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Cross-dehydrocoupling: A Novel Synthetic Route to P−B−P−B Chains

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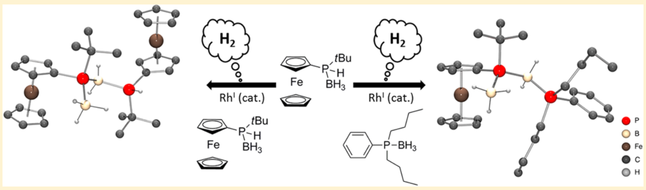
Supporting Information

ABSTRACT: Transition-metal-catalyzed dehydrocoupling of *tert*-butylferrocenylphosphine−borane (**2**) with $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (cod = cyclooctadiene) as the catalyst gave the homocoupled product $[Fc(tBu)(H)P(BH_2)P(Fc)(tBu)(BH_2X)]$ [**3**; Fc = $Fe(C_5H_5)(C_5H_4)$, X = H/Cl], while cross-dehydrocoupling with the tertiary phosphine−boranes $P(tBu)(nBu)_2(BH_3)$ (**2a**) and $PPh(nBu)_2(BH_3)$ (**2b**) using $[Rh(1,5\text{-}cod)_2]OTf$ (OTf = trifluoromethanesulfonate) gave the first cross-dehydrocoupled products reported to date, $[Fc(tBu)(BH_3)P(BH_2)P(tBu)(nBu)_2]$ (**4**) and $[Fc(tBu)(BH_3)P(BH_2)PPh(nBu)_2]$ (**5**), in moderate yields. Compounds **2**−**5** were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{31}P, and ^{11}B), IR spectroscopy, mass spectrometry, and single-crystal X-ray structure determination.

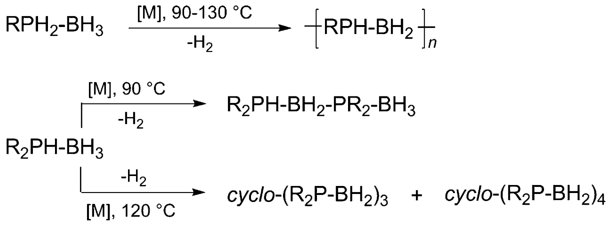


INTRODUCTION

Polymers are one of the major areas of molecular and materials science with uses as plastics,[1] thermosets, elastomers, fibers, films, and structural materials.[2] So far, most commercial polymers[3] are petroleum-based organic materials,[4] with polysiloxanes[5] being a notable exception. Importantly, during the last two decades, as suitable monomeric building blocks became available, polymers with backbone elements other than carbon are increasingly being applied in high-end technologies where materials with a combination of specific properties are required.[6] Silicon-based polymers,[7] polythiazyls,[8] polysulfides,[9] polystannanes,[10] and polyphosphazenes[11] are excellent examples in this regard,[12] and poly(aminoboranes) (N−B as the backbone)[13−15] and poly(phosphinoboranes) (P−B as the backbone)[15] are showing promise as potentially useful materials.[16] The latter can be obtained by dehydrocoupling of amine−boranes or phosphine−boranes.[15,17] These precursors are also of interest as hydrogen-storage[14,18] and hydrogen-transfer materials.[19]

Thermal dehydrocoupling of phosphine−borane adducts was pioneered in the early 1950s by Wagner and Burg,[20] who reported the formation of poly(phosphinoborane) and in some cases cross-linked materials.[20−22] In the late 1990s, Manners et al. reported the transition-metal-catalyzed dehydrocoupling of primary phosphine−borane adducts, which resulted in well-characterized, predominantly linear poly(phosphinoboranes), while secondary phosphine−borane adducts[23] gave dimers and six- or eight-membered rings (Scheme 1).[24,25]

Scheme 1. Transition-Metal-Catalyzed Dehydrocoupling of Primary and Secondary Phosphine−Borane Adducts



[M] = transition metal catalyst, R = aryl, alkyl

It was claimed earlier that the presence of amines promotes the formation of linear rather than cyclic products by coordination to the terminal BH_2 group.[26] For example, thermolysis of $Me_2P{-}PMe_2{-}BH_3$ or $RMePH{-}BH_3$ (R = Me or Et) at 175−200 °C in the presence of catalytic amounts of triethylamine gave polymers $[RMeP{-}BH_2]_n$ with molecular weights of 1800−6000 Da.[22,26] An alternative approach to obtaining poly(diorganylphosphinoboranes) is alkylation of $[RPH{-}BH_2]_n$;[27] for example, poly(phenylphosphinoborane), $[PhPH{-}BH_2]_n$, reacts with *n*BuLi(TMEDA) (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) followed by butyl chloride to give poly[(phenyl-*n*-butylphosphino)borane], $[Ph(nBu)P{-}BH_2]_n$.[28]

