Rhodium-Catalyzed Dehydrocoupling of the Sterically Encumbered Phosphine−Borane Adduct tBu$_2$PH·BH$_3$: Synthesis of the Linear Dimers tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_3$ and tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_2$Cl

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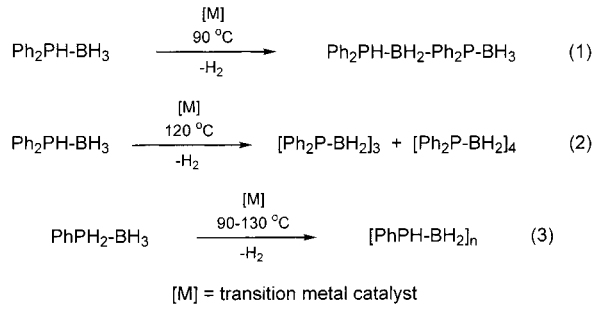
The dehydrocoupling of the sterically hindered phosphine−borane adduct tBu$_2$PH·BH$_3$ above 140 °C is catalyzed by the rhodium complexes [Rh(1,5-cod)$_2$][OTf] or Rh$_6$(CO)$_{16}$ to give the four-membered chain tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_3$ (**1**), which was isolated in 60% yield and characterized by multinuclear NMR spectroscopy, mass spectrometry, and elemental analysis. Thermolysis of **1** in the temperature range 175−180 °C led to partial decomposition and the formation of tBu$_2$PH·BH$_3$. When the dehydrocoupling of tBu$_2$PH·BH$_3$ was performed in the presence of [{Rh(μ-Cl)(1,5-cod)}$_2$] or RhCl$_3$ hydrate, the chlorinated compound tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_2$-Cl (**2**) was formed which could not be obtained free of **1**. The molecular structures of tBu$_2$PH·BH$_3$, tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_3$ (**1**), and tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_2$Cl (**2**) together with **1** were determined by single-crystal X-ray diffraction studies.

Introduction

The development of new and efficient synthetic procedures for the formation of bonds between main group elements is of importance for the construction of inorganic polymer chains and also for the general development of p-block chemistry. In recent years, transition-metal-catalyzed dehydrocoupling routes have been established for the preparation of homonuclear and heteronuclear bonds between main group elements.[1] Species containing Si−Si,[1,2] Ge−Ge,[1,3] Sn−Sn,[1,4] P−P,[1,5] B−Si,[6] P−Si,[7] and O−Si[8] bonds have received particular attention.

As part of our continuing program to develop novel extended structures based on main group elements, we are currently exploring compounds with four-coordinate phosphorus and boron atoms. Cyclic phosphinoboranes of the general formula [R$_2$P−BH$_2$]$_x$ (R = alkyl or aryl, x = 3) are well-known as a result of the pioneering work of Burg and Wagner in the 1950s.[9,10] In contrast, the synthesis of well-characterized linear and polymeric phosphinoboranes represents a relatively unexplored area of research.[11] We have recently reported the transition-metal-catalyzed dehydrocoupling of the phosphine−borane adducts Ph$_2$PH·BH$_3$ and RPH$_2$·BH$_3$ (R = Ph or *i*Bu) to yield novel linear and cyclic phosphinoboranes, as well as the first high molecular weight polyphosphinoboranes (Scheme 1).[12−15] For example, dehydrocoupling of Ph$_2$PH·BH$_3$ at 90 °C in the presence of rhodium complexes such as [Rh(1,5-cod)$_2$][OTf] (cod = cyclooctadiene) or [{Rh(μ-Cl)(1,5-cod)}$_2$] was found to result in the quantitative formation of the four-membered chain Ph$_2$PH−BH$_2$−Ph$_2$P−BH$_3$, whereas at more elevated temperatures (120 °C) a mixture of the rings [Ph$_2$P−BH$_2$]$_3$ and [Ph$_2$P−BH$_2$]$_4$ is formed. In contrast, rhodium-catalyzed dehydrocoupling of the primary phosphine−borane adduct PhPH$_2$·BH$_3$ afforded the high molecular weight poly-

