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Linear Hybrid Aminoborane/Phosphinoborane Chains: Synthesis, Proton-Hydride Interactions, and Thermolysis Behavior

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The reaction of the lithiated phosphine–borane adducts Li[PPhR•BH_3] or Li[CH_2–PR_2•BH_3] with Me_2NH•BH_2Cl afforded the hybrid linear species Me_2NH–BH_2–PPhR–BH_3 (**1**, R = Ph; **2**, R = H) or Me_2NH–BH_2–CH_2–PR_2–BH_3 (**3**, R = Ph; **4**, R = Me). Single-crystal X-ray diffraction studies on **1** and **3**, the first for linear hybrid aminoborane/phosphinoborane adducts, confirmed the expected four-coordinate N–B–P–B and N–B–C–P–B frameworks. In addition, interactions between the protic N–H and hydridic B–H hydrogen atoms resulted in short *intermolecular* H•••H contacts for **1**, whereas **3** was found to possess an exceptionally short *intramolecular* H•••H distance of 1.95 Å. Solution and solid state infrared studies on **3** and **4** also suggest that these dihydrogen interactions were maintained even in dilute solution. Hydrogen bond strengths in the range of 7.9 to 10.9 kJ mol^{-1} indicate the presence of a relatively weak interaction. The thermal and catalytic dehydrocoupling reactivities of **1**–**4** were also investigated. Chain cleavage reactions were observed for **1** and **2** upon thermolysis at 130 °C to afford species such as Me_2NH•BH_3, [Me_2N–BH_2]$_2$, PhPRH•BH_3 (R = Ph, H), PhPRH (R = Ph, H), Ph_2PH–BH_2–PPh_2–BH_3, and also the low molecular weight polyphosphinoborane [PhPH–BH_2]$_n$ ($M_w \sim 5000$). Similar products were observed for the attempted catalytic dehydrocoupling reactions but under milder reaction conditions (50 °C). Thermolysis of **3** at 130 °C yielded the six-membered ring [BH_2–CH_2–PPh_2]$_2$ (**5**), which presumably results from the dissociation of Me_2NH•BH_3 from **3**. Thermolysis of **4** at 90 °C afforded Me_2NH•BH_3 and Me_3P•BH_3, in addition to a product tentatively assigned as [BH_2–CH_2–PMe_2]$_2$ (**6**).

Introduction

Thermal and transition-metal-catalyzed dehydrocoupling of main-group hydrides has recently emerged as a promising synthetic method for the synthesis of new cyclic and linear species involving group 13 and group 15 elements.[1−11] For example, phosphorus macrocycles such as $(C_6H_4P_2)_8$ have been prepared from the Zr-catalyzed homodehydrocoupling of bis(phosphine) precursors.[3] In addition, tetraphenyldiphosphine (Ph_2P-PPh_2) has been found to result from the dehydrocoupling of Ph_2PH in the presence of a Rh catalyst,[4]

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and the thermal dehydrocoupling of P−H and Al/Ga−H bonds has been employed to yield donor stabilized phosphanylalane and -gallane species.[5] Thermal heterodehydrocoupling of borazine has also been shown to afford polyborazylene, which is a useful polymeric precursor for the synthesis of boron nitride ceramics.[6] Our group has recently reported that the catalytic dehydrocoupling of secondary phosphine−borane adducts yields either linear or cyclic oligophosphinoboranes, while the primary adducts give high molecular weight polyphosphinoboranes of the type $[\mathrm{RPH{-}BH_2}]_n$ (R = Ph, ^{i}Bu, etc.).[7−9] We have also shown that secondary amine−borane adducts undergo dehydrocoupling at 25 °C in the presence of Rh precatalysts to yield the cyclic dimers $[\mathrm{R_2N{-}BH_2}]_2$, while reactions with primary adducts or $\mathrm{NH_3{\cdot}BH_3}$ yield borazine $[\mathrm{RN{-}BH}]_3$ derivatives.[9−11]

During the course of our work on amine−boranes, we discovered that the catalytic dehydrocoupling of the linear adducts $\mathrm{R_2NH{-}BH_2{-}NR_2{-}BH_3}$ yields the cyclic $[\mathrm{R_2N{-}BH_2}]_2$.[11] This suggested that if the dehydrocoupling of analogous linear species could be induced by either thermal or catalytic methods, the formation of novel heterocyclic or polymeric products would result. In the early 1970s, Keller and co-workers reported the synthesis of the hybrid adducts $\mathrm{R_3N{-}BH_2{-}PMe_2{-}BH_3}$ (R = H, Me) from the reaction of the appropriate amine $\mathrm{R_3N}$ with the salt $\mathrm{Li[BH_3{-}PMe_2{-}BH_3]}$.[12] High temperature (150−240 °C) thermolysis of these compounds resulted in the formation of $[\mathrm{Me_2P{-}BH_2}]_3$ in all cases, and the appropriate amine−borane adduct $\mathrm{R_3N{\cdot}BH_3}$ or their thermal decomposition products (e.g. $[\mathrm{Me_2N{-}BH_2}]_2$, $[\mathrm{MeN{-}BH}]_3$, $[\mathrm{HN{-}BH}]_3$). However, the compounds were not structurally characterized, and lower temperature (e.g. <150 °C) thermal and catalytic dehydrocoupling reactions were not investigated. In this paper, we present the synthesis and characterization of a series of new linear hybrid adducts with N−B−P−B (**1** and **2**) and N−B−C−P−B (**3** and **4**) frameworks, as well as an exploration of their thermal and catalytic dehydrocoupling chemistry.

As a further consideration, the presence of unconventional proton−hydride[13] bonds ($\mathrm{H}^{\delta+}\cdots{}^{\delta-}\mathrm{H}$) have been detected in the solid state structures of the linear amine−borane adducts $\mathrm{R_2NH{-}BH_2{-}NR_2{-}BH_3}$.[11,14] This unique type of hydrogen bonding between protic and hydridic hydrogen atoms has been found to be highly directional in nature and moderately strong (13−29 kJ mol^{-1}) and can exert an influence on solid state physical and chemical properties.[15−18] Such proton−hydride interactions would be anticipated in species **1**−**4**, and would be expected to influence the thermal or catalytic dehydrocoupling reactivity. Correlation between proton−hydride bonding and the observed dehydrocoupling chemistry is of clear interest and will also be discussed.

Results and Discussion

Synthesis and Characterization of $\mathrm{Me_2NH{-}BH_2{-}PPhR{-}BH_3}$ (1, R = Ph; 2, R = H). Recently, we have found that reaction of $\mathrm{R_2NH{\cdot}BH_2Cl}$ with $\mathrm{Li[NR_2{\cdot}BH_3]}$ results in the linear adducts $\mathrm{R_2NH{-}BH_2{-}NR_2{-}BH_3}$ (R = Me; R = 1,4-$\mathrm{C_4H_8}$) in moderate yields.[11] This appears to be a general method for the synthesis of linear adducts with various *N*-substituents, particularly on the internal nitrogen atom. When the same method was applied but a lithiated phosphine−borane adduct was used, the linear hybrid adducts $\mathrm{Me_2NH{-}BH_2{-}RPPh{-}BH_3}$ (**1**, R = Ph; **2**, R = H) were synthesized (eq 1). For example, the treatment of $\mathrm{Ph_2PH{\cdot}BH_3}$ with ^{n}BuLi gave $\mathrm{Li[PPh_2{\cdot}BH_3]}$, which was then reacted with $\mathrm{Me_2NH{\cdot}BH_2Cl}$ to give **1** in 48% yield. Compound **1** was fully characterized by ^{1}H, ^{11}B, ^{13}C, and ^{31}P NMR, mass spectrometry, infrared spectroscopy, elemental analysis, and also single-crystal X-ray diffraction. The ^{11}B NMR spectrum of **1** shows two resonances at δ −11.3 and −39.9 ppm, which were assigned to the internal ($\mathrm{N{-}BH_2{-}P}$) and terminal ($\mathrm{P{-}BH_3}$) boron atoms, respectively. These chemical shifts agree with those found for $\mathrm{R_3N{-}BH_2{-}PMe_2{-}BH_3}$, which vary between δ −6.2 and −11.2 ppm for the $\mathrm{BH_2}$ group, and δ −35.2 and −37.6 ppm for the $\mathrm{BH_3}$ group.[12] The ^{31}P NMR spectrum displays one resonance at δ −19.9 ppm, which is indicative of a $\mathrm{PPh_2}$ unit between two boron atoms.[7a−c]

$$\mathrm{Me_2NH{-}BH_2Cl} + \mathrm{LiRPhP{-}BH_3} \xrightarrow[\text{- LiCl}]{} \mathrm{Me_2NH{-}BH_2{-}PPhR{-}BH_3} \qquad (1)$$