A wide range of substituents can be introduced at phosphorus and boron, and thus the properties of poly(phosphinoboranes) were enriched with versatility.[29] Computationally, it has been shown that poly(phosphinoboranes) have great potential to serve as nonlinear-optical (NLO) materials because of their high electronic first hyperpolarizabilities β.[30] Optically active single-handed polymeric chains can be obtained by introducing enantiomerically pure chiral building blocks.[31] In this respect, ferrocene derivatives are excellent

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candidates to introduce diversity into a polymer (e.g., chirality,[32] electrochemical properties, etc.)[33] because of their high thermal and photochemical stability and rich chemistry.[33] Ferrocene itself is an effective NLO chromophore. Therefore, by the introduction of different substituents, especially ferrocenyl groups, on the phosphorus atoms of poly(phosphinoboranes), β can be tuned, and these compounds could thus be suitable as NLO materials.[34]

Here we describe the selective dehydrocoupling between two different phosphine−borane adducts: a secondary ferrocenylphosphine−borane and a tertiary phosphine−borane adduct. The tertiary phosphine blocks one end and thus prevents cyclization.[35] We have termed this extended version of a dehydrocoupling reaction, which allows systematic building of the P−B chain, cross-dehydrocoupling.

■ EXPERIMENTAL DETAILS

General Consideration. All reactions and manipulations were performed under an atmosphere of dry nitrogen by using a Schlenk technique or in a glovebox. Diethyl ether, toluene, and *n*-hexane were dried and purified with an MBraun MB SPS-800 solvent purification system; tetrahydrofuran (THF) was distilled from sodium/benzophenone. All solvents were nitrogen-saturated and stored over a potassium mirror. Ferrocene, *t*BuOK, *t*BuLi, $LiAlH_4$, $PhPCl_2$, Na_2SO_4, and $tBuPCl_2$ are commercially available and were used as purchased. $BH_3(THF)$ (1 M in THF) was purchased and purified by bulb-to-bulb vacuum distillation. Tertiary phosphine−boranes $P(tBu)(nBu)_2(BH_3)$ (**2a**) and $PPh(nBu)_2(BH_3)$ (**2b**)[37] and $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$[38] were synthesized according to published procedures. $[Rh(1,5\text{-}cod)_2]OTf$ was received from Umicore AG & Co. KG (Germany).

The NMR spectra (^1H, ^{11}B, ^{13}C, and ^{31}P) were recorded on a Bruker AVANCE DRX 400 spectrometer. The chemical shifts of ^1H, ^{11}B, ^{13}C, and ^{31}P are reported in parts per million (ppm) at 400.1, 128.4, 100.6, and 161.9 MHz, respectively. Tetramethylsilane was used as the internal standard for ^1H NMR spectroscopy and for referencing the ^{11}B, ^{31}P, and ^{13}C NMR spectra to the unified scale.[36] Electron impact mass spectra (EI-MS) were recorded on a ZAB-HSQ-VG12−520 Analytical Manchester spectrometer or a MASPEC II spectrometer; electrospray ionization mass spectra (ESI-MS) were recorded on a Bruker-Daltonics FT-ICR-MS APEX II. Fourier transform infrared spectra were recorded on a PerkinElmer Spectrum 2000 spectrometer. Melting points were determined in sealed glass capillaries under nitrogen.

***tert*-Butylferrocenylphosphine [FcP(*t*Bu)H] [1; Fc = Fe(C_5H_5)(C_5H_4)].** A suspension of ferrocenyllithium in THF (50 mL) [prepared from ferrocene (3.73 g, 20 mmol), *t*BuOK (0.28 g, 0.025 mmol), and *t*BuLi (27 mL, 40 mmol)] was added dropwise to a solution of $tBuPCl_2$ (3.58 g, 22.5 mmol) in THF (60 mL) at −78 °C. The mixture was stirred for 4 h at this temperature and then slowly warmed to room temperature overnight. The reaction mixture was filtered, and the solvent was evaporated in a vacuum (10^{-1} Pa). Diethyl ether was added to the red-orange residue. The orange suspension was filtered to remove alkali-metal salts. An orange residue was obtained after removal of the solvent and dried for 1 h in a vacuum (10^{-1} Pa) to give *tert*-butylferrocenylchlorophosphine (**1a**) in an almost pure state (5.85 g, 94%). Further purification of **1a** was almost impossible because it was always accompanied by unconverted ferrocene (which can be removed in the next step, i.e., the formation of **1**) and other impurities, such as the disubstituted product $[Fe\{C_5H_4P(tBu)Cl\}_2]$. Sublimation resulted in decomposition of the products. However, **1a** could be obtained as deep-orange crystals from diethyl ether at −16 °C. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 4.40 (br s, 2H, C_5H_4), 4.36 (br s, 2H, C_5H_4), 4.25 (s, 5H, C_5H_5), 1.00 (d, $^3J_{P,H}$ = 13.6 Hz, 9H, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz): δ 113.0 (s, Fc*P*(*t*Bu)Cl). EI-MS [+14 eV, *m*/*z* (%)]: 308 (30) [M^+], 251 (100) [M^+ − *t*Bu], 215 (15) [$C_5H_5FeP^+$], 185 (30) (Fc−H^+).