Scheme 1



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(1) For a recent review on catalytic dehydrocoupling, see: Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363.
(2) (a) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc*. **1986**, *108*, 4059. (b) Tilley, T. D. *Acc. Chem. Res*. **1993**, *26*, 22.
(3) For catalytic demethanative coupling, see: Katz, S. M.; Reichl, J. A.; Berry, D. H. *J. Am. Chem. Soc*. **1998**, *120*, 9844.
(4) (a) Imori, T.; Tilley, T. D. *J. Chem. Soc., Chem. Commun*. **1993**, 1607. (b) Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc*. **1995**, *117*, 9931. (c) Babcock, J. R.; Sita, L. R. *J. Am. Chem. Soc*. **1996**, *118*, 12481.
(5) Etkin, N.; Fermin, M. C.; Stephan, D. W. *J. Am. Chem. Soc.* **1997**, *119*, 2954.
(6) Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1993**, *12*, 177.
(7) Shu, R.; Hao, L.; Harrod, J. F.; Woo, H.-G.; Samuel, E. *J. Am. Chem. Soc*. **1998**, *120*, 12988.
(8) Zhang, R.; Mark, J. E.; Pinhas, A. R. *Macromolecules* **2000**, *33*, 3508.
(9) Burg, A. B.; Wagner, R. I. *J. Am. Chem. Soc*. **1953**, *75*, 3872.
(10) For reviews, see: (a) Parshall, G. W. In *The Chemistry of Boron and its Compounds*; Muetterties, E. L., Ed.; Wiley: New York, 1967; p 617. (b) Haiduc, I. *The Chemistry of Inorganic Ring Systems*; Wiley: New York, 1970; p 349.
(11) See, for example: (a) Wagner, R. I.; Caserio, F. F. *J. Inorg. Nucl. Chem.* **1959**, *11*, 259. (b) Burg, A. B. *J. Inorg. Nucl. Chem.* **1959**, *11*, 258.
(12) Dorn, H.; Singh, R. A.; Massey, J. A.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed.* **1999**, *38*, 3321.
(13) 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.
(14) Dorn, H.; Jaska, C. A.; Singh, R. A.; Lough, A. J.; Manners, I. *Chem. Commun*. **2000**, 1041.
(15) For a recent report of N−B bond formation by catalytic dehydrocoupling, see: Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *Chem. Commun*., in press.

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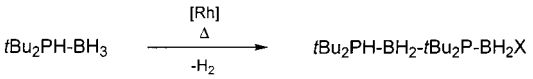
Table 1. Dehydrocoupling of tBu$_2$PH·BH$_3$[a]

entry	catalyst	cat. load (mol % Rh)	temp (°C)	time (h)	conversion[b] (%)	products[b] (%)
1	[Rh(1,5-cod)$_2$][OTf]	3	140	16	75	**1** (70), others (5)[c]
2	none		140	16	0	
3	[Rh(1,5-cod)$_2$][OTf]	3	160	3	40	**1** (35), others (5)[c]
4	Rh$_6$(CO)$_{16}$	3	160	3	60	**1** (60)
5	[{Rh(μ-Cl)(1,5-cod)}$_2$]	3	160	3	80	**1** (70), **2** (3), others (7)
6	RhCl$_3$ hydrate	3	160	3	50	**1** (40), **2** (7), others (3)
7	none		160	3	10	**1** (10)
8	Rh$_6$(CO)$_{16}$	5	160	63	85	**1** (80), others (5)
9	none		160	63	65−70	**1** (50), others (15−20)[c,d]
10	[{Rh(μ-Cl)(1,5-cod)}$_2$]	10	160	16	85	**1** (60), **2** (10), others (15)[e]
11	RhCl$_3$ hydrate	10	160	16	85−90	**1** (55), **2** (25), others (5−10)[e]

[a] All reactions performed without solvent, using ca. 200−250 mg of tBu$_2$PH·BH$_3$. [b] Estimated from the integrals of the ^{31}P NMR spectra. However, product ratios could not always be determined to high accuracy (ca. ±5%) as small amounts of tBu$_2$PH·BH$_3$ and **1** were found to sublime out of the reaction mixture at high temperatures. Also, small amounts of tBu$_2$P(O)H (δ 67.0 ppm) and tBu$_2$PH (δ 21.0 ppm) were sometimes detected. [c] A broad resonance at δ 28−29 ppm (unknown compound(s)) was observed. [d] A broad resonance at δ 33−34 ppm (unknown compound(s)) was observed. [e] A broad resonance at δ 8.5 ppm (unknown compound(s)) was observed.

Scheme 2



1: X = H
2: X = Cl

phosphinoborane [PhPH−BH$_2$]$_n$. These results indicate that there is considerable potential for the development of molecular and polymeric phosphinoborane chemistry based on metal-catalyzed dehydrocoupling procedures.

As part of our efforts to examine the scope and limitations of this novel catalytic chemistry, in this paper we report full details of our dehydrocoupling studies of the highly sterically encumbered phosphine−borane adduct tBu$_2$PH·BH$_3$.

Results and Discussion

Dehydrocoupling of tBu$_2$PH·BH$_3$ in the Presence of [Rh(1,5-cod)$_2$][OTf] or Rh$_6$(CO)$_{16}$. Similar to the formation of Ph$_2$PH−BH$_2$−Ph$_2$P−BH$_3$ from Ph$_2$PH·BH$_3$,[12,13] the dehydrocoupling of tBu$_2$PH·BH$_3$ is catalyzed by the rhodium complexes [Rh(1,5-cod)$_2$][OTf] or Rh$_6$(CO)$_{16}$ to give the linear dimer tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_3$ (**1**), as is shown in Scheme 2. The results are summarized in Table 1.