1: R = Ph
2: R = H

Further characterization of **1** was performed using X-ray crystallography, and this species represents the first example of a structurally characterized, linear hybrid adduct with a N−B−P−B backbone. The molecular structure of **1** is shown in Figure 1a, while a list of the selected bond lengths and angles can be found in Table 1. Bond lengths of 1.598(2), 1.964(2), and 1.935(2) Å were found for the terminal N−B, internal B−P, and terminal P−B bonds, respectively. A similar arrangement of longer internal/shorter terminal B−P bonds was found in the crystal structures of other linear phosphine−borane adducts.[7a−c,19] The angles around the four-coordinate nitrogen, boron, and phosphorus atoms were all found to be approximately tetrahedral. An interesting feature is the association of the chains in the solid state. Proton−hydride bonds ($\mathrm{H}^{\delta+}\cdots{}^{\delta-}\mathrm{H}$) between N−H and B−H hydro-

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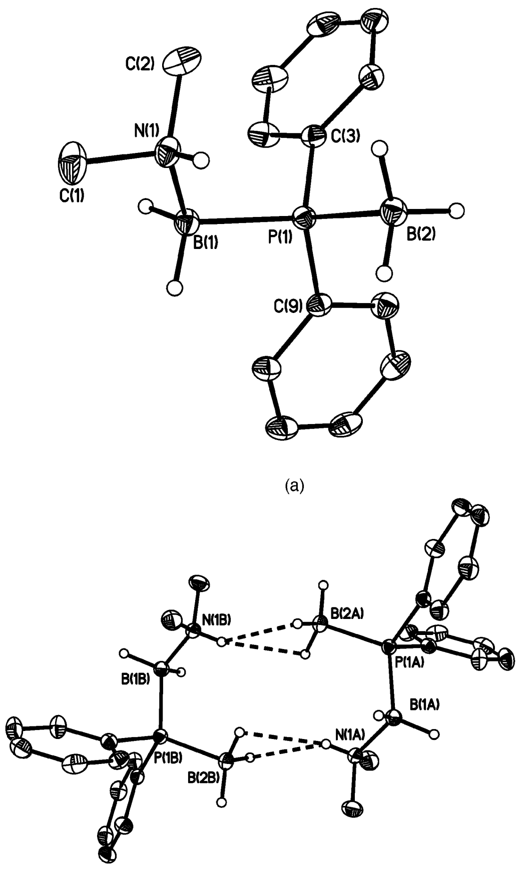

(a)

(b)

Figure 1. Molecular structure of **1**. All hydrogen atoms bonded to carbon are omitted for clarity. Selected bond lengths and angles are presented in Table 1.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1** and $[\mathbf{1}]_2$

N(1)−B(1)	1.598(2)	N(1)−B(1)−P(1)	110.25(9)
B(1)−P(1)	1.964(2)	B(1)−P(1)−B(2)	115.19(7)
P(1)−B(2)	1.935(2)	C(1)−N(1)−C(2)	110.6(1)
N(1)−H(1N)	0.81(2)	C(1)−N(1)−B(1)	109.8(1)
N(1)−C(1)	1.493(2)	C(2)−N(1)−B(1)	114.3(1)
N(1)−C(2)	1.471(2)	B(1)−P(1)−C(9)	107.48(6)
P(1)−C(3)	1.828(1)	B(1)−P(1)−C(3)	109.49(7)
P(1)−C(9)	1.821(1)	B(2)−P(1)−C(9)	110.16(7)
		B(2)−P(1)−C(3)	111.15(7)
H(1N)−H(3*)	2.24[a]	N(1*)−H(1N)−H(3)	131.3[a]
H(1N)−H(4*)	2.06[a]	N(1*)−H(1N)−H(4)	159.2[a]
H(1N)−H(5*)	2.99[a]	B(2)−H(4)−H(1N*)	85.4[a]
		B(2)−H(3)−H(1N*)	94.0[a]

[a] Using the normalized bond distances of d(N−H) = 1.03 Å and d(B−H) = 1.21 Å.

gen atoms link two molecules together to form a dimeric structure as shown in Figure 1b. Normalizing the N−H and B−H bond distances to 1.03 and 1.21 Å,[16a] respectively, two short interaction distances of 2.24 and 2.06 Å were found. A third distance of 2.99 Å was found but is well beyond the sum of the van der Waals radii for two hydrogen atoms (2.40 Å).[20] Linear N−H···H angles of 131.3° and 159.2° and bent B−H···H angles of 85.4° and 94.0° were found and are consistent with other N−H···H−B proton−hydride bonded structures.[11,14,16a] Proton−hydride bonding interactions to yield dimeric species in the solid state have also been observed in the structures of $Me_2NH-BH_2-NMe_2-BH_3$[14] and $(1,4\text{-}C_4H_8)NH-BH_2-N(1,4\text{-}C_4H_8)-BH_3$.[11]

For compound **2**, which was synthesized in 83% yield, similar chemical shifts were observed in the ^{11}B (δ −12.8 and −41.5 ppm) and ^{31}P (δ −54.8 ppm) NMR spectra. In addition, further evidence for a P−H bond was found in the ^{1}H-coupled ^{31}P NMR spectrum, in which the resonance at δ −54.8 ppm was found to split into a doublet (J_{PH} = 344 Hz). In the ^{1}H NMR spectrum, the P−H resonance occurs as a doublet of sextets resulting from coupling to one phosphorus nucleus and five adjacent protons on boron (J_{HH} = 6 Hz). The crystal structure of **2** was also of interest as N−H···H−B and P−H···H−B contacts may be present simultaneously in the solid state, leading to a highly aggregated, proton−hydride bonded network. A low resolution X-ray structure was obtained which showed that the packing of the molecules did not allow for a favorable alignment for any P−H···H−B or N−H···H−B proton−hydride interactions. However, numerous attempts to obtain a more accurate X-ray analysis were hampered by the formation of low quality crystals.

Attempted Thermal and Catalytic Dehydrocoupling of 1 and 2. Previous work has shown that thermolysis of the linear hybrid adducts $R_3N-BH_2-PMe_2-BH_3$ (R = H or Me) at temperatures of 150−240 °C results in skeletal bond cleavage (vide supra).[12] We found that thermolysis of **1** at 130 °C for 20 h also resulted in backbone cleavage, with the formation of a complex mixture of products (eq 2a). Ph_2PH (trace), $Ph_2PH-BH_2-PPh_2-BH_3$ (ca. 15%), $Me_2NH\cdot BH_3$ (ca. 10%), $[Me_2N-BH_2]_2$ (ca. 40%), $Ph_2PH\cdot BH_3$ (ca. 35%), and unreacted **1** were all identified by their respective ^{11}B and ^{31}P NMR shifts. In contrast, we found that the thermolysis of **2** was complete in only 2 h at 130 °C, resulting solely in the formation of $[Me_2N-BH_2]_2$ and the polymer $[PhPH-BH_2]_n$ (eq 2c), which was isolated in quantitative yield after precipitation into pentane. The polymer $[PhPH-BH_2]_n$ was characterized by ^{1}H, ^{11}B, and ^{31}P NMR spectroscopy, which gave spectra identical with those of samples previously synthesized in our group by the Rh-catalyzed dehydrocoupling of $PhPH_2\cdot BH_3$ at 90−130 °C.[7a,b,d] Dynamic light scattering (DLS) on a solution of $[PhPH-BH_2]_n$ in THF resulted in a bimodal size distribution with peak values of $D_h \approx 1.8$ and 163 nm. As previously observed, the two peaks may arise from the presence of single polymer chains ($D_h \approx 1.8$ nm) and large polymer aggregates ($D_h \approx 163$ nm).[7b] Indeed, after 4 days only a single size distribution was observed with $D_h \approx 1.4$ nm, indicating that the larger aggregates had dissociated in a manner similar to that noted previously.[7b] The small D_h values of 1−2 nm suggest that low molecular weight polymer is formed. Previous work on $[PhPH-BH_2]_n$ has shown that samples with a D_h of 1 nm correspond to an absolute weight-average molecular weight (M_w) value of ca. 5000 by static light scattering (SLS).[7b] We hoped that by utilizing a transition-metal catalyst, dehydrocoupling of **1** might proceed at lower temperatures to yield cyclic or polymeric $[Me_2N-BH_2-RPPh-BH_2]_n$ species. However, when **1** was treated with 1.5 mol % of $[Rh(1,5\text{-}cod)(\mu\text{-}Cl)]_2$ (1,5-cod = 1,5-cyclooctadiene), chain cleavage

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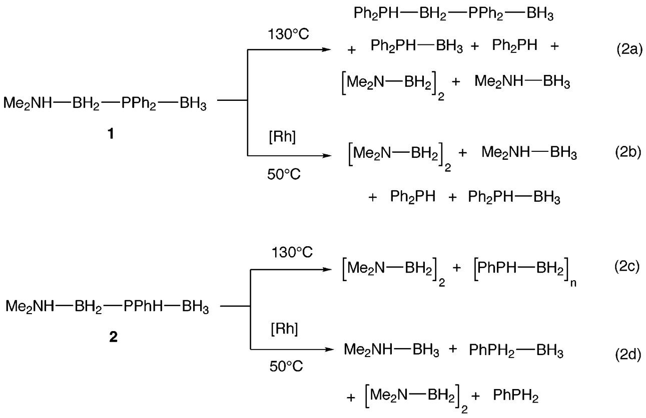
products were again observed (eq 2b). Thus, after 24 h at 50 °C, signals associated with $Me_2NH{\cdot}BH_3$ (ca. 5%), $[Me_2N{-}BH_2]_2$ (ca. 45%), and $Ph_2PH{\cdot}BH_3$ (ca. 50%) as well as unreacted **1** were observed in the ^{11}B and ^{31}P NMR spectra. After 48 h, an additional resonance due to free Ph_2PH (trace) was observed in the ^{31}P NMR. Compound **1** was found to be completely consumed after 10 days. In contrast, under the same conditions in the absence of catalyst, only 35% conversion of **1** was detected. Similarly, when **2** was treated with 1.3 mol % of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ at 50 °C, complete conversion to $Me_2NH{\cdot}BH_3$ (ca. 10%), $PhPH_2$ (trace), $[Me_2N{-}BH_2]_2$ (ca. 40%), and $PhPH_2{\cdot}BH_3$ (ca. 50%) was detected after 10 days (eq 2d). In contrast, under the same conditions in the absence of catalyst, only 10% conversion of **2** was detected.