1a was added to a suspension of $LiAlH_4$ (0.93 g, 25 mmol) in diethyl ether (60 mL) at 0 °C over 1 h. The reaction mixture was stirred overnight at room temperature and was carefully hydrolyzed with slightly basic degassed water at 0 °C. The solution was stirred for 2 h at room temperature and then left for the layers to separate (ca. 1 h). The clear orange organic layer was collected and dried over Na_2SO_4. The solution was filtered, and the solvent was removed in a vacuum (10^{-1} Pa) to give **1** as a fine, orange, crystalline solid. The crude product was recrystallized from diethyl ether at 0 °C to give orange crystals. The crude product can also be purified by sublimation (70 °C, 10^{-1} Pa). Yield: 4.4 g, 82%. Mp: 65−67 °C. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 4.22 (br m, 3H, C_5H_4), 4.08 (br s, 1H, C_5H_4, and 5H, C_5H_5), 3.75 (d, $^1J_{P,H}$ = 212 Hz, 1H, PH), 0.96 (d, $^3J_{P,H}$ = 12.5 Hz, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 76.2 (d, $J_{C,P}$ = 33 Hz, C_5H_4), 74.8 (d, $J_{C,P}$ = 8 Hz, C_5H_4), 70.9 (d, $J_{C,P}$ = 7 Hz, C_5H_4), 70.4 (s, C_5H_4), 69.9 (d, $J_{C,P}$ = 11 Hz, C_5H_4), 68.9 (s, C_5H_5), 29.6 (d, $^2J_{C,P}$ = 13 Hz, $C(CH_3)_3$), 28.7 (d, $^1J_{C,P}$ = 6.7 Hz, $C(CH_3)_3$). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ −25.9 (dm, $^1J_{P,H}$ = 212 Hz, $^3J_{P,H}$ = 13 Hz, Fc*P*H). EI-MS [+14 eV; *m*/*z* (%)]: 274 (30) [M^+], 217 (100) [M^+ − *t*Bu], 152 (15) [$C_5H_5FeP^+$], 121 (40) [$C_5H_5Fe^+$]. Elem anal. Calcd for $C_{14}H_{19}FeP$: C, 61.34; H, 6.99. Found: C, 60.86; H, 6.74.

(*tert*-Butyl)ferrocenylphosphine−borane [FcP(*t*Bu)H(BH_3)] (2). **1** (2.3 g, 8.4 mmol) was dissolved in 50 mL of diethyl ether and cooled to −20 °C. $BH_3(THF)$ (10 mL, 1 M solution in THF, 10 mmol) in diethyl ether (20 mL) was added dropwise, and the solution was stirred for 1 h at −20 °C and then 2 h at room temperature. The reaction mixture was filtered, and the solvent was removed in a vacuum (10^{-1} Pa). The crude product was dried in a vacuum for 1 h in a water bath (40 °C). Orange-red crystals of **2** were obtained from diethyl ether at −16 °C within a few days. Yield: 2.1 g, 90%. Mp: 119−121 °C. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 5.05 (br dq, $^1J_{P,H}$ = 365.9 Hz, $^3J_{HH}$ = 6.5 Hz, 1H, P*H*), 4.59 (s, 1H, C_5H_4), 4.47 (s, 1H, C_5H_4), 4.44 (m, 1H, C_5H_4), 4.29 (br s, 5H, C_5H_5, and 1H, C_5H_4), 1.11 (d, $^3J_{P,H}$ = 14.7 Hz, 9H, $C(CH_3)_3$), 0.35−1.15 (br q, BH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 74.5 (d, $^3J_{C,P}$ = 17.0 Hz, C_5H_4), 72.7 (s, C_5H_4), 71.7 (d, $^3J_{C,P}$ = 16.8 Hz, C_5H_4), 71.6 (d, $J_{C,P}$ = 11.4 Hz, C_5H_4), 68.9 (s, C_5H_5), 28.8 (d, $^1J_{C,P}$ = 33.4 Hz, $C(CH_3)_3$), 26.5 (d, $^2J_{C,P}$ = 2.9 Hz, $C(CH_3)_3$). ^{31}P NMR ($CDCl_3$, 161.98 MHz): δ 20.5 (br dq, $^1J_{P,H}$ = 366 Hz, $^1J_{P,B}$ = 50 Hz, H_2P−B). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128.3 MHz): δ −42.6 (br d, $^1J_{P,B}$ = 50 Hz, P−BH_3). EI-MS [+14 eV; *m*/*z* (%)]: 288 (15) [M^+], 274 (75) [M^+ − BH_3], 217 (100) [M^+ − *t*Bu], 152 (10) [$C_5H_5FeP^+$], 121 (30) [$C_5H_5Fe^+$]. Elem anal. Calcd for $C_{14}H_{22}FePB$: C, 58.33; H, 7.70. Found: C, 57.30; H, 7.76.