[Rh(1,5-cod)$_2$][OTf] acts as an efficient catalyst for the dehydrogenative coupling of tBu$_2$PH·BH$_3$ at 140 °C (16 h) to give compound **1** in ca. 70% yield, whereas no reaction occurred in the absence of any catalyst under these conditions (entries 1 and 2, respectively). Entries 3−7 confirm the catalytic activity of various rhodium complexes when the reaction is performed at 160 °C for 3 h: 35% of compound **1** was produced when [Rh(1,5-cod)$_2$][OTf] (entry 3) was used as dehydrocoupling catalyst, and 60% of compound **1** was obtained in the presence of Rh$_6$(CO)$_{16}$ (entry 4), while the control experiment without catalyst showed only 10% conversion to **1** (entry 7). Under these conditions, the chlorine-containing rhodium complexes [{Rh(μ-Cl)(1,5-cod)}$_2$] and RhCl$_3$ hydrate were also found to give high conversions of tBu$_2$PH·BH$_3$ (entries 5 and 6, respectively), which is further discussed below. On heating tBu$_2$PH·BH$_3$ to 160 °C for 63 h in the presence of Rh$_6$(CO)$_{16}$, compound **1** was obtained in 80% yield (entry 8). In the blank experiment at 160 °C (63 h) ca. 65−70% conversion of tBu$_2$PH·BH$_3$ was observed; however, only 50% of compound **1** was produced together with 15−20% of other compounds (entry 9).

Pure compound **1** was obtained from a larger scale experiment following the dehydrocoupling conditions outlined in entry 8 (Table 1) and subsequent crystallization from diethyl ether. The isolated yield of the colorless, air- and moisture stable dimer **1** was approximately 60% (based on tBu$_2$PH·BH$_3$). ^{31}P{^{1}H} NMR spectroscopy in CDCl$_3$ showed two broad resonances centered at δ 39.5 ppm (tBu$_2$PH) and δ 13.2 ppm (tBu$_2$P); the resonance at δ 39.5 ppm split further into a doublet when the proton-coupled spectrum was recorded (J_{PH} = 371 Hz). In the ^{1}H NMR spectrum, the proton attached to phosphorus was observed at δ 4.57 ppm, with a PH coupling constant of 371 Hz. The protons of the tBu groups were detected as two doublets at δ 1.37 ppm and δ 1.22 ppm, respectively. The BH$_3$ protons appeared as a broad quartet around δ 0.45 ppm (J_{BH} ca. 95 Hz) while the BH$_2$ protons could not be observed. In the ^{11}B{^{1}H} NMR spectrum of **1**, only one broad multiplet in the region δ −37.2 to −40.8 ppm was detected, indicating that the two boron environments are quite similar. The ^{31}P and ^{11}B NMR spectra of **1** may be compared to those of the related compound Ph$_2$PH−BH$_2$−Ph$_2$P−BH$_3$. The ^{31}P{^{1}H} NMR chemical shifts of the latter appear at higher field and are both negative (δ −3.3 ppm, Ph$_2$PH, and δ −17.7 ppm, Ph$_2$P), which is in agreement with the relative chemical shifts observed for the free phosphines (tBu$_2$PH, δ 21.0 ppm; Ph$_2$PH, δ −41.1 ppm). The ^{11}B{^{1}H} NMR spectrum of Ph$_2$PH−BH$_2$−Ph$_2$P−BH$_3$ displayed two distinct broad signals, one at δ −33.2 ppm (BH$_2$) and another at δ −37.3 ppm (BH$_3$). In the EI mass spectrum (70 eV) of **1** a peak at m/z 317 (19%) is attributable to loss of one hydrogen from the molecular ion. The 100% intensity peak corresponds to tBu$_2$PH (m/z 146).

Thermal Decomposition of tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_3$ (1). A sample of pure compound **1** was heated at 175−180 °C for 16 h. The resulting off-white residue was dissolved in CDCl$_3$ and analyzed by ^{31}P NMR spectroscopy. The complex spectrum showed major signals at δ 39.5 and 13.2 ppm (**1**), and at δ 48.9 ppm (q, tBu$_2$PH·BH$_3$). Broad resonances of lower intensity found at δ 53.8, 34.0, 26.5, and 8.5 ppm are characteristic of phosphinoborane compounds; however, these species could not be identified. In addition, small amounts of tBu$_2$P(O)H (δ 67.0 ppm) and tBu$_2$PH (δ 21.0 ppm) were detected. Clearly, compound **1** decomposed partially upon heating with breaking of P−B bonds, since a significant amount of the starting material tBu$_2$PH·BH$_3$ and traces of tBu$_2$P(O)H and tBu$_2$PH were formed during the reaction. Recently, Gaumont et al. reported on the flash vacuum pyrolysis of tBu$_2$PH·BH$_3$ above 300 °C, and the only volatile products that could be detected by mass spectrometry were tBu$_2$PH, BH$_3$ and isobutene, while the nonvolatile products were not analyzed.[16]

Dehydrocoupling of tBu$_2$PH·BH$_3$ in the Presence of Chlorine-Containing Rhodium Complexes. A new product, tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_2$Cl (**2**), was identified when chlorine-

