (m, 2 H, PCH_2), 1.70 (m, 6 H, β-/δ-Cy), 1.50 (m, 4 H, γ-Cy), 1.45–1.36 (m, 4 H, α-Cy, PCH_2CH_2B), 1.33–1.15 (m, 6 H, β-/δ-Cy), 1.07 (m, 4 H, γ-Cy). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 140.0 (d, $^1J_{CP}$ = 16.1 Hz, *ipso*-Ph), 133.3 (d, $^2J_{CP}$ = 18.1 Hz, *o*-Ph), 128.7 (d, $^3J_{CP}$ = 6.2 Hz, *m*-Ph), 128.7 (*p*-Ph), 36.1 (vbr, α-Cy), 27.8 (β-Cy), 27.4 (γ-Cy), 27.3 (δ-Cy), 22.1 (d, $^1J_{CP}$ = 14.1 Hz, PCH_2), 20.1 (vbr, Cy_2BCH_2). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 83.0 ppm. $^{31}P\{^1H\}$ NMR (benzene-d_6): δ –8.5 ppm. Anal. Calcd for $C_{26}H_{36}BP$ (mol wt 390.35): C, 80.00; H, 9.30. Found: C, 80.29; H, 8.91.

$Ph_2PCH_2CH_2$[BBN] (1b). By the procedure presented above, vinyldiphenylphosphine (1.139 g, 5.37 mmol) and recrystallized 9-BBN (655 mg, 5.37 mmol) were combined with stirring. The mixture was heated to 60 °C and kept for 3 h at this temperature. Then, the solvent was removed in vacuo. The crude product was washed with hexanes (3 × 5 mL) and dried under vacuum to give **1b** as a white powder in 55.5% yield (996 mg, 2.98 mmol). IR (Nujol, KBr): 1961 w, 1901 w, 1821 w, 1774 w, 1586 w, 1482 s, 1434 s, 1306 w, 1264 m, 1200 w, 1188 m, 1106 s, 1071 m, 1028 m, 999 w, 949 w, 896 m, 837 w, 771 w, 747 s, 699 s, 634 w, 562 w, 523 m, 502 m cm^{-1}. ^1H NMR (benzene-d_6): δ 7.50 (m, 4 H, *o*-Ph), 7.10 (4 H, *m*-Ph), 7.05 (m, 2 H, *p*-Ph), 2.24 (m, 2 H, PCH_2), 1.84–1.77 (m, 6 H, β-/γ-BBN), 1.70 (m, 2 H, α-BBN), 1.69–1.62 (m, 4 H, β-BBN), 1.55 (m, 2H, CH_2B), 1.18 ppm (m, 2 H, γ-BBN). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 139.9 (d, $^1J_{CP}$ = 15.1 Hz, *ipso*-Ph), 133.2 (d, $^2J_{CP}$ = 17.6 Hz, *o*-Ph), 128.7 (d, $^3J_{CP}$ = 6.3 Hz, *m*-Ph), 128.6 (*p*-Ph), 33.5 (β-BBN), 31.4 (vbr, α-BBN), 23.6 (γ-BBN), 23.5 (vbr, CH_2B), 22.9 ppm (d, $^1J_{CP}$ = 11.3 Hz, PCH_2). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 86.4 ppm. $^{31}P\{^1H\}$ NMR (benzene-d_6): δ –11.5 ppm. Anal. Calcd. for $C_{22}H_{28}BP$ (mol wt 334.24): C, 79.06; H, 8.44. Found: C, 79.28; H, 8.56.