Dehydrocoupling of 2: Synthesis of [Fc(*t*Bu)(H)P(BH_2)P(Fc)(*t*Bu)(BH_2X)] [3a (R_P,S_P/S_P,R_P), 3b (R_P,R_P/S_P,S_P), X = H/Cl]. A mixture of neat phosphine−borane adduct **2** (0.1 g, 0.35 mmol) and $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (ca. 3 mg, 3 mol % rhodium) was heated at 160 °C for 3 h. After cooling to room temperature, the mixture was dissolved in *n*-hexane (20 mL) and filtered. The filtrate was collected, and the solvent was removed in a vacuum (10^{-1} Pa). The crude product was purified by column chromatography (silica gel). Elution with *n*-hexane/diethyl ether (4/1, v/v) gave first an orange fraction, which contained mostly impurities and unconverted starting material (identified by NMR spectroscopy). The second yellow fraction (R_f value: 0.52) contained pure **3a** (yield: 0.015 g, 14%) and the third fraction (R_f value: 0.45) pure **3b** (yield: 0.037 g, 37%). **3a** and **3b** were recrystallized from *n*-hexane at 0 °C.

3a (R_P,S_P/S_P,R_P). ^1H NMR (C_6D_6, 400.1 MHz): δ 5.39 (br, d, $^1J_{P,H}$ = 388 Hz, 1H, P*H*), 4.92 (s, 1H, C_5H_4), 4.62 (s, 1H, C_5H_4), 4.55 (s, 1H, C_5H_4), 4.41 (br s, 5H, C_5H_5), 4.22 (s, 2H, C_5H_4), 4.20 (br s, 5H, C_5H_5), 4.10 (1H, C_5H_4), 3.99 (s, 1H, C_5H_4), 3.89 (br m, 1H, C_5H_4), 1.35 (d, $^3J_{P,H}$ = 16.1 Hz, 0.5H, $C(CH_3)_3$), 1.33 (d, $^3J_{P,H}$ = 16.1 Hz, 9H, $C(CH_3)_3$), 1.08 (d, $^3J_{P,H}$ = 12.3 Hz, 0.5H, $C(CH_3)_3$), 1.05 (br d, $^3J_{P,H}$ = 12.3 Hz, 9H, $C(CH_3)_3$), 0.3−2.1 (br m, 5H, BH_2 and BH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 74.5, 74.2, 73.9, 73.7, 73.2, 71.7, 71.2 (C_5H_4), 70.6, 70.5, 70.3, 70.0 (s, C_5H_5), 32.4, 32.3 (br, $C(CH_3)_3$), 30.2, 27.6, 26.9 ($C(CH_3)_3$). ^{31}P NMR (C_6D_6, 161.98 MHz): δ 11.7 (br d, $^1J_{P,H}$ = 370 Hz, 1P, Fc(*t*Bu)*P*H), 8.2 (br d, $^1J_{P,H}$ = 385 Hz, 0.06P, Fc(*t*Bu)*P*H), −6.2 (br s, 1P, Fc(*t*Bu)*P*), −19.2 (br s, 0.06P, Fc(*t*Bu)*P*). $^{11}B\{^1H\}$ NMR (C_6D_6, 128.3 MHz): δ −35 to −39 (br, BH_2 and BH_3). MS [CH_2Cl_2/MeOH, ESI(−)]: 573 ([$C_{28}H_{41}Fe_2P_2B_2$]$^-$, 100%), 607 ([$C_{28}H_{40}ClFe_2P_2B_2$]$^-$, 8%). Elem anal. Calcd for

$C_{28}H_{41.74}Fe_2P_2B_2Cl_{0.26}$ (composition calculated from single-crystal X-ray data): C, 57.66; H, 7.21; Cl, 1.58. Found: C, 58.23; H, 7.46; Cl, 0.30 (corresponds to the formula $C_{28}H_{41.95}Fe_2P_2B_2Cl_{0.05}$, which is in agreement with the NMR spectra of the bulk material).