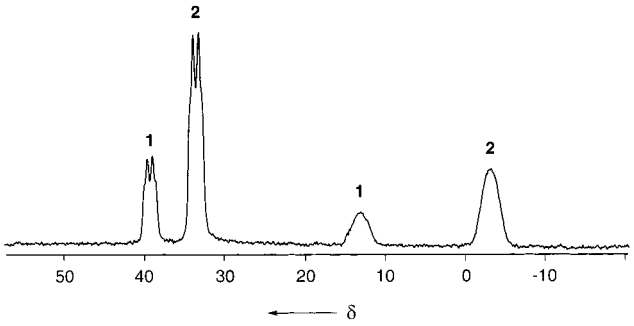


Figure 1. ^{31}P{^{1}H} NMR spectrum of a mixture of tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_2$Cl (**2**) and tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_3$ (**1**) in CDCl$_3$.

containing rhodium complexes were used to promote the dehydrocoupling of tBu$_2$PH·BH$_3$ (Scheme 2). Entries 5 and 6 of Table 1 demonstrate that [{Rh(μ-Cl)(1,5-cod)}$_2$] and RhCl$_3$ hydrate are suitable dehydrocoupling catalysts; however, this was accompanied by a chlorination reaction at the terminal BH$_3$ group of compound **1**. The amount of compound **2** could be increased using higher catalyst loads. For example, the use of [{Rh(μ-Cl)(1,5-cod)}$_2$] as catalyst (ca. 10 mol % Rh) gave a mixture of ca. 60% **1** and 10% **2** at 160 °C after 16 h (entry 10); however, small amounts of byproducts were also detected by ^{31}P NMR spectroscopy. A higher amount of the chlorinated product **2** (ca. 25%, along with ca. 55% **1**) was formed in the presence of RhCl$_3$ hydrate (ca. 10 mol % Rh) after 16 h at 160 °C (entry 11). After crystallization from diethyl ether, compound **2** was obtained as the major component (ca. 3:1 ratio, based on integration of ^{1}H NMR spectra). These crystals were also selected for X-ray diffraction experiments, which are discussed below. Unfortunately, compound **2** could not be isolated free of **1**. Consequently, multinuclear NMR spectroscopy of this mixture also displayed all signals characteristic for **1**. In the ^{31}P NMR spectrum, signals centered at δ 33.5 and −3.3 ppm were assigned to the tBu$_2$PH (J_{PH} = 380 Hz) and tBu$_2$P groups of **2**, respectively (Figure 1).

In addition, a new resonance at δ −15.8 ppm in the ^{11}B{^{1}H} NMR spectrum was assigned to the BH$_2$Cl group and reflects the electron-deficient environment of the latter. The ^{1}H NMR resonance for the PH proton of **2** (δ 5.01 ppm, J_{PH} = 380 Hz) was shifted downfield by about δ 0.4 ppm from that observed for **1**, while the resonances of the tBu protons (δ 1.39 ppm and δ 1.31 ppm) were similar. BH$_2$ and BH$_3$ proton signals appeared just above the baseline, and chemical shifts could not be extracted from the ^{1}H NMR spectrum. The EI mass spectrum (70 eV) of this sample exhibited the molecular ion peak for **2** at m/z 352 (5%) and for **1** at m/z 318 (16%).

Discussion. Our results clearly show that the dehydrocoupling of tBu$_2$PH·BH$_3$ is much more sluggish than that observed for Ph$_2$PH·BH$_3$ and requires higher temperatures. Also, it should be noted that the amount of byproducts (tBu$_2$P(O)H, tBu$_2$PH, and compounds of unknown composition) is higher and that we did not find reaction conditions that allowed for full conversion of tBu$_2$PH·BH$_3$; in fact, the heating of neat compound **1** led to the starting material tBu$_2$PH·BH$_3$ (along with other products). This difference in ease of dehydrocoupling was also observed previously for the catalytic dehydropolymerization of iBuPH$_2$·BH$_3$ and PhPH$_2$·BH$_3$, where the alkyl-substituted adduct required heating at 120 °C for 13 h and the aryl-substituted adduct required only 6 h at 90−130 °C for complete conversion.[12,13] The exact reasons for this difference in rate are not known, but it is very likely that steric problems contribute in the case of tBu$_2$PH·BH$_3$. Consistent with this idea is the observation that cyclic or polymeric phosphinoboranes could not be isolated from our experiments and are obviously not a major product. Besides these steric factors, we believe that the ease of P−B bond formation also depends on the polarity of the P−H bond (and thus inductive effects). Since alkyl substituents are generally more effective donors than aryl substituents, the P−H(δ+) bond in tBu$_2$PH should be less polar than that in Ph$_2$PH or PhPH$_2$. With the hydrogens attached to boron having a partial negative charge (B−H(δ−)), the dehydrocoupling (i.e., elimination of H$_2$) of phosphine−borane adducts should occur at a faster rate with increasing polarity of the P−H bond.[17,18]

Another interesting feature is the chlorination at the terminal BH$_3$ group of **1** to give tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_2$Cl (**2**), when the dehydrocoupling reaction is catalyzed by [{Rh(μ-Cl)(1,5-cod)}$_2$] or RhCl$_3$ hydrate. This may be a consequence of the high temperatures, causing chlorine ligand displacement from the rhodium center accompanied by chlorination at the sterically less shielded BH$_3$ group; this phenomenon was not observed during our studies of the catalytic dehydrocoupling of Ph$_2$PH·BH$_3$.[19] However, the chlorination of a borane fragment by a rhodium complex has been observed previously, e.g., in the reaction of BH$_3$·THF with [{(η^5-C$_5$Me$_5$)RhCl$_2$}$_2$] to give BH$_2$Cl.[20]

X-ray Crystallographic Studies. The molecular structures of tBu$_2$PH·BH$_3$, tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_3$ (**1**), and a mixture of tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_2$Cl (**2**) and **1** were determined by X-ray crystallography, and SHELXTL drawings are shown in Figures 2, 3, and 4, respectively. Crystallographic data and details of the structural determination are given in Table 2.