(dmpe)NiMe($Ph_2PCH_2CH_2BCy_2Me$) (2a). In a drybox, (dmpe)NiMe$_2$[16] (126.2 mg, 0.53 mmol) was dissolved in 8 mL of a toluene/THF mixture (1:1). A solution of 206.2 mg of $Ph_2PCH_2CH_2BCy_2$ (0.53 mmol) in 4 mL of toluene was slowly added with stirring at ambient temperature. The mixture was stirred at ambient temperature for 3 h. Then, the solvents were removed in vacuo, and the residue was washed with toluene (1 × 3 mL) and hexanes (3 × 3 mL) and dried under vacuum to give 264.7 mg (0.42 mmol, 79%) of analytically pure **5a** as a light yellow powder. Crystallization from toluene/THF mixtures (1:2) at –30 °C gave single crystals suitable for an X-ray structure determination. IR (Nujol, KBr): 1586 w, 1463 s, 1328 w, 1301 m, 1285 m, 1260 m, 1240 s, 1227 m, 1197 m, 1175 m, 1161 m, 1147 w, 1118 m, 1100 s, 1070 m, 1022 m, 987 m, 876 m, 852 w, 829 m, 797 m, 737 s, 698 s, 655 m, 522 m, 512 m cm^{-1}. ^1H NMR (400.1 MHz, dichloromethane-d_2): δ 7.59 (m, 4 H, *o*-Ph), 7.36 (m, 6 H, *m*-Ph, *p*-Ph), 2.43 (m, 2 H, PCH_2CH_2B), 1.75–1.40 (br m, 18 H, Cy^{β}, Cy^{γ}, Cy^{δ}, PCH_2CH_2B, PMe_2), 1.25–0.80 (br m, 18 H, Cy^{α}, Cy^{β}, Cy^{γ}, Cy^{δ}, PMe_2), 0.60 (br, 2 H, PCH_2CH_2P), 0.11 (br, 2 H, PCH_2CH_2P), –0.07 (s, 3 H, NiMe), –0.75 ppm (br s, 3 H, BMe). ^1H NMR (400.1 MHz, benzene-d_6): δ 7.58 (m, 4 H, *o*-Ph), 7.01 (m, 4 H, *m*-Ph), 6.95 (m, 2 H, *p*-Ph), 2.90 (m, 2 H, PCH_2CH_2B), 2.50–2.15 (m, 10 H, Cy^{β}, Cy^{γ}, Cy^{δ}), 1.90–1.65 (m, 10 H, Cy^{β}, Cy^{γ}, Cy^{δ}), 1.08 (m, 2 H, PCH_2CH_2B), 0.99 (m, 2 H, Cy^{α}), 0.91 (m, 10 H, PCH_2CH_2P, PMe_2), 0.56 (m, 6 H, PMe_2), 0.23 (s, 3 H, NiMe), 0.10 (br s, 3 H, BMe). $^{13}C\{^1H\}$ NMR (100.6 MHz, dichloromethane-d_2): δ 137.0 (br, *ipso*-Ph), 132.9 (d, $^2J_{CP}$ = 8.8 Hz, *o*-Ph), 130.1 (*p*-Ph), 128.9 (d, $^3J_{CP}$ = 5.9 Hz, *m*-Ph), 36.8 (m, PCH_2CH_2P), 32.8 (Cy^{β}), 32.7 (Cy^{β}), 31.3 (Cy^{γ}), 29.6 (Cy^{δ}), 26.6 (m, PCH_2CH_2P), 24.7 (d, $^1J_{CP}$ = 19.0 Hz, PCH_2CH_2B), 12.2 (d, $^1J_{CP}$ = 23.4 Hz, PMe_2), 12.1 (d, $^1J_{CP}$ = 29.2 Hz, PMe_2), 5.9 (br m, BMe), 0.2 ppm (br m, NiMe). $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 137.1 (br, *ipso*-Ph), 132.6 (*o*-Ph), 129.5 (*p*-Ph), 128.6 (*m*-Ph), 37.1 (vbr, Cy^{α}), 33.3 (Cy^{β}), 33.2 (Cy^{β}), 31.7 (Cy^{γ}), 30.0 (Cy^{δ}), 27.8 (br, PCH_2CH_2P), 