3b (R_P,R_P/S_P,S_P). ^{1}H NMR (C_6D_6, 400.1 MHz): δ 5.31 (br d, $^1J_{P,H}$ = 396 Hz, 1H, P*H*), 5.20 (br d, $^1J_{P,H}$ = 381 Hz, 0.08H, P*H*), 4.63 (s, 1H, C_5H_4), 4.47 (s, 1H, C_5H_4), 4.45 (s, 1H, C_5H_4), 4.43 (br s, 5H, C_5H_5), 4.41 (s, 1H, C_5H_4), 4.23 (s, 1H, C_5H_4), 4.12 (br s, 5H, C_5H_5), 4.10 (s, 1H, C_5H_4), 3.99 (s, 1H, C_5H_4), 3.89 (s, 1H, C_5H_4), 1.38 (d, $^3J_{P,H}$ = 16.1 Hz, 9H, $C(CH_3)_3$), 1.19 (d, $^3J_{P,H}$ = 16.1 Hz, 0.7H, $C(CH_3)_3$), 1.08 (br d, $^3J_{P,H}$ = 12.3 Hz, 9H, $C(CH_3)_3$), 1.05 (br d, $^3J_{P,H}$ = 12.3 Hz, 0.7H, $C(CH_3)_3$), 0.3–2.1 (br m, 5H, BH_2 and BH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 74.1 (d, $J_{C,P}$ = 13.7 Hz, C_5H_4), 73.9, 73.8, 73.5, 73.1 (s, C_5H_4), 72.9 (d, $J_{C,P}$ = 3.7 Hz, C_5H_4), 71.5 (d, $J_{C,P}$ = 8.1 Hz, C_5H_4), 70.0 (s, C_5H_5), 69.8 (s, C_5H_5), 69.6, 69.5 (s, C_5H_4), 69.4 (s, C_5H_5), 29.8 (d, $J_{C,P}$ = 36 Hz, $C(CH_3)_3$), 29.2 (d, $J_{C,P}$ = 30 Hz, $C(CH_3)_3$), 27.8, 26.5 (d, $^2J_{C,P}$ = 2.9 Hz, $C(CH_3)_3$). ^{31}P NMR (C_6D_6, 161.98 MHz): δ 12.7 (br d, $^1J_{P,H}$ = 370 Hz, 1P, Fc(*t*Bu)*P*H), 8.2 (br d, $^1J_{P,H}$ = 385 Hz, 0.09P, Fc(*t*Bu)*P*H), −6.2 (br s, 1P, Fc(*t*Bu)*P*), −19.2 (br s, 0.09P, Fc(*t*Bu)*P*). $^{11}B\{^1H\}$ NMR (C_6D_6, 128.3 MHz): δ −35 to −39 (br, BH_2 and BH_3). MS [CH_2Cl_2/MeOH, ESI(−)]: 573 ([$C_{28}H_{41}Fe_2P_2B_2$]$^-$, 100%), 607 ([$C_{28}H_{40}ClFe_2P_2B_2$]$^-$, 5%). Elem anal. Calcd for $C_{28}H_{41.87}Fe_2P_2B_2Cl_{0.13}$ (composition calculated from single-crystal X-ray data): C, 58.11; H, 7.29; Cl, 0.80. Found: C, 58.40; H, 7.41; Cl, 0.66 (corresponds to the formula $C_{28}H_{41.89}Fe_2P_2B_2Cl_{0.11}$, which is in agreement with the NMR spectra of the bulk material).