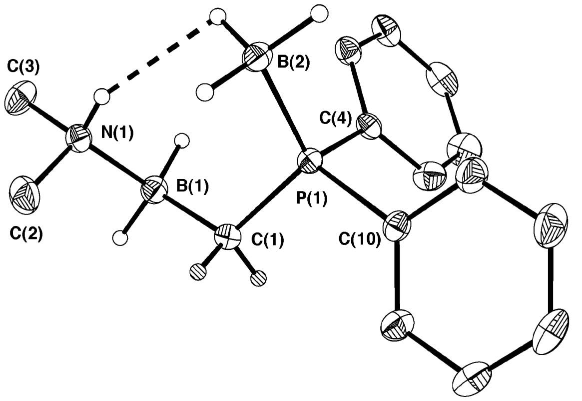


Figure 2. Molecular structure of **3**. All hydrogen atoms bonded to carbon in the phenyl rings are omitted for clarity. Selected bond lengths and angles are presented in Table 2.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**

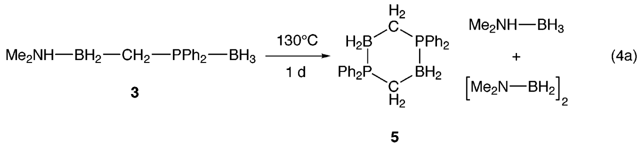
N(1)−B(1)	1.619(2)	N(1)−B(1)−C(1)	112.4(1)
B(1)−C(1)	1.634(2)	B(1)−C(1)−P(1)	114.6(1)
C(1)−P(1)	1.801(2)	C(1)−P(1)−B(2)	113.40(8)
P(1)−B(2)	1.928(2)	N(1)−H(1N)−H(5)	151.8(2)
N(1)−H(1N)	0.85(2)	N(1)−H(1N)−H(5)	149.5[a]
B(2)−H(5)	1.12(2)	B(2)−H(5)−H(1N)	105.0(1)
H(1N)−H(5)	2.13(2)	B(2)−H(5)−H(1N)	102.9[a]
H(1N)−H(5)	1.95[a]		

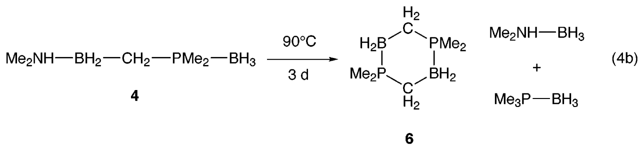
[a] Using the normalized bond distances of $d(N{-}H) = 1.03$ Å and $d(B{-}H) = 1.21$ Å.

Synthesis and Characterization of $Me_2NH{-}BH_2{-}CH_2{-}PR_2{-}BH_3$ (3, R = Ph; 4, R = Me). The incorporation of a spacer unit into the skeleton of compounds **1** and **2** may prevent chain cleavage and might potentially allow the formation of larger cyclic species or polymeric products via dehydrocoupling. A methylene group can be easily incorporated through the use of a tertiary phosphine−borane adduct containing a methyl group $MePR_2{\cdot}BH_3$ (R = Ph, Me). Treatment with ^nBuLi affords $Li[CH_2{-}PR_2{\cdot}BH_3]$, which was then reacted with $Me_2NH{\cdot}BH_2Cl$ to yield $Me_2NH{-}BH_2{-}CH_2{-}PR_2{-}BH_3$ (**3**, R = Ph; **4**, R = Me) in yields of 20% and 32%, respectively (eq 3). The low yields result from a side reaction between the N−H proton of $Me_2NH{\cdot}BH_2Cl$ and $Li[CH_2{-}PR_2{\cdot}BH_3]$ regenerating $MePR_2{\cdot}BH_3$ and forming $Li[NMe_2{\cdot}BH_2Cl]$. The latter product then eliminates LiCl to form $[Me_2N{-}BH_2]_2$, which was frequently detected in the reaction mixture. The ^{31}P NMR spectra of **3** and **4** showed broad quartets and at δ 16.6 ($J_{PB} = 79$ Hz) and 3.1 ppm ($J_{PB} = 70$ Hz), respectively. The ^{11}B NMR spectrum of **3** showed two resonances for the BH_2 and BH_3 groups at δ −11.7 and −40.2 ppm, respectively. Similar ^{11}B shifts were observed for **4**, but with resolved B−H couplings; a triplet at δ −9.9 ($J_{BH} = 98$ Hz) and a quartet of doublets at δ −40.2 ppm ($J_{BP} = 70$ Hz, $J_{BH} = 94$ Hz). The most interesting feature of the ^{13}C NMR spectra arises from the resonance associated with the internal CH_2 group, which gave broad signals at δ 10.9 and 14.2 ppm for **3** and **4**, respectively, due to the nearby quadrupolar boron nucleus. The ^1H NMR spectra of **3** and **4** also show the presence of a broad resonance due to the internal CH_2 group at δ 1.31 and 0.54 ppm, respectively. Further characterization of **3** was performed using X-ray crystallography, the molecular structure of which is shown in Figure 2. A list of the selected bond lengths and angles for **3** can be found in Table 2. The terminal N−B and P−B adduct bonds were determined to be 1.619(2) and 1.928(2) Å, respectively, and are typical of N−B and P−B adduct bond distances. The internal B−C and C−P distances were found to be 1.634(2) and 1.801(2) Å, respectively, which are also normal distances for these types of bonds. One noteworthy feature of interest was the presence of an *intramolecular* proton−hydride interaction between the terminal N−H and B−H hydrogen atoms, effectively giving a seven-membered heterocycle. Using normalized B−H and N−H bond distances (vide supra), a H···H contact distance of 1.95Å was found. This is much shorter than the H···H distances found in **1** (2.06 and 2.24 Å), in which the bonding interaction is intermolecular in nature. This distance is also shorter than the shortest H···H distance (2.02(3) Å) found in the neutron diffraction study of $NH_3{\cdot}BH_3$.[16a]

$$\begin{array}{l} Me_2NH{-}BH_2Cl + LiCH_2{-}R_2P{-}BH_3 \xrightarrow[\text{- LiCl}]{} \\ \qquad Me_2NH{-}BH_2{-}CH_2{-}PR_2{-}BH_3 \qquad (3) \\ \qquad \mathbf{3}\text{: R = Ph} \\ \qquad \mathbf{4}\text{: R = Me} \end{array}$$

Attempted Thermal and Catalytic Dehydrocoupling of 3 and 4. Thermolysis of **3** at 130 °C for 6 h was found to result in solidification of the initially liquid reactant. The NMR spectra of the reaction mixture indicated partial conversion to a new product **5**, with the presence of new resonances at δ 7.7 (^{31}P) and −33.6 ppm (^{11}B). The ^{11}B NMR spectrum also showed resonances at δ 3.5 and −13.4 ppm which were assigned to $[Me_2N-BH_2]_2$ and $Me_2NH{\cdot}BH_3$, respectively. Further heating of the solid for 24 h was found to result in full conversion to the six-membered cyclic dimer $[BH_2-CH_2-PPh_2]_2$ (**5**) in 98% yield (eq 4a). The ^{13}C NMR of **5** showed a broad resonance at δ 6.3 ppm attributed to the internal CH_2 group. The mass spectrum of **5** was also indicative of a dimeric species, with the parent ion for both the dimer and monomer occurring at m/z = 424 (10%) and 212 (6%), respectively. Heating of **4** at 90 °C in the absence of solvent for 3 days was found to result in mainly sublimation of the volatile starting material. However, ^{1}H, ^{11}B, and ^{31}P NMR spectra of the reaction mixture indicated partial conversion (ca. 50%) of **4** to $Me_2NH{\cdot}BH_3$, $Me_3P{\cdot}BH_3$, and a product that may be the cyclic dimer $[BH_2-CH_2-PMe_2]_2$ (**6**). Evidence for the formation of **6** was obtained from the ^{1}H (δ 1.52 (d), Me), ^{11}B (δ −30.5 (dt)), ^{13}C (δ 10.6 (d), Me), and ^{31}P NMR (δ 6.0 (q)) spectra. This assignment is tentative, as the anticipated broad ^{1}H and ^{13}C resonances for the CH_2 group were not observed due to overlapping signals. Attempts to isolate **6** from the reaction mixture by fractional sublimation were unsuccessful. Heating of **4** at 130 °C in solution was found to result in complete conversion to $[Me_2N-BH_2]_2$ and $Me_3P{\cdot}BH_3$. The presence of $Me_3P{\cdot}BH_3$ in the thermolysis reaction of **4** suggests that a different chain cleavage pathway is operating compared to that of **3**, as $MePPh_2{\cdot}BH_3$ was not observed in the latter case.