Crystals of tBu$_2$PH·BH$_3$ suitable for X-ray analysis were obtained by overnight sublimation at room temperature under an atmosphere of nitrogen. The four molecules in the unit cell are separated by the normal van der Waals distances; no intermolecular hydrogen bonding was observed. The geometry around phosphorus and boron is approximately tetrahedral, and their substituents are oriented in a staggered conformation (Figure 2). The smallest angle at phosphorus is 99.4(7)° (H1P−P1−C5), and the largest is 115.45(8)° (C1−P1−C5), while the angles at boron range from 105.4(12)° to 114.9(16)°. The P−B bond length of 1.936(2) Å is somewhat longer than those reported for, e.g., (cHex)$_2$PH·BH$_3$ (1.919(3) Å)[21] or Ph$_3$P·BH$_3$ (av 1.917 Å),[22] but shorter than the one in RR′PH·BH$_3$ (1.944(8) Å, R = mesityl, R′ = menthyl) which bears organic substituents of significant size.[23]

An X-ray diffraction study of **1** was carried out on a single crystal grown from diethyl ether over a period of several days

(16) Gaumont, A.-C.; Bourumeau, K.; Denis, J.-M.; Guenot, P. *J. Organomet. Chem*. **1994**, *484*, 9.

(17) The differences in dehydrocoupling rates were also confirmed by heating equimolar mixtures of Ph$_2$PH·BH$_3$ and tBu$_2$PH·BH$_3$ in the presence of Rh catalysts, showing that Ph$_2$PH·BH$_3$ reacts much faster than tBu$_2$PH·BH$_3$.

(18) Generally, the literature on P−B bond features is surprisingly limited and, to our knowledge, studies explaining the differences in reactivity between various phosphine−borane adducts have not been reported. For recent reviews on phosphine−borane chemistry, see: (a) Brunel, J. M.; Faure, B.; Maffei, M. *Coord. Chem. Rev*. **1998**, *178*−*180*, 665. (b) Carboni, B.; Monnier, L. *Tetrahedron* **1999**, *55*, 1197.

(19) A referee has pointed out that chlorination of tBu$_2$PH·BH$_3$ to give tBu$_2$PH·BH$_2$Cl may precede the dehydrocoupling events. We were unable to observe tBu$_2$PH·BH$_2$Cl by ^{31}P or ^{11}B NMR spectroscopy; however, it is possible that it is formed during the initial stages of the reaction and then undergoes fast dehydrocoupling with tBu$_2$PH·BH$_3$ to give compound **2**.

(20) Lei, X.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc*. **1998**, *120*, 2686.

(21) Day, M. W.; Mohr, B.; Grubbs, R. H. *Acta Crystallogr*. **1996**, *C52*, 3106.

(22) Huffman, J. C.; Skupinski, W. A.; Caulton, K. G. *Cryst. Struct. Commun.* **1982**, *11*, 1435.

(23) Bader, A.; Pabel, M.; Willis, A. C.; Wild, S. B. *Inorg. Chem*. **1996**, *35*, 3874.

Table 2. Crystallographic Data and Structure Refinement

	tBu$_2$PH·BH$_3$	**1**	**2** and **1**
formula	$C_8H_{22}BP$	$C_{16}H_{42}B_2P_2$	$C_{16}H_{41.21}B_2Cl_{0.79}P_2$
fw	160.04	318.06	345.18
temp, K	150(1)	150(1)	240(1)
cryst syst	orthorhombic	triclinic	monoclinic
space group	*Pna*2(1)	$P\bar{1}$	*P*2(1)/*n*
a, Å	15.9731(3)	8.8850(2)	8.7446(3)
b, Å	8.7103(4)	11.1510(4)	24.6411(9)
c, Å	7.8725(7)	11.3390(4)	10.4574(5)
α, deg	90	87.2910(14)	90
β, deg	90	76.9920(16)	101.857(2)
γ, deg	90	70.411(2)	90
vol, Å^3	1095.30(11)	1030.76(6)	2205.25(15)
Z	4	2	4
density, g cm^{-3}	0.970	1.025	1.040
abs coeff., mm^{-1}	0.191	0.202	0.286
F(000)	360	356	762
cryst size, mm	0.25 × 0.20 × 0.16	0.34 × 0.28 × 0.26	0.27 × 0.25 × 0.22
θ range, deg	2.55−27.48	2.60−27.54	2.59−30.04
index ranges	$-20 \le h \le 20$, $-11 \le k \le 11$, $-10 \le l \le 10$	$0 \le h \le 11$, $-13 \le k \le 14$, $-14 \le l \le 14$	$-9 \le h \le 12$, $-34 \le k \le 0$, $-10 \le l \le 14$
reflns collected	6569	11323	16496
indep reflns	2344 ($R_{int} = 0.043$)	4705 ($R_{int} = 0.040$)	6348 ($R_{int} = 0.028$)
GOF on F^2	1.023	1.055	1.035
R1[a] ($I > 2\sigma(I)$)	0.0350	0.0396	0.0535
wR2[b] (all data)	0.0821	0.0975	0.1381
peak/hole, e Å^{-3}	0.156/−0.193	0.267/−0.315	0.365/−0.282