Cross-dehydrocoupling between 2 and 2a with [Rh(1,5-cod)$_2$]OTf as the Catalyst: Synthesis of [Fc(*t*Bu)(BH$_3$)P(BH$_2$)P(*t*Bu)(*n*Bu)$_2$] (4). Neat **2** (0.062 g, 0.21 mmol) was mixed with a slight excess of di-*n*-butyl-*tert*-butylphosphine–borane (**2a**; 0.07 g, 0.32 mmol) and [Rh(1,5-cod)$_2$]OTf (ca. 8 mg, 4 mol %), and the mixture was heated at 160 °C. The reaction was monitored through thin-layer chromatography (TLC; *n*-hexane/Et$_2$O, 7/1, v/v). After 3 h, **2** was completely consumed. After cooling to room temperature, the mixture was dissolved in *n*-hexane (20 mL) and filtered. The solvent was removed in a vacuum (10^{-1} Pa). The crude product was heated in a vacuum (10^{-1} Pa) at 70 °C for 6 h to eliminate impurities by sublimation. The almost pure product remained. Purification could also be achieved by column chromatography on silica gel with *n*-hexane/diethyl ether (10/1, v/v) as the eluent. The first orange fraction contained mostly impurities, and the second yellow-orange fraction contained the product **4** (yield: 0.036 g, 35%). Orange crystals were obtained from *n*-hexane at 0 °C.

4. Mp: 168–171 °C. ^{1}H NMR (C_6D_6, 400.1 MHz): δ 4.91 (br s, 1H, C_5H_4), 4.54 (br s, 1H, C_5H_4), 4.37 (s, 5H, C_5H_5), 4.17 (br s, 2H, C_5H_4), 2.02–2.03 (br m, 4H, CH_2), 1.75 (br m, 4H, CH_2), 1.41 (br m, 4H, CH_2), 1.23 (d, $^3J_{P,H}$ = 12.5 Hz, 9H, *t*Bu), 0.95 (d, $^3J_{P,H}$ = 13.0 Hz, 9H, *t*Bu), 0.89 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3, *n*Bu), 0.85 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, *n*Bu), 0.35–2.25 (br, overlapped with methyl protons, BH_2 and BH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 76.5 (dd, $^1J_{C,P}$ = 60.0 Hz, $^3J_{C,P}$ = 10.0 Hz, C_5H_4), 73.7 (d, $J_{C,P}$ = 16.0 Hz, C_5H_4), 73.6 (d, $J_{C,P}$ = 4.0 Hz, C_5H_4), 69.6 (d, $J_{C,P}$ = 5.0 Hz, C_5H_4), 69.5 (d, $J_{C,P}$ = 4.5 Hz, C_5H_4), 69.4 (s, C_5H_5), 29.7 (dd, $^1J_{C,P}$ = 36.0 Hz, $^3J_{C,P}$ = 7.0 Hz, CCH_3), 28.9 (br d, $^1J_{C,P}$ = 25.0 Hz, CCH_3), 26.7 (br d, $^3J_{C,P}$ = 3.0 Hz CCH_3), 26.5 (s, CCH_3), 25.9 (d, $J_{C,P}$ = 5.0 Hz, *n*Bu), 25.8 (d, $J_{C,P}$ = 5.0 Hz, *n*Bu), 24.8 (d, $J_{C,P}$ = 14.0 Hz, *n*Bu), 24.7 (d, $J_{C,P}$ = 14.0 Hz, *n*Bu), 21.2 (d, $J_{C,P}$ = 30.0 Hz, *n*Bu), 20.8 (d, $J_{C,P}$ = 30.0 Hz, *n*Bu), 13.5, 13.3 (s, *n*Bu). ^{31}P NMR (C_6D_6, 161.98 MHz): δ 22.1 (br s, *P*(*t*Bu)(*n*Bu)$_2$), −8.8 (br s, Fc(*t*Bu)*P*). $^{11}B\{^1H\}$ NMR (C_6D_6, 128.3 MHz): δ −36.0 to −38.6 (br s, BH_2, BH_3). MS [CH_2Cl_2/MeOH, ESI(+)]: 502 ([M$^+$], 100%). Elem anal. Calcd for $C_{26}H_{50}FeP_2B_2$: C, 62.19; H, 10.03. Found C, 62.21; H, 10.01.

Cross-dehydrocoupling between 2 and 2a with [{Rh(μ-Cl)(1,5-cod)}$_2$] as the Catalyst: Synthesis of [Fc(*t*Bu)(BH$_2$X)P(BH$_2$)P(*t*Bu)(*n*Bu)$_2$] [4′; X = H/Cl (ca. 0.96/0.04)]. The same reaction procedure as that for **4** with [{Rh(μ-Cl)(1,5-cod)}$_2$] (2 mol % rhodium) instead of [Rh(1,5-cod)$_2$]OTf as the catalyst was followed. The product was recrystallized from *n*-hexane at 0 °C. An X-ray crystal structure determination showed the presence of varying amounts of chlorine [the molecular structure of **4′** (a crystal of composition $C_{26}H_{49.96}FeP_2B_2Cl_{0.04}$) is shown in Figure S5 in the Supporting Information, SI]. The spectroscopic data of the obtained product are similar to those of **4**. The signals for the minor chlorine-containing product **4′** were not observed in the NMR spectra even after scanning for a longer time. 0.14% Cl was found in the elemental analysis and indicates the formula $C_{26}H_{49.98}FeP_2B_2Cl_{0.02}$.