Catalytic dehydrocoupling trials performed on both **3** and **4** with $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (1−5 mol %) at either 25 or 50 °C were found to result in no observable reaction. Upon heating to 90 °C, **3** and **4** were completely consumed after 20 h. The only products that could be identified by NMR were $MePPh_2{\cdot}BH_3$ (for **3**) and $Me_3P{\cdot}BH_3$ (for **4**). Blank reactions for both **3** and **4** at 90 °C in the absence of catalyst were found to result in no significant conversion after 20 h.

The cyclic **5** was further characterized by X-ray crystallography, the molecular structure of which is shown in Figure 3. A list of the selected bond lengths and angles for **5** can be found in Table 3. The six-membered ring adopts a chair conformation, with typical B−P, P−C, and B−C bond lengths of 1.937(2), 1.800(2), and 1.645(3)Å, respectively. The angles around the four-coordinate P and B atoms are all approximately tetrahedral, ranging from 104.89(9)° to 113.2(1)° for phosphorus and 102.8(1)° to 113.5(1)° for boron. There are three previous examples describing the synthesis of six-membered BCP rings,[21] with $[EtBR-CH_2-RPPh]_2$ (R = 1,3-EtC=CMe−SiMe$_2$) being the lone example which has been characterized by X-ray crystallography to date.[21a] Interestingly, the synthesis of $[BH_2-CHPh\text{-}PHMes^*]_2$ (Mes* = 2,4,6-tri-*tert*-butylphenyl) is facilitated via dissociation of BH_3 and THF from the linear adduct $BH_3-PHMes^*-CHPh-BH_2-THF$.[21c]

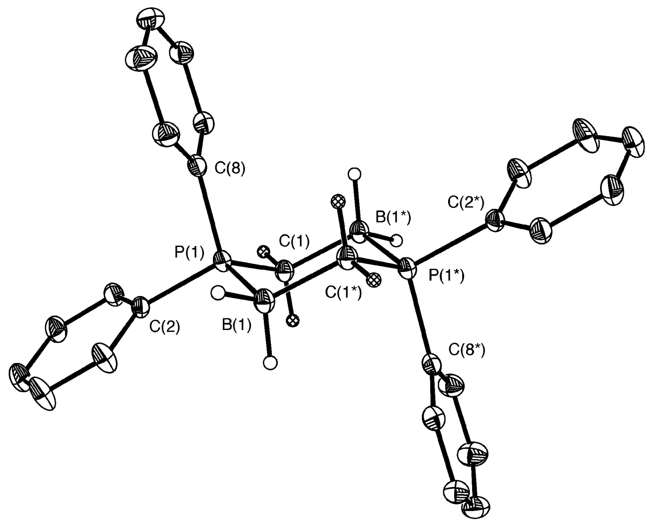


Figure 3. Molecular structure of **5**. All hydrogen atoms bonded to carbon in the phenyl rings are omitted for clarity. Selected bond lengths and angles are presented in Table 3.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **5**

P(1)−B(1)	1.937(2)	C(1)−P(1)−B(1)	110.4(1)
P(1)−C(1)	1.800(2)	C(1)−P(1)−C(2)	108.28(9)
P(1)−C(2)	1.816(2)	C(1)−P(1)−C(8)	108.3(1)
P(1)−C(8)	1.815(2)	B(1)−P(1)−C(2)	111.5(1)
B(1)−C(1)*	1.645(3)	B(1)−P(1)−C(8)	113.2(1)
		P(1)−B(1)−C(1)*	109.4(2)
		P(1)−C(1)−B(1)*	112.1(1)

Evaluation of Solid State Intra- or Intermolecular Proton−Hydride Interactions in 1−4 by Infrared Spectroscopy. To confirm the presence of proton−hydride bonding interactions in **1**−**4**, solid state and solution IR spectroscopy was used. It has been acknowledged that the presence of hydrogen bonding in molecules can be inferred from the appearance of broadened, lower frequency stretching absorptions when compared with non-H-bonded systems. In particular, amine−borane adducts have been shown to participate in proton−hydride bonding through either self-association[11,14,16a] or the presence of protic H atom sources (e.g. O−H or N−H).[22−25] In these cases, the hydrogen bond acceptor becomes the hydridic H atoms attached to boron (or the B−H bond itself),[26] despite the lack of a lone pair of

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Table 4. Selected IR Stretching Frequencies for Compounds **1**−**4**[a]

compound	ν(NH)	$\nu(\text{BH})_{\text{asym}}$	$\nu(\text{BH})_{\text{sym}}$
$Me_3N{\cdot}BH_3$		2382	2263
$Me_2NH{\cdot}BH_3$	3204	2372	2260
$Me_2NH{\cdot}BH_3$ (pure liquid)[b]	3180	2366	2265
$Me_2NH{\cdot}BH_3$ (0.0021 M in CCl_4)[c]	3300		
$NH_3{\cdot}BH_3$[d]	3317	2329	2281
$NH_3{\cdot}BH_3$[e]	3386	2427	2340
1	3178	2337	2260
1 (0.005 M)[f]	3224	2376	2279
2	3178	2342	2267
2 (0.005 M)[f]	3232	2391	2271
3	3215	2370	2282
3 (0.005 M)[f]	3209	2380	2284
4	3200	2345	2286
4 (0.005 M)[f]	3204	2363	2285

[a] Spectra were obtained as Nujol mulls unless otherwise specified. ν reported in cm^{-1}. [b] Reference 24. [c] Reference 22. [d] Spectra obtained as a pressed KBr pellet. [e] Spectra obtained as isolated $NH_3{\cdot}BH_3$ in an argon matrix on a CsI window at liquid hydrogen temperature. Reference 28. [f] Solution spectra were obtained in dry CH_2Cl_2.

electrons or a π system. However, to establish these proton−hydride interactions, values for the non-H-bonding N−H and B−H stretching absorption were required. This was accomplished by obtaining the ν_{NH} and ν_{BH} stretching absorptions for the amine−borane adducts $Me_3N{\cdot}BH_3$, $Me_2NH{\cdot}BH_3$, and $NH_3{\cdot}BH_3$, and also **1**−**4** (Table 4). For $Me_3N{\cdot}BH_3$, which lacks ν_{NH}, non-H-bonded values of ν_{BH} were observed at 2382 and 2263 cm^{-1}, for the asymmetric (asym) and symmetric (sym) modes, respectively. For $Me_2NH{\cdot}BH_3$, in which intermolecular N−H···H−B interactions are present in the solid state, values of 3204 cm^{-1} and of 2372 and 2260 cm^{-1} were found for ν_{NH} and ν_{BH} (asym and sym), respectively. Brown has reported a value of 3300 cm^{-1} for the non-H-bonded ν_{NH} for $Me_2NH{\cdot}BH_3$ in dilute CCl_4 (0.0021 M).[22] Thus, there is a frequency shift of $\Delta\nu = 96$ cm^{-1} for ν_{NH} in H-bonded and non-H-bonded samples of $Me_2NH{\cdot}BH_3$.[27] There appears to be little difference in the values of ν_{BH} between $Me_3N{\cdot}BH_3$ and $Me_2NH{\cdot}BH_3$, with $\Delta\nu$ values of 10 (asym) and 3 cm^{-1} (sym). The proton−hydride interactions in $Me_2NH{\cdot}BH_3$ are also preserved in the liquid state, with values of 3180 cm^{-1} for ν_{NH}, and 2366 and 2265 cm^{-1} for ν_{BH} (asym and sym), respectively.[24] To confirm that ν_{BH} does shift to lower frequency upon association via dihydrogen bonding, the spectrum of $NH_3{\cdot}BH_3$ was obtained as a KBr disk yielding values of 2329 and 2281 cm^{-1}.[28] This was compared with that of an unassociated sample obtained in a rare gas matrix, which yielded values of 2427 and 2340 cm^{-1}.[29] Thus, there is a large frequency shift of $\Delta\nu = 98$ and 59 cm^{-1} for ν_{BH} on going from unassociated to associated samples of $NH_3{\cdot}BH_3$. In addition, a large shift of $\Delta\nu = 69$ cm^{-1} results for ν_{NH}. These $\Delta\nu$ values are reasonable as the solid state structure of $NH_3{\cdot}BH_3$ has been shown to be highly associated, with the presence of many long and short-range H···H interactions.[16a,30]