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

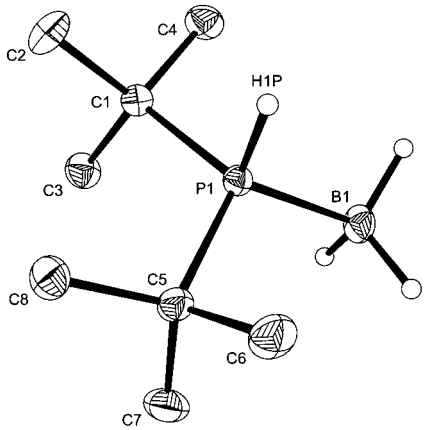


Figure 2. Molecular structure of tBu$_2$PH·BH$_3$. Selected bond lengths (Å) and angles (deg): P1−B1 1.936(2), P1−C1 1.8568(18), P1−C5 1.8627(18), P1−H1P 1.350(16); H1P−P1−B1 113.4(7), C1−P1−B1 113.03(10), C5−P1−B1 112.76(10). Hydrogen atoms attached to carbon atoms are omitted.

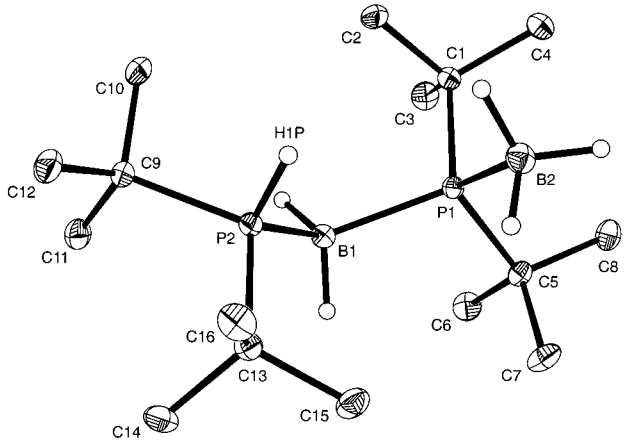


Figure 3. Molecular structure of tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_3$ (**1**). Selected bond lengths (Å) and angles (deg): P2−B1 1.9544(19), P1−B1 1.9794(18), P1−B2 1.9536(19), P2−H1P 1.303(15), P1−C1 1.8881(15), P1−C5 1.8882(16), P2−C9 1.8718(15), P2−C13 1.8805(15); P2−B1−P1 114.36(9), B2−P1−B1 116.39(8), H1P−P2−B1 113.1(7). Hydrogen atoms attached to carbon atoms are omitted.

at room temperature. Compound **1** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of **1** (Figure 3) is very similar to that of Ph$_2$PH−BH$_2$−Ph$_2$P−BH$_3$.[12,13] The internal P1−B1 bond length is 1.9794(18) Å, while the terminal P−B distances are slightly shorter (P2−B1 1.9544(19) Å, P1−B2 1.9536(19) Å). This pattern of short−long−short P−B distances was also observed in Ph$_2$PH−BH$_2$−Ph$_2$P−BH$_3$ (P2−B1 1.923(2) Å, P1−B1 1.944(2) Å, P1−B2 1.932(2) Å), as well as for the two P−B bonds closest to the P terminus in Ph$_2$PCl−BH$_2$−Ph$_2$P−BH$_2$Cl (1.907(6), 1.959(6), 1.953(6) Å);[24] however, the overall values are larger in compound **1**. Also, the P−B bonds in **1** are significantly longer than in the starting material tBu$_2$PH·BH$_3$ (1.936(2) Å). The bond angles around P1 (105.89(7)−116.39(8)°) and P2 (101.4(6)−114.39(7)°), as well as B1 (105.3(9)−114.36(9)°) and B2 (104.9(10)−115.2(14)°), deviate quite significantly from the tetrahedral value of 109.5°. The conformation adopted by **1** has a torsion angle of 14.41(13)° in the P−B−P−B chain, which minimizes the steric interactions between the tBu groups attached to P1 and P2, respectively. For comparison, the torsion angle in Ph$_2$PH−BH$_2$−Ph$_2$P−BH$_3$ is 39.35(17)°, and it is ca. 60° in Ph$_2$PCl−BH$_2$−Ph$_2$P−BH$_2$Cl.[24] Furthermore, the P−C distances in **1** (av P−C(tBu) 1.8822(16) Å) are longer than those found in Ph$_2$PH−BH$_2$−Ph$_2$P−BH$_3$ (av P−C(Ph) 1.812(2) Å). The sterically highly encumbered phosphorus centers and carbon hybridization effects are the most likely explanation for the long P−B and P−C distances in **1**, respectively.