26.3 (vbr, PCH_2CH_2B), 25.7 (vbr, PCH_2CH_2P), 25.3 (br, 27.8 (br, PCH_2CH_2B), 11.5 (d, $^1J_{CP}$ = 23.1 Hz, PCH_3), 11.1 (d, $^1J_{CP}$ = 42.3 Hz, PCH_3), 8.6 (vbr, NiMe), 1.1 ppm (vbr, BCH_3). $^{11}B\{^1H\}$ NMR (128.4 MHz, dichloromethane-d_2): δ –15.7 ppm. $^{11}B\{^1H\}$ NMR (128.4 MHz, benzene-d_6): δ –14.9 ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz, dichloromethane-d_6): δ 40.0 (br, *trans*-P^{dmpe}), 30.8 (br), 28.8 ppm (*cis*-P^{dmpe}). $^{31}P\{^1H\}$ NMR (162.0 MHz, benzene-d_6): δ 38.7 (dd, $^2J_{PP}$ = 255.6 Hz, $^2J_{PP}$ = 15.9 Hz, *trans*-P^{dmpe}), 31.6 (br d, $^2J_{PP}$ = 255.6 Hz, PPh_2), 27.9 ppm (dd, $^2J_{PP}$ = 33.7 Hz, $^2J_{PP}$ =

15.9 Hz, *cis*-P^{dmpe}). Anal. Calcd for $C_{34}H_{58}BNiP_3$ (mol wt 629.25): C, 64.90; H, 9.29. Found: C, 64.94; H, 9.52.

(dmpe)NiMe($Ph_2PCH_2CH_2$[BBN]Me) (2b). In a drybox, (dmpe)NiMe$_2$ (130.8 mg, 0.55 mmol) was dissolved in 15 mL of a toluene/THF mixture (3:1) and the resulting solution was stirred at ambient temperature. Solid $Ph_2PCH_2CH_2BBN$ (183.0 mg, 0.55 mmol) was slowly added, and the brownish mixture was stirred for 3 h. The yellow precipitate was separated, washed with toluene (1 × 3 mL) and hexanes (4 × 3 mL), and dried under vacuum to give 129.6 mg (0.23 mmol, 41%) of analytically pure **5b** as a yellow powder. IR (Nujol, KBr): 1428 m, 1280 w, 1259 m, 1176 w, 1144 w, 1101 w, 1060 w, 1010 w, 941 s, 901 m, 841 w, 817 w, 796 w, 741 m, 655 w, 521 m, 487 m cm^{-1}. ^{1}H NMR (400.1 MHz, dichloromethane-d_2): δ 7.60 (m, 4 H, *o*-Ph), 7.36 (m, 6 H, *m*-Ph, *p*-Ph), 2.4 (m, 2 H, PCH_2CH$_2$B), 2.07–1.85 (br m, 4 H, BBN$^\beta$), 1.85–1.60 (br m, 6 H, BBN$^\gamma$, BBN$^\alpha$, PCH$_2$CH_2B), 1.52 (d, $^2J_{HP}$ = 9.2 Hz, 6 H, PMe$_2$), 1.47 (m, 6 H, BBN$^\beta$, BBN$^\gamma$), 0.93 (d, $^2J_{HP}$ = 8.0 Hz, 6 H, PMe$_2$), 0.77 (br, 2 H, PCH_2CH$_2$P), 0.17 (br, 2 H, PCH$_2$CH_2P), –0.05 (br d, 3 H, NiMe), –0.42 ppm (br, 3 H, *Me*BBN). ^{13}C{^{1}H} NMR (100.6 MHz, dichloromethane-d_2): δ 137.1 (d, $^1J_{CP}$ = 34.2 Hz, *ipso*-Ph), 132.9 (d, $^2J_{CP}$ = 9.1 Hz, *o*-Ph), 130.1 (*p*-Ph), 128.9 (d, $^3J_{CP}$ = 8.0 Hz, *m*-Ph), 34.0 (BBN$^\beta$), 33.8 (BBN$^\beta$), 29.5 (m, PCH$_2$*C*H$_2$P), 28.8 (br m, PCH$_2$*C*H$_2$B), 28.0 (m, P*C*H$_2$CH$_2$P), 27.8 (BBN$^\gamma$), 27.4 (BBN$^\gamma$), 26.7 (vbr, BBN$^\alpha$), 23.2 (d, $^1J_{CP}$ = 18.1 Hz, P*C*H$_2$CH$_2$B), 12.3 (d, $^1J_{CP}$ = 21.1 Hz, PMe$_2$), 11.9 (d, $^1J_{CP}$ = 28.2 Hz, PMe$_2$), 9.8 (br m, *Me*BBN), 1.0 ppm (br m, NiMe). ^{11}B{^{1}H} NMR (128.4 MHz, dichloromethane-d_2): δ –17.3 ppm. ^{11}B{^{1}H} NMR (128.4 MHz, benzene-d_6): δ –16.3 ppm. ^{31}P{^{1}H} NMR (162.0 MHz, dichloromethane-d_2): δ 40.4 (br d, $^2J_{PP}$ = 244 Hz, *trans*-P^{dmpe}), 30.3 (br d, $^2J_{PP}$ = 244 Hz, PPh$_2$), 28.8 ppm (br, *cis*-P^{dmpe}). ^{31}P{^{1}H} NMR (162.0 MHz, benzene-d_6): δ 38.5 (dd, $^2J_{PP}$ = 256 Hz, $^2J_{PP}$ = 16.2 Hz, *trans*-P^{dmpe}), 31.3 (br d, $^2J_{PP}$ = 256 Hz, PPh$_2$), 27.8 ppm (dd, $^2J_{PP}$ = 34.0 Hz, $^2J_{PP}$ = 16.2 Hz, *cis*-P^{dmpe}). Anal. Calcd for $C_{30}H_{50}BNiP_3$ (mol wt 573.14): C, 62.87; H, 8.79. Found: C, 63.02; H, 8.90.

NMR-Scale Reaction of (dmpe)NiMe($Ph_2PCH_2CH_2BCy_2Me$) with B(C_6F_5)$_3$ (3). In a drybox, a solution of 12.6 mg of **5a** (20 μmol) in 0.5 mL of benzene-d_6 was added to 10.2 mg of B(C_6F_5)$_3$ (20 μmol). A few drops of THF were added to completely dissolve the brownish mixture, which was then transferred into a 5 mm Wilmad NMR tube equipped with a J. Young Teflon valve seal. Proton, boron, fluorine, and phosphorus NMR spectroscopy confirmed the clean formation of one new product. ^{1}H NMR (benzene-d_6): δ 7.31 (m, 4 H, *o*-Ph), 7.10 (m, 6 H, *m*-Ph, *p*-Ph), 2.28 (m, 2 H, PCH_2CH$_2$B), 1.74 (m, 4 H, Cy), 1.50–0.90 (br m, 10 H, Cy, PCH$_2$CH_2B, PCH_2CH_2P), 0.83 (d, $^2J_{HP}$ = 9.6 Hz, 6 H, PMe$_2$), 0.34 (d, $^2J_{HP}$ = 8.4 Hz, 6 H, PMe$_2$), –0.04 (m, 3 H, NiMe). ^{11}B{^{1}H} NMR (benzene-d_6): δ 82.1 (vbr, BCy$_2$), –14.4 ppm (MeB(C_6F_5)$_3$). ^{19}F{^{1}H} NMR (376.5 MHz, benzene-d_6): δ –130.8 (d), –163.4 (t), –165.8 ppm (t). ^{31}P{^{1}H} NMR (benzene-d_6): δ 41.0 (dd, $^2J_{PP}$ = 257.5 Hz, $^2J_{PP}$ = 17.8 Hz, *trans*-P^{dmpe}), 29.3 (dd, $^2J_{PP}$ = 257.5 Hz, $^2J_{PP}$ = 30.8 Hz, PPh$_2$), 27.7 ppm (dd, $^2J_{PP}$ = 29.3 Hz, $^2J_{PP}$ = 17.8 Hz, *cis*-P^{dmpe}).

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Supporting Information Available: CIF files giving crystallographic data for **1b** and **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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