In the case of **1**, the solid state IR spectrum shows absorptions at 3178 cm^{-1} due to ν_{NH}, and at 2337 and 2260 cm^{-1} due to ν_{BH} (asym and sym) vibrations, respectively. Compared with unassociated $Me_2NH{\cdot}BH_3$ in CCl_4, there is a large frequency shift of $\Delta\nu = 122$ cm^{-1} in the value of ν_{NH}. When compared with $Me_3N{\cdot}BH_3$, $\Delta\nu$ values of 45 and 3 cm^{-1} are obtained for ν_{BH} (asym and sym, respectively). It has been noted that the asymmetric B−H stretch is affected by H-bonding to a greater extent than the symmetric stretch, resulting in a larger $\Delta\nu$ value.[23] When the solution IR spectrum of **1** was obtained in CH_2Cl_2 (0.005 M), there was an observed increase in the frequencies of the stretching absorptions to 3224 cm^{-1} for ν_{NH}, and to 2376 and 2279 cm^{-1} for ν_{BH} (asym and sym), respectively. This results in $\Delta\nu$ values between the solid and solutions samples of 46, 39, and 19 cm^{-1}, respectively. Thus, in dilute solution the intermolecular proton−hydride interactions in **1** are disrupted, as the stretching frequencies approach values for that of the unassociated molecules. For **2**, similar $\Delta\nu$ values of 54 cm^{-1} for ν_{NH}, and 49 and 4 cm^{-1} for ν_{BH} (asym and sym), respectively, between the solid state and solution IR spectra were obtained, indicating the presence of proton−hydride interactions only in the solid state.

In the case of **3**, the solid state IR spectrum shows absorptions at 3215 cm^{-1} for ν_{NH}, and at 2370 and 2282 cm^{-1} for ν_{BH} (asym and sym), respectively. Again, there is a large $\Delta\nu$ value of 85 cm^{-1} for ν_{NH} when compared to the value of the free N−H stretch in $Me_2NH{\cdot}BH_3$. However, a small $\Delta\nu$ value of 12 cm^{-1} results for the asymmetric ν_{BH}, while the symmetric ν_{BH} shows an increase in frequency ($\Delta\nu = -19$ cm^{-1}) when compared to the values obtained for $Me_3N{\cdot}BH_3$. When the solution IR spectrum was obtained in CH_2Cl_2 (0.005 M), only minor frequency shifts are observed. In fact, the frequency of ν_{NH} decreases to 3209 cm^{-1}, resulting in a $\Delta\nu$ value of -6 cm^{-1}, while the frequency of ν_{BH} increases to 2380 and 2284 cm^{-1}, resulting in $\Delta\nu$ values of 10 and 2 cm^{-1} for the asymmetric and symmetric modes, respectively. For **4**, similar minor shifts in the stretching frequencies ($\Delta\nu = 4$ cm^{-1} for ν_{NH}, 18 and -1 cm^{-1} for ν_{BH} (asym and sym), respectively) were also observed between the solid state and solution samples. One explanation for the small changes in ν from solid state to solution may be due to the type of proton−hydride interaction present in **3** and **4** compared to **1** and **2**. In **1** and **2**, intermolecular proton−hydride bonding is present between molecules, which can easily be disrupted by high dilution. However, in **3** and **4**, intramolecular proton−hydride bonding is present within the same molecule. High dilution would have little effect as the N−H and B−H bonds are still in close proximity to one another and the proton−hydride bonding would be unaffected.

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(26) Li, J.; Zhao, F.; Jing, F. *J. Chem. Phys.* **2002**, *116*, 25.

(27) The frequency shift ($\Delta\nu$) can be defined as $\Delta\nu = \nu(\text{XH})_{\text{free}} - \nu(\text{XH})_{\text{H-bonded}}$ where X = N or B.

(28) A reviewer suggested the possible formation of $K[BH_3Br]$ from KBr and $NH_3{\cdot}BH_3$. However, evidence for a N−B stretch was observed at ca. 950 cm^{-1} in the IR spectrum. In addition, solid state CP-MAS ^{11}B NMR on samples of $NH_3{\cdot}BH_3$ and KBr/$NH_3{\cdot}BH_3$ (from the KBr pellet) showed identical resonances at $\delta = -35$ ppm.

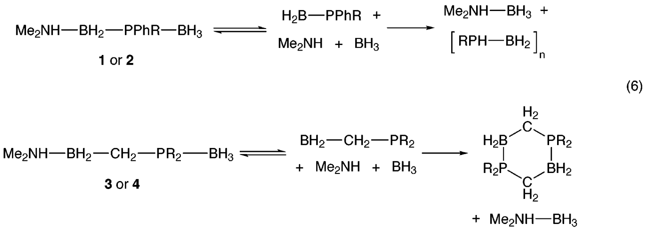
(29) Smith, J.; Seshadri, K. S.; White, D. *J. Mol. Spectrosc.* **1973**, *45*, 327.

(30) Additional evidence for $H^{\delta+}\cdots{}^{\delta-}H$ interactions in $NH_3{\cdot}BH_3$ has been provided by Raman spectroscopy: Trudel, S.; Gilson, D. F. R. *Inorg. Chem.* **2003**, *42*, 2814.

The frequency shifts ($\Delta\nu$) can be used to estimate the hydrogen bond strengths of **1**−**4** in the solid state by using an empirical equation proposed by Ioganson (eq 5),[31] which correlates ΔH° with the change in the stretching absorption upon hydrogen-bond formation. For **1** and **2**, values of $\Delta\nu = 122\ \text{cm}^{-1}$ result in proton−hydride bond strengths of $\Delta H^\circ = -2.61\ \text{kcal mol}^{-1}$ ($-10.9\ \text{kJ mol}^{-1}$). Compounds **3** and **4** ($\Delta\nu = 85$ and $100\ \text{cm}^{-1}$, respectively) yield values of -1.9 and $-2.20\ \text{kcal mol}^{-1}$ (-7.9 and $-9.20\ \text{kJ mol}^{-1}$) for ΔH°, respectively. These hydrogen bond strengths are on the lower end of the range of values (3−7 kcal mol^{-1}; 12.6−29.3 kJ mol^{-1}) determined for unconventional $\text{H}^{\delta+}\cdots{}^{\delta-}\text{H}$ hydrogen bonds, and are thus considered to be weak interactions.

$$\Delta H^\circ = \frac{-18\Delta\nu}{\Delta\nu + 720} \qquad (5)$$

Mechanism for the Skeletal Cleavage Reactions for 1−4. Although the thermolysis chemistry of **1**−**4** led to a complex range of products, many of these can be explained by simple mechanistic considerations. The mechanism for the chain cleavage reactions of **1**−**4** in the presence or absence of catalyst may involve the initial dissociation of Me_2NH and BH_3 from the termini. The dissociation may occur simultaneously, or as a two-step process, to yield the monomers $\text{PhPR}{-}\text{BH}_2$ (R = Ph, H; from **1** and **2**) or $\text{BH}_2{-}\text{CH}_2{-}\text{PR}'_2$ (R′ = Ph, Me; from **3** and **4**) as transient species (eq 6). Oligomerization of these species would then give, for example, low molecular weight $[\text{PhPH}{-}\text{BH}_2]_n$ (from **2**) or the cyclic $[\text{BH}_2{-}\text{CH}_2{-}\text{PPh}_2]_2$ (from **3**). The free Me_2NH and BH_3 would be expected to combine to form $\text{Me}_2\text{NH}\cdot\text{BH}_3$, which has been previously shown to undergo dehydrocoupling at 130 °C[32] or in the presence of Rh precatalysts[10,11] to yield $[\text{Me}_2\text{N}{-}\text{BH}_2]_2$. In the uncatalyzed chain cleavage reactions, products such as $\text{PhPH}_2\cdot\text{BH}_3$ and $\text{Ph}_2\text{PH}\cdot\text{BH}_3$ cannot be explained by the dissociative mechanism postulated. These species may form as a result of complex thermally induced hydrogen transfer reactions. In the case of the catalytic chain cleavage reactions, the mechanistic scenario is even more complex as oxidative addition/reductive elimination reactions at the transition-metal center may also lead to the formation of the observed products.



The lack of catalytic chain cleavage at 50 °C for compounds **3** and **4**, in contrast to the cases of **1** and **2**, may be due to the *intramolecular* proton−hydride bonding present in solution. The N−H···H−B interactions between the chain ends may effectively prevent dissociation at lower temperatures, and also help to sterically shield the active sites from the catalyst, thereby preventing chain cleavage. At higher temperatures (>90°C), the proton−hydride interactions may be disrupted, enabling dissociation and/or catalytic chain cleavage to occur.