Single crystals of a mixture of compounds **2** and **1** were grown from a diethyl ether solution at room temperature. The crystal was monoclinic with space group *P*(2)1/*n*. The final refinement of the site occupancy factors proceeded to give 0.79 for BH$_2$Cl (compound **2**) and 0.21 for BH$_3$ (compound **1**). This ratio is in good agreement with the integration ratio of the ^{1}H NMR spectra, as discussed above. The molecular structure is

(24) Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1978**, 40.

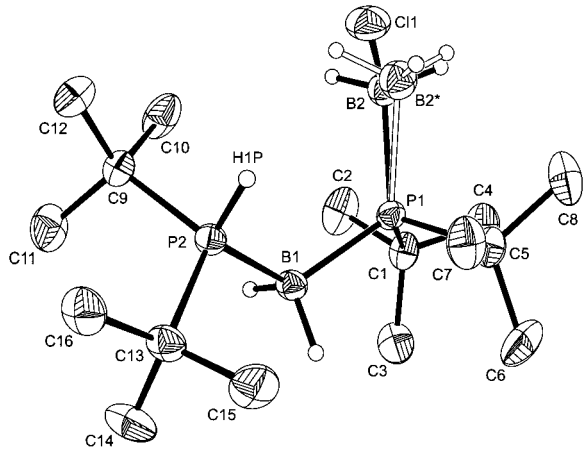


Figure 4. Molecular structure of the mixture of tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_2$Cl (**2**) and tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_3$ (**1**). Selected bond lengths (Å) and angles (deg): P2−B1 1.954 (2), P1−B1 1.967(2), P1−B2 1.955(3), P2−H1P 1.305(19), B2−Cl1 1.898(4); P2−B1−P1 119.23(11), B2−P1−B1 120.98(11), H1P−P2−B1 115.2(8), P1−B2−Cl1 110.32(16). Hydrogen atoms attached to carbon atoms are omitted.

shown in Figure 4. It is the least precise of those reported here, and only the major component **2** is discussed.

The terminal bond lengths P2−B1 (1.954(2) Å) and P1−B2 (1.955(3) Å) are comparable to those observed in **1**, while the internal bond length P1−B1 (1.967(2) Å) is slightly shorter. The phosphorus and boron environments in **2** also exhibit distortion from the ideal tetrahedral geometry (P1, 102.42(13)−120.98(11)°; P2, 101.4(8)−115.2(8)°; B1, 103.4(10)−119.23(11)°); the P1−B2−Cl1 angle is 110.32(16)°. The B−Cl bond in **2** of 1.898(4) Å is somewhat longer than that reported for the related four-membered chain Ph$_2$PCl−BH$_2$−Ph$_2$P−BH$_2$Cl (B−Cl 1.877(7) Å).[24]

Summary

With the synthesis of tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_3$ (**1**) and tBu$_2$PH−BH$_2$−tBu$_2$P−BH$_2$Cl (**2**) we have demonstrated again the usefulness of rhodium complexes in the catalytic formation of phosphorus−boron bonds. In contrast to the catalytic dehydrocoupling of Ph$_2$PH·BH$_3$, tBu$_2$PH·BH$_3$ reacts much slower and does not yield appreciable amounts of cyclic species. This may primarily be due to the high steric requirements of the tBu$_2$ groups but may also be attributed to the low polarity of the P−H bond in tBu$_2$PH·BH$_3$.

Experimental Section

General Information. All reactions were performed under an atmosphere of dry nitrogen while workup procedures were carried out in air. tBu$_2$PH, [Rh(1,5-cod)$_2$][OTf], Rh$_6$(CO)$_{16}$ (Strem), and RhCl$_3$ hydrate (Pressure Chemical Co.) were purchased and used as received. [{Rh(μ-Cl)(1,5-cod)}$_2$] was prepared following a literature procedure.[25] tBu$_2$PH·BH$_3$ was prepared following a procedure analogous to that for iBuPH$_2$·BH$_3$.[13] NMR spectra were recorded on a Varian Gemini or Mercury 300 MHz spectrometer. Chemical shifts are referenced to solvent peaks (^{1}H) or external BF$_3$·Et$_2$O (^{11}B) or H$_3$PO$_4$ (^{31}P). Mass spectra were obtained with a VG 70-250S mass spectrometer operating in electron impact (EI) mode. Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ.

X-ray Structural Characterization. Crystal data and details of the data collection are provided in Table 2. Diffraction data were collected on a Nonius Kappa-CCD using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A combination of 1° ϕ and ω (with κ offsets) scans were used collect sufficient data. The structures were solved and refined with the SHELXTL-PC V5.1 software package.[26] The data frames were integrated and scaled using the Denzo-SMN package.[27] Refinement was by full-matrix least squares on F^2 using all data (negative intensities included). Molecular structures are presented with ellipsoids at a 30% probability level. In all structures hydrogens bonded to carbon atoms were included in calculated positions and treated as riding atoms. Hydrogens attached to boron and phosphorus atoms were refined with isotropic thermal parameters, except for hydrogens attached to B2 in the mixture of compounds **2** and **1**, which were also included in calculated positions. Crystallographic data were deposited in the Cambridge Crystallographic Data Centre with codes CCDC-166925 (tBu$_2$PH·BH$_3$), CCDC-166926 (**1**), and CCDC-166927 (**2** and **1**).