Cross-dehydrocoupling between 2 and 2b with [Rh(1,5-cod)$_2$]OTf as the Catalyst: Synthesis of [Fc(*t*Bu)(BH$_3$)P(BH$_2$)PPh(*n*Bu)$_2$] (5). Neat **2** (0.087 g, 0.3 mmol), di-*n*-butylphenylphosphine–borane (**2b**; 0.07 g, 0.3 mmol), and [Rh(1,5-cod)$_2$]OTf (ca. 11.0 mg, 4 mol % rhodium) were mixed, and the mixture was heated at 160 °C. The reaction was monitored through TLC (*n*-hexane/Et$_2$O, 7/1, v/v). After 5 h, **2** was completely consumed. After cooling to room temperature, the mixture was dissolved in *n*-hexane (30 mL) and filtered. The solvent was removed in a vacuum (10^{-1} Pa). The crude product was heated in a vacuum (10^{-1} Pa) at 70 °C for 6 h to eliminate impurities by sublimation. The almost pure product remained. Purification could also be achieved by column chromatography on silica gel with *n*-hexane/diethyl ether (10/1, v/v) as the eluent. The first orange fraction contained mostly impurities, and the second yellow-orange fraction contained the product **5** (yield: 0.036 g, 35%). Orange crystals were obtained from *n*-hexane at 0 °C.

5. Mp: 123–125 °C. ^{1}H NMR (C_6D_6, 400.1 MHz): δ 7.52 (br m, 2H, *o*-H in C_6H_5), 7.06 (br m, 3H, *m*-H in C_6H_5 and *p*-H in C_6H_5), 4.88 (br s, 1H, C_5H_4), 4.56 (s, 1H, C_5H_4), 4.34 (s, 5H, C_5H_5), 4.19 (br m, 2H, C_5H_4), 1.95–2.35 (br m, 8H, CH_2, *n*Bu), 1.15–1.50 (br m, 4H, CH_2), 1.11 (d, $^3J_{P,H}$ = 12.6 Hz, 9H, $C(CH_3)_3$), 0.79 (t, $^3J_{H,H}$ = 6.9 Hz, 3H, CH_3, *n*Bu), 0.74 (t, $^3J_{H,H}$ = 6.9 Hz, 3H, CH_3, *n*Bu), 0.96–2.51 (br, overlapped with methyl protons, BH_2 and BH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 131.6 (d, $J_{C,P}$ = 7.0 Hz, C_6H_5), 131.1 (d, $J_{C,P}$ = 2.1 Hz, C_6H_5), 129.8 (d, $J_{C,P}$ = 9.2 Hz, C_6H_5), *ipso*-C in C_6H_5 was not observed probably because of overlap with the solvent (C_6D_6), 76.0 (dd, $^1J_{C,P}$ = 64.0 Hz, $^3J_{C,P}$ = 14.0 Hz, C_5H_4), 74.0 (br d, $^1J_{C,P}$ = 12.0 Hz, C_5H_4), 73.6 (br d, $^1J_{C,P}$ = 5.0 Hz, C_5H_4), 70.0 (d, $^1J_{C,P}$ = 5.0 Hz, C_5H_4), 69.8 (d, $^1J_{C,P}$ = 4.3 Hz, C_5H_4), 69.8 (s, C_5H_5), 28.9 (d, $^1J_{C,P}$ = 40.0 Hz, $C(CH_3)_3$), 26.9 (d, $J_{C,P}$ = 2.9 Hz, $C(CH_3)_3$), 24.9 (d, $J_{C,P}$ = 5 Hz, *n*Bu), 24.8 (d, $J_{C,P}$ = 5 Hz, *n*Bu), 24.5 (d, $J_{C,P}$ = 3 Hz, *n*Bu), 24.3 (d, $J_{C,P}$ = 3 Hz, *n*Bu), 22.8 (s, *n*Bu), 22.3 (s, *n*Bu). ^{31}P NMR (C_6D_6, 161.98 MHz): δ 11.6 (br, *P*Ph(*n*Bu)$_2$), −7.9 (br, Fc(*t*Bu)*P*). $^{11}B\{^1H\}$ NMR (C_6D_6, 128.3 MHz): δ −35.1 (br, BH_2), −37.8 (br, BH_3). MS [CH_2Cl_2/MeOH, ESI(+)]: 522 ([M$^+$], 100%]. Elem anal. Calcd for $C_{28}H_{46}FeP_2B_2$: C, 64.42; H, 8.88. Found: C, 64.37; H, 8.89.