Summary

Novel examples of linear hybrid aminoborane/phosphinoborane species have been synthesized and structurally characterized by X-ray crystallography. The compounds **1** and **2** possess intermolecular proton−hydride interactions in the solid state, as indicated by both single-crystal X-ray diffraction and IR studies, which are disrupted in solution. Compounds **3** and **4** possess intramolecular proton−hydride interactions in the solid state, which are preserved even in dilute solution as indicated by negligible IR frequency shift ($\Delta\nu$) values for the N−H and B−H stretching absorptions between solid state and solution samples. The hydrogen bond strengths of **1**−**4** have been estimated to be in the range of 7.9 to 10.9 kJ mol^{-1}, which is indicative of weak interactions. The thermolysis of **2** and **3** yields, for example, low molecular weight poly(phenylphosphinoborane) $[\text{PPhH}{-}\text{BH}_2]_n$ (M_w = ca. 5000) and the six-membered ring **5** as chain cleavage products, respectively. Rather than catalytic dehydrocoupling, catalytic chain cleavage reactions were observed for **1**−**4** in the presence of [Rh(1,5-cod)(μ-Cl)]$_2$, yielding mixtures of amine−boranes, aminoboranes, and phosphine−boranes. Interestingly, these results suggest that transition metals may be capable of inducing the *cleavage* of B−N and B−P bonds, and this possibility will be the subject of more detailed studies.

Experimental Section

General Procedures and Materials. All reactions and product manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox. All solvents were dried over the appropriate drying agents such as Na/benzophenone (toluene, hexanes, THF, Et_2O) or CaH_2 (CH_2Cl_2) and distilled prior to use. $\text{BH}_3\cdot\text{SMe}_2$, $\text{BH}_3\cdot\text{THF}$ (1.0 M in THF), ^{n}BuLi (1.6 M in hexane), HCl (1.0 M in Et_2O) (Aldrich), $\text{Me}_2\text{NH}\cdot\text{BH}_3$, Me_3P, MePPh_2, Ph_2PH, and PhPH_2 (Strem Chemicals) were purchased and used as received. $\text{Ph}_2\text{PH}\cdot\text{BH}_3$,[7b] $\text{PhPH}_2\cdot\text{BH}_3$,[7b] $\text{Me}_3\text{P}\cdot\text{BH}_3$,[33] and [Rh(1,5-cod)($\mu$-Cl)]$_2$[34] were synthesized via literature procedures.

Equipment. NMR spectra were recorded on either a Varian Gemini 300 MHz or a Unity 400 MHz (^{13}C) spectrometer. Chemical shifts are reported relative to residual protonated solvent peaks (^{1}H, ^{13}C) or external $\text{BF}_3\cdot\text{Et}_2\text{O}$ (^{11}B) and H_3PO_4 (^{31}P) standards. Spectra were obtained at 300 MHz (^{1}H), 96 MHz (^{11}B), 75 or 100 MHz (^{13}C), and 121 MHz (^{31}P). Infrared spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr windows. Mass spectra were obtained with a VG 70-250S mass spectrometer operating in electron impact (EI) mode. Melting point determinations were performed in sealed capillaries and are uncorrected. Elemental analyses were performed by Quantitative

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(31) Ioganson, A. V. *Hydrogen Bond*; Nauka: Moscow, 1981, as cited in: Beringhelli, T.; D'Alfonso, G.; Panigati, M.; Mercandelli, P.; Sironi, A. *Chem. Eur. J.* **2002**, *8*, 5340. Equation has units of kcal mol^{-1}.

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Table 5. Crystallographic Data and Summary of Data Collection and Refinement for Structures **1**, **3**, and **5**

	1	**3**	**5**
emp formula	$C_{14}H_{22}B_2NP$	$C_{15}H_{24}B_2NP$	$C_{13}H_{14}BP$
fw	256.92	270.94	424.04
temp (K)	150(1)	150(1)	150(1)
λ (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	*Pbca*	$P2_1/n$
cryst size (mm)	0.30 × 0.30 × 0.20	0.40 × 0.35 × 0.30	0.22 × 0.10 × 0.08
a (Å)	11.2250(3)	11.9203(2)	6.7219(3)
b (Å)	9.3830(3)	9.6239(3)	21.27300(10)
c (Å)	15.3070(5)	28.7897(7)	8.4366(5)
α (deg)	90	90	90
β (deg)	106.4140(13)	90	102.033(2)
γ (deg)	90	90	90
V (Å^3)	1546.49(8)	3302.75(14)	1179.88(9)
Z	4	8	2
D_C (g/cm^3)	1.103	1.090	1.194
μ (mm^{-1})	0.160	0.153	0.195
F(000)	552	1168	448
θ range (deg)	3.61−27.49	2.81−27.48	2.65−25.09
index ranges	$-14 \leq h \leq 14$ $-10 \leq k \leq 12$ $-19 \leq l \leq 19$	$0 \leq h \leq 15$ $0 \leq k \leq 12$ $-37 \leq l \leq 0$	$0 \leq h \leq 8$ $0 \leq k \leq 25$ $-10 \leq l \leq 9$
reflns collected	11694	20296	8458
indep reflns	3523	3776	2083
R_{int}	0.0404	0.042	0.067
GOF on F^2	1.034	1.020	1.056
$R1^a$ ($I > 2\sigma(I)$)	0.0373	0.0405	0.0422
$wR2^b$ (all data)	0.0982	0.1038	0.1082
peak/hole (e Å^{-3})	0.244/−0.319	0.252/−0.266	0.268/−0.312

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Technologies Inc., Whitehouse, NJ, or were obtained on a Perkin-Elmer Series 2400 CHNS analyzer maintained by the Analest facility at the University of Toronto. Dynamic light scattering was performed using a wide-angle laser light scattering photometer from Brookhaven Instruments Corp. See ref 7b for details on sample preparation and data analysis.

X-ray Structural Characterization. Crystallographic data and the summary of data collection and refinement for structures **1**, **3**, and **5** are presented in Table 5. Diffraction data were collected on a Nonius Kappa-CCD using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were integrated and scaled using the Denzo-SMN package.[35] The structures were solved and refined with the SHELXTL-PC V5.1 software package.[36] Refinement was by full-matrix least squares on F^2 using all data (negative intensities included). Molecular structures are presented with thermal ellipsoids at a 30% probability level. In all structures, hydrogen atoms bonded to carbon were included in calculated positions and treated as riding atoms, while those attached to nitrogen or boron were located and refined with isotropic thermal parameters. CCDC-211991 (**1**), CCDC-211992 (**3**), and CCDC-211993 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax, (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Synthesis of $MePPh_2 \cdot BH_3$. To a solution of $MePPh_2$ (13.616 g, 68.0 mmol) in THF (200 mL) cooled to −30 °C was added $BH_3 \cdot SMe_2$ (6.7 mL, 5.367 g, 70.6 mmol) dropwise via syringe over 5 min. The mixture was slowly warmed to 25 °C and stirred overnight. The volatiles were removed in vacuo to give $MePPh_2 \cdot BH_3$ as a colorless oil, which occasionally crystallized upon standing at 25 °C. Yield: 13.146 g, 90%. Mp: 48−50 °C. ^1H NMR ($CDCl_3$): δ 7.71−7.64 (m, Ph), 7.50−7.45 (m, Ph), 1.88 (d, $J_{HP} = 10$ Hz, Me), 1.02 (q, br, $J_{BH} = 93$ Hz, BH_3). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −38.2 (d, $J_{BP} = 56$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 131.9 (d, $J_{CP} = 10$ Hz, Ar), 131.4 (d, $J_{CP} = 2$ Hz, Ar), 130.7 (d, $J_{CP} = 56$ Hz, *ipso*-C), 129.0 (d, $J_{CP} = 10$ Hz, Ar), 12.1 (d, $J_{CP} = 40$ Hz, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.2 (q, $J_{PB} = 56$ Hz). EI-MS (70 eV): 211 ($M^+ - 3H$, 17%), 200 ($MePPh_2$, 100%), 185 (PPh_2, 30%).

Synthesis of $Me_2NH \cdot BH_2Cl$. To a solution of $Me_2NH \cdot BH_3$ (6.570 g, 111.5 mmol) in Et_2O (125 mL) cooled to 0 °C was added a solution of HCl in Et_2O (113 mL, 113 mmol) dropwise over 30 min. The mixture was stirred for 1 h at 0 °C, then warmed to 25 °C, and stirred for a further 1 h. The solvent was removed in vacuo to give a pale yellow oil, which was transferred to the bottom of a sublimation apparatus. The oil was distilled under dynamic vacuum (ca. 10^{-3} mmHg) and condensed onto a −15 °C coldfinger, which solidified to give $Me_2NH \cdot BH_2Cl$ as a white solid. The purified product was stored at −30 °C in the glovebox to prevent melting. Yield: 7.663 g, 74%. ^1H NMR ($CDCl_3$): δ 4.52 (br, NH), 2.61 (d, $J_{HH} = 5.8$ Hz, Me), 2.56 (q, br, $J_{BH} = 120$ Hz, BH_2). ^{11}B NMR ($CDCl_3$): δ −3.4 (t, $J_{BH} = 120$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 40.7 (Me).