***t*Bu$_2$PH−BH$_2$−*t*Bu$_2$P−BH$_3$ (1).** Neat tBu$_2$PH·BH$_3$ (0.84 g, 5.25 mmol) and Rh$_6$(CO)$_{16}$ (ca. 20 mg, 2 mol % Rh) were stirred at 160 °C for 63 h (Table 1, entry 8). The dark brown reaction mixture became liquid upon heating and solidified when cooled to room temperature. Recrystallization from diethyl ether gave colorless crystals of **1** which were suitable for single-crystal X-ray analysis. Isolated yield: 0.50 g (60%). Mp: 130−131 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.57 (dm, J_{PH} = 371 Hz, PH), 1.37 (d, J_{PH} = 14.0 Hz, tBu), 1.22 (d, J_{PH} = 11.8 Hz, tBu), 1.10 to −0.10 (br q, J_{BH} ca. 95 Hz, BH$_3$), BH$_2$ not observed. ^{11}B{^{1}H} NMR (96 MHz, CDCl$_3$): δ = −37.2 to −40.8 (br m, BH$_2$ and BH$_3$). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ = 39.5 (br, tBu$_2$PH), 13.2 (br, tBu$_2$P). MS (EI, 70 eV): m/z (%) 317 (19) [M$^+$ − H], 304 (35) [M$^+$ − BH$_3$], 146 (100) tBu$_2$PH. Anal. Calcd for C$_{16}$H$_{42}$B$_2$P$_2$: C, 60.4; H, 13.3. Found: C, 59.7; H, 12.8.

Thermal Decomposition of *t*Bu$_2$PH−BH$_2$−*t*Bu$_2$P−BH$_3$ (1). A sample of **1** (0.10 g) was loaded into a sublimator and heated and maintained at 175−180 °C for 16 h. A small amount of a colorless sublimate was noted on the coldfinger and was subsequently identified as tBu$_2$P(O)H (^{31}P NMR). The off-white residue in the sublimator was analyzed by ^{31}P NMR spectroscopy without further purification. ^{31}P-{^{1}H} NMR (121 MHz, CDCl$_3$): δ = 67.0 (s, tBu$_2$P(O)H), 53.8 (br), 48.9 (q, tBu$_2$PH·BH$_3$), 39.5 (br, tBu$_2$PH, **1**), 34.0 (br), 26.5 (br), 21.0 (s, tBu$_2$PH), 13.2 (br, tBu$_2$P, **1**), 8.5 (br).

***t*Bu$_2$PH−BH$_2$−*t*Bu$_2$P−BH$_2$Cl (2) and *t*Bu$_2$PH−BH$_2$−*t*Bu$_2$P−BH$_3$ (1).** Neat tBu$_2$PH·BH$_3$ (0.27 g, 1.69 mmol) and RhCl$_3$ hydrate (ca. 45 mg, 10 mol % Rh) were stirred at 160 °C for 16 h (Table 1, entry 11). After cooling to room temperature the dark brown reaction mixture was recrystallized from diethyl ether to give colorless crystals of a mixture of compounds **2** and **1** which were suitable for single-crystal X-ray analysis. Isolated yield 0.18 g. These compounds could not be separated by fractional crystallization and could not be distinguished by their crystal habits. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 5.01 (dm, J_{PH} = 380 Hz, PH, **2**), 4.56 (dm, J_{PH} = 371 Hz, PH, **1**), 1.39 (d, J_{PH} = 14.0 Hz, tBu, **2**), 1.37 (d, J_{PH} = 14.0 Hz, tBu, **1**), 1.31 (d, J_{PH} = 12.1 Hz, tBu, **2**), 1.22 (d, J_{PH} = 11.8 Hz, tBu, **1**), 1.10 to −0.10 (br q, J_{BH} ca. 95 Hz, BH$_3$), BH$_2$ not observed. ^{11}B{^{1}H} NMR (96 MHz, CDCl$_3$): δ = −15.8 (br, BH$_2$Cl, **2**), −36.0 to −41.5 (br m, BH$_2$ and BH$_3$, **2** and **1**). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ = 39.3 (br, tBu$_2$PH, **1**), 33.5 (br, tBu$_2$PH, **2**), 13.0 (br, tBu$_2$P, **1**), −3.3 (br, tBu$_2$P, **2**). MS (EI, 70 eV): m/z (%) 352 (5) [M$^+$(**2**)], 318 (16) [M$^+$(**1**)], 57 (100) tBu.

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Supporting Information Available: Figures giving ^{1}H and ^{31}P-{^{1}H} NMR spectra of compound **1**. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

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

(27) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.