Synthesis of $Me_2NH{-}BH_2{-}PPh_2{-}BH_3$ (1). A solution of ^{n}BuLi in hexanes (3.0 mL, 4.8 mmol) was added dropwise to a solution of $Ph_2PH \cdot BH_3$ (0.967 g, 4.83 mmol) in THF (15 mL) cooled to 0 °C. The reaction mixture was stirred at 0 °C for 30 min, followed by warming to 25 °C. After 2 h, the reaction mixture showed complete conversion to $Li[PPh_2 \cdot BH_3]$. $^{11}B\{^1H\}$ NMR (THF): δ −31.6 (d, $J_{BP} = 45$ Hz). $^{31}P\{^1H\}$ NMR (THF): δ −32.4 (q, $J_{PB} = 45$ Hz). The mixture was recooled to 0 °C, and a solution of $Me_2NH \cdot BH_2Cl$ (0.464 g, 4.97 mmol) in THF (10 mL) was added dropwise over 5 min. The mixture was allowed to warm to 25 °C and stirred overnight. The solvent was removed in vacuo, and the resulting solid was dissolved in toluene (50 mL) and filtered to remove LiCl. The solvent was removed to give **1** as a white powder. X-ray quality crystals of **1** were obtained from a toluene/hexanes (10:1) solution cooled to −30 °C. Yield: 0.591 g, 48%. Mp: 121−123 °C. ^1H NMR ($CDCl_3$): δ 7.76−7.68 (m, Ph), 7.36−7.30 (m, Ph), 4.76 (br, NH), 2.53 (d, $J_{HH} = 5.1$ Hz, Me), 2.3 (br, BH_2), 0.93 (q, br, $J_{BH} = 106$ Hz, BH_3). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −11.3 (d, $J_{BP} = 76$ Hz, BH_2), −39.9 (d, $J_{BP} = 59$ Hz, BH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 133.6 (d, $J_{CP} = 48$ Hz, *ipso*-C), 133.0 (d, $J_{CP} = 8$ Hz, Ar), 129.5 (d, $J_{CP} = 2$ Hz, Ar), 128.5 (d, $J_{CP} = 9$ Hz, Ar), 45.0 (d, $J_{CP} = 7$ Hz, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −19.9 (br, no resolved J_{PB} coupling). EI-MS (70 eV): *m*/*z* 243 ($M^+ - BH_3$, 99%), 186 (Ph_2PH, 100%). Elemental anal. Calcd (%) for $C_{14}H_{22}B_2NP$ (256.92): C 65.45, H 8.63, N 5.45. Found: C 65.81, H 8.86, N 5.33.

Synthesis of $Me_2NH{-}BH_2{-}PPhH{-}BH_3$ (2). **2** was synthesized by a procedure analogous to that used for **1**. After filtration and solvent removal, the residue was washed with hexanes (15 mL) and extracted with Et_2O (20 mL). Recrystallization from toluene/hexanes (10:1) at −30 °C afforded **2** as a white solid.

For $Li[PPhH \cdot BH_3]$. $^{11}B\{^1H\}$ NMR (THF): δ −34.6 (d, $J_{BP} = 32$ Hz). ^{31}P NMR (THF): δ −93.8 (dq, $J_{PB} = 34$ Hz, $J_{PH} = 202$ Hz).

For 2. Yield: 0.922 g, 83%. Mp: 70−71 °C. ^1H NMR ($CDCl_3$): δ 7.74−7.64 (m, Ph), 7.40−7.34 (m, Ph), 4.67 (br, NH), 4.61 (d (sextet), $J_{HP} = 344$ Hz, $J_{HH} = 6$ Hz, PH), 2.61 (dd, $J_{HP} = 35$ Hz, $J_{HH} = 5.8$ Hz, Me), 2.0 (br, BH_2), 0.74 (q, br, $J_{BH} = 98$ Hz, BH_3).

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(36) Sheldrick, G. M. *SHELXTL-PC V5.1*; Bruker Analytical X-Ray Systems Inc.: Madison, WI, 1997.

$^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −12.8 (d, J_{BP} = 70 Hz, BH_2), −41.5 (d, J_{BP} = 50 Hz, BH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 133.4 (d, J_{CP} = 7 Hz, Ar), 129.7 (d, J_{CP} = 2 Hz, Ar), 128.9 (d, J_{CP} = 50 Hz, *ipso*-C), 128.6 (d, J_{CP} = 9 Hz, Ar), 44.7 (d, J_{CP} = 8 Hz, Me). ^{31}P NMR ($CDCl_3$): δ −54.8 (d, br, J_{PH} = 344 Hz, no resolved J_{PB} coupling). EI-MS (70 eV): *m*/*z* 180 (M^+ − H, 9%), 167 (M^+ − BH_3, 58%), 123 ($PhPH-BH_3$, 4%), 110 ($PhPH_2$, 51%), 58 (Me_2NH-BH_2, 100%). Elemental anal. Calcd (%) for $C_8H_{18}B_2NP$ (180.83): C 53.14, H 10.03, N 7.75. Found: C 52.40, H 10.10, N 8.00.

Thermolysis of 1. A sample of **1** (0.151 g, 0.588 mmol) was heated at 130 °C under nitrogen for 20 h in the absence of solvent. The reaction mixture showed the presence of the following products by NMR ($CDCl_3$): Ph_2PH ($^{31}P\{^1H\}$ NMR δ −40.3; trace), $Ph_2PH{\cdot}BH_3$ ($^{11}B\{^1H\}$ NMR δ −40.0; $^{31}P\{^1H\}$ NMR δ 1.5; ca. 35%), $Ph_2PH-BH_2-PPh_2-BH_3$ ($^{11}B\{^1H\}$ NMR δ −33.3 (BH_2), −37.4 (BH_3); $^{31}P\{^1H\}$ NMR δ −3.5 (Ph_2PH), −18.6 (PPh_2); ca. 15%), $[Me_2N-BH_2]_2$ (^{11}B NMR δ 4.9 (t); ca. 40%), $Me_2NH{\cdot}BH_3$ (^{11}B NMR δ −14.1 (q); ca. 10%), unreacted **1** and an unidentified product ($^{11}B\{^1H\}$ NMR δ −35.6; $^{31}P\{^1H\}$ NMR δ −26.8; ca. 5%).

Thermolysis of 2. A sample of **2** (2.569 g, 14.21 mmol) was heated at 130 °C under nitrogen for 2 h in the absence of solvent. The ^{11}B and ^{31}P NMR spectra of the reaction mixture showed the presence of only $[Me_2N-BH_2]_2$ and $[PhPH-BH_2]_n$. The semisolid was evacuated at 25 °C for 24 h to remove $[Me_2N-BH_2]_2$. The residue was then dissolved in $CHCl_3$ and precipitated into hexanes, giving $[PhPH-BH_2]_n$ as a white solid. Yield: 1.724 g, 99%. ^1H NMR ($CDCl_3$): δ 7.5−6.9 (br, Ph), 4.4 (br d, J_{HP} = 309 Hz, PH), 2.1−1.1 (br, BH_2). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −33.6 (br). ^{31}P NMR ($CDCl_3$): δ −49.5 (br d, J_{PH} = 309 Hz). Dynamic light scattering (THF): after 3 h, D_h = 1.8 nm, 163 nm; after 4 days: 1.43 nm. The peak at D_h = 1.4−1.8 nm corresponds to an absolute value of M_w of ca. 5000.[7b]

Attempted Catalytic Dehydrocoupling of 1. (a) To a solution of **1** (0.319 g, 1.24 mmol) in toluene (2 mL) was added $[Rh(1,5\text{-}cod)(\mu\text{-}Cl)]_2$ (0.009 g, 0.02 mmol, 1.5 mol %). The mixture was heated to 50 °C and monitored periodically by ^{11}B and ^{31}P NMR spectroscopy. Complete conversion of **1** to form $[Me_2N-BH_2]_2$ (ca. 45%), $Me_2NH{\cdot}BH_3$ (ca. 5%), $Ph_2PH{\cdot}BH_3$ (ca. 50%), and Ph_2PH (trace) was observed after 10 days. (b) Blank reaction: A sample of **1** heated at 50 °C in toluene in the absence of catalyst indicated the presence of chain cleavage products (35%) after 10 days. The chain cleavage products were found to be the same as those identified above, with the exception of $[Me_2N-BH_2]_2$, which was not formed from $Me_2NH{\cdot}BH_3$ in the absence of a transition-metal catalyst.[11]

Attempted Catalytic Dehydrocoupling of 2. (a) To a solution of **2** (0.086 g, 0.48 mmol) in toluene (2 mL) was added $[Rh(1,5\text{-}cod)(\mu\text{-}Cl)]_2$ (0.003 g, 0.006 mmol, 1.3 mol %). The mixture was heated to 50 °C and monitored periodically by ^{11}B and ^{31}P NMR spectroscopy. Complete conversion of **2** to form $[Me_2N-BH_2]_2$ (ca. 40%), $Me_2NH{\cdot}BH_3$ (ca. 10%), $PhPH_2{\cdot}BH_3$ ($^{11}B\{^1H\}$ NMR δ −40.8 (br); $^{31}P\{^1H\}$ NMR δ −49 (v br); ca. 50%), and $PhPH_2$ ($^{31}P\{^1H\}$ NMR δ −123.8, trace) was observed after 10 days. (b) Blank reaction: A sample of **2** heated at 50 °C in toluene in the absence of catalyst indicated the presence of chain cleavage products (ca. 10%) after 10 days. The chain cleavage products were found to be the same as those identified above, with the exception of $[Me_2N-BH_2]_2$, which was not formed from $Me_2NH{\cdot}BH_3$ in the absence of a transition-metal catalyst.[11]

Synthesis of $Me_2NH-BH_2-CH_2-PPh_2-BH_3$ (3). To a solution of $MePPh_2{\cdot}BH_3$ (1.168 g, 5.46 mmol) in THF (10 mL) cooled to 0 °C was added a solution of ^nBuLi in hexanes (3.6 mL, 5.8 mmol) dropwise via syringe. The mixture was stirred for 30 min at 0 °C, then warmed to 25 °C, and stirred for a further 90 min. ^{11}B and ^{31}P NMR of the reaction mixture indicated complete conversion to $Li[CH_2-PPh_2{\cdot}BH_3]$: $^{11}B\{^1H\}$ NMR (THF), δ −36.1 (d, J_{BP} = 76 Hz); $^{31}P\{^1H\}$ NMR (THF), δ 19.2 (q, J_{PB} = 76 Hz). The mixture was recooled to −30 °C, and a solution of $Me_2NH{\cdot}BH_2Cl$ (0.526 g, 5.63 mmol) in THF (5 mL) was added. The mixture was allowed to warm slowly to 25 °C and stirred overnight. The volatiles were removed in vacuo, and the resulting oil was redissolved in toluene (15 mL) and filtered to remove LiCl. The solution was concentrated to ca. 5 mL, added to hexanes (20 mL), and filtered. Upon standing at 25 °C, colorless crystals of X-ray quality were formed over 3−4 days. Yield: 0.294 g, 20%. Mp: 106−108 °C. ^1H NMR ($CDCl_3$): δ 7.74−7.66 (m, Ph), 7.44−7.36 (m, Ph), 5.12 (br, NH), 2.53 (d, J_{HH} = 5.7 Hz, Me), 1.31 (m, br, CH_2), 0.97 (m, br, BH_2 and BH_3). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −11.7 (BH_2), −40.2 (BH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 132.9 (d, J_{CP} = 55 Hz, *ipso*-C), 132.1 (d, J_{CP} = 8 Hz, Ar), 130.5 (d, J_{CP} = 2 Hz, Ar), 128.6 (d, J_{CP} = 10 Hz, Ar), 42.4 (s, Me), 10.9 (s, br, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16.6 (q, J_{PB} = 79 Hz). EI-MS (70 eV): *m*/*z* 257 (M^+ − BH_3, 75%). Elemental anal. Calcd (%) for $C_{15}H_{24}B_2NP$ (270.94): C 66.49, H 8.93, N 5.17. Found: C 66.44, H 8.95, N 5.03.

Synthesis of $Me_2NH-BH_2-CH_2-PMe_2-BH_3$ (4). A procedure analogous to that of **3** was used. After filtration to remove LiCl, the oily residue was recrystallized (Et_2O/hexanes (5:1), −30 °C) to afford a mixture of **4** and $Me_3P{\cdot}BH_3$. The solid mixture was fractionally sublimed at 25 °C: $Me_3P{\cdot}BH_3$ was first removed under static vacuum, followed by sublimation of the residue under dynamic vacuum, which afforded **4** as a white solid.

For $Li[CH_2-PMe_2{\cdot}BH_3]$. $^{11}B\{^1H\}$ NMR (THF): δ −34.1 (d, J_{BP} = 85 Hz). $^{31}P\{^1H\}$ NMR (THF): δ 1.7 (q, J_{PB} = 85 Hz).

For 4. Yield: 0.506 g, 32%. Mp: 71−73 °C. ^1H NMR (C_6D_6): δ 4.89 (br, NH), 2.16 (q, br, BH_3), 1.88 (d, J_{HH} = 5.7 Hz, NMe), 1.14 (q, br, BH_2), 1.00 (d, J_{HP} = 10.6 Hz, PMe), 0.54 (m, br, CH_2). ^{11}B NMR (C_6D_6): δ −9.9 (t, J_{BH} = 98 Hz, BH_2), −40.2 (dq, J_{BP} = 70 Hz, J_{BH} = 94 Hz, BH_3). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 41.8 (s, NMe), 14.2 (m, br, CH_2), 13.4 (d, J_{CP} = 38 Hz, PMe). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 3.1 (q, J_{PB} = 70 Hz). EI-MS (70 eV): *m*/*z* 133 (M^+ − BH_3, 100%), 88 ($CH_2-PMe_2-BH_2$, 24%). Elemental anal. Calcd (%) for $C_5H_{20}B_2NP$ (146.82): C 40.90, H 13.73, N 9.54. Found: C 41.14, H 13.49, N 9.68.

Thermolysis of 3; Synthesis of $[BH_2-CH_2-PPh_2]_2$ (5). A sample of **3** (0.166 g, 0.613 mmol) was heated at 130 °C for 24 h in the absence of solvent. The mixture was cooled to 25 °C, giving **5** as a white solid. X-ray quality crystals were grown from an ether solution at −20 °C. Yield: 0.127 g, 98%. Mp: 253 °C. ^1H NMR ($CDCl_3$): δ 7.71 (m, Ph), 7.38 (m, Ph), 1.62 (br, CH_2), 2.3−0.8 (br, BH_2). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −33.6 (br, BH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 132.0 (d, J_{CP} = 9 Hz, Ar), 131.4 (d, J_{CP} = 54 Hz, *ipso*-C), 130.6 (s, Ar), 128.8 (d, J_{CP} = 9 Hz, Ar), 6.3 (br, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 7.7 (br, PPh_2). EI-MS (70 eV): *m*/*z* 424 (M^+, 10%), 346 (M^+ − C_6H_6, 33%), 313 (M^+ − PPhH − H_2, 36%), 237 (M^+ − PPh_2 − H_2, 100%), 212 (M^+/2, 6%). Elemental anal. Calcd (%) for $C_{13}H_{14}BP$ (212.02): C 73.64, H 6.65. Found: C 73.23, H 6.57.

Attempted Catalytic Dehydrocoupling of 3. (a) A sample of **3** (0.035 g, 0.13 mmol) and $[Rh(1,5\text{-}cod)(\mu\text{-}Cl)]_2$ (0.003 g, 0.006 mmol, 5 mol %) were dissolved in toluene in a 5 mm NMR tube with a D_2O insert. No reaction was observed by ^{11}B or ^{31}P NMR after 24 h at 25 °C, or after 24 h at 50 °C. Heating at 90 °C for 20 h resulted in chain cleavage, with the only identified product being $MePPh_2{\cdot}BH_3$. (b) Blank reaction: Heating of **3** in toluene at 90 °C in the absence of catalyst resulted in no reaction after 20 h.

Thermolysis of 4. (a) A sample of **4** (0.143 g, 0.974 mmol) was heated at 90 °C for 3 days in the absence of solvent. Colorless crystals of **4** were observed to sublime to the top of the reaction vessel. Partial decomposition (ca. 50%) to give $Me_2NH{\cdot}BH_3$ (ca. 20%), $Me_3P{\cdot}BH_3$ (^{11}B NMR δ −37.4 (qd); ^{31}P{^{1}H} NMR δ −1.89 (q); ca. 20%) and a product tentatively assigned as $[BH_2{-}CH_2{-}PMe_2]_2$ (**6**) was observed. Selected NMR characterization for **6**: yield (11% by NMR); ^{1}H NMR (C_6D_6) δ 1.52 (d, $J_{HP} = 13$ Hz, Me); ^{11}B NMR (C_6D_6) δ −30.5 (dt, $J_{BP} = 61$ Hz, $J_{BH} =$ ca. 91 Hz); ^{13}C{^{1}H} NMR (C_6D_6) δ 10.6 (d, $J_{CP} = 37$ Hz, Me); ^{31}P{^{1}H} NMR (C_6D_6) δ 6.0 (q, br). (b) A sample of **4** (0.048 g, 0.33 mmol) was heated at 130 °C in DMF-d_7. After 5 h, the mixture contained only $[Me_2N{-}BH_2]_2$ and $Me_3P{\cdot}BH_3$.

Attempted Catalytic Dehydrocoupling of 4. (a) A sample of **4** (0.061 g, 0.42 mmol) and $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (0.003 g, 0.006 mmol, 1 mol %) were dissolved in THF and stirred at 25 °C for 2 days. No reaction was observed according to the ^{11}B and ^{31}P spectra obtained. Heating at 90 °C in toluene for 20 h resulted in chain cleavage, with the only identified product being $Me_3P{\cdot}BH_3$. (b) Blank reaction: Heating of **4** in toluene at 90 °C in the absence of catalyst resulted in no reaction after 20 h.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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