Cross-dehydrocoupling between 2 and 2b with [{Rh(μ-Cl)(1,5-cod)}$_2$] as the Catalyst: Synthesis of [Fc(*t*Bu)(BH$_2$X)P(BH$_2$)PPh(*n*Bu)$_2$] [5′; X = H/Cl (ca. 0.907/0.093)]. The same reaction procedure as that for **5** with [{Rh(μ-Cl)(1,5-cod)}$_2$] (2 mol % rhodium) instead of [Rh(1,5-cod)$_2$]OTf as the catalyst was followed. The product was recrystallized from *n*-hexane at 0 °C. An X-ray crystal structure determination showed the presence of varying amounts of chlorine [the molecular structure of **5′** (a crystal of composition $C_{28}H_{45.91}FeP_2B_2Cl_{0.09}$) is shown in Figure S5 in the SI]. The spectroscopic data of the obtained product are similar to those of **5**. The signals for the minor chlorine-containing product **5′** were not observed in the NMR spectra even after scanning for a longer time. 0.14% Cl was found in the elemental analysis and indicates the composition $C_{28}H_{45.97}FeP_2B_2Cl_{0.03}$.

X-ray Data Collection and Refinement. Single-crystal X-ray crystallography for structural analysis was performed with an Oxford Gemini S CCD diffractometer (Agilent Technologies) and Mo$_{K\alpha}$ irradiation (λ = 0.71073 Å). The structures were solved by direct methods with *SIR-92*,[39] *SHELXS-97*, or *SHELX-2013*.[40] Anisotropic refinement of all non-hydrogen atoms was performed with *SHELXL-97* or *SHELXL-2013*.[40] Disordered fragments of the structures of **2** (*t*Bu substituent) and **3a** and **3b** (cyclopentadienyl ring and BH$_3$/BH$_2$Cl disorder) were refined isotropically. Hydrogen atoms of disordered structure fragments and the hydrogen atoms for **3a** (except: P–H and B–H) were calculated on idealized positions using the riding model. The hydrogen atoms of all other structures were located on difference Fourier maps calculated at the final stage of the structure refinement. Structure figures were generated with ORTEP-3 (thermal ellipsoids are drawn at 50% probability).[41] CCDC 958420 (**1a**), 958421 (**1**), 958422 (**2**), 1005264 [**3a** (R_P,S_P/S_P,R_P)], 958423 [**3b** (R_P,R_P/S_P,S_P)], 958424 (**4′**), 958425 (**5′**), 1005265 (**4**), and 1005266 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data, details of data collection, and structure refinement parameters for compounds **1a**, **1**, **3a**, **3b**, **4′**, and **5′** are listed in Table S2 (in the SI) and those for **2**, **4**, and **5** in Table 1.

Table 1. Crystallographic Data, Details of Data Collection, and Structure Refinement Parameters for Compounds 2, 4, and 5

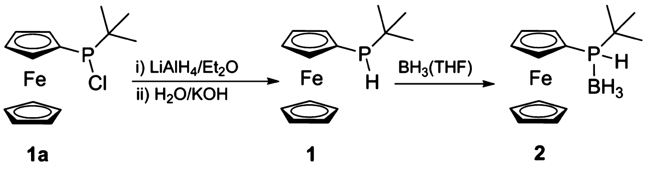
	2	4	5
empirical formula	$C_{14}H_{22}BFeP$	$C_{26}H_{50}B_2FeP_2$	$C_{28}H_{46}B_2FeP_2$
MW	287.95	502.07	522.06
T (K)	130(2)	130(2)	130(2)
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pnma*	$P2_1/n$	$P2_1/n$
a (Å)	12.9033(1)	14.0331(5)	14.5112(5)
b (Å)	10.8595(1)	10.5026(3)	10.9711(3)
c (Å)	10.6321(1)	20.1121(6)	19.1066(7)
α (deg)	90	90	90
β (deg)	90	107.140(3)	110.500(4)
γ (deg)	90	90	90
V (Å^3)	1489.81(2)	2832.6(2)	2849.2(2)
Z	4	4	4
ρ_{calcd} (Mg·m^{-3})	1.284	1.177	1.217
θ range (deg)	3.11−30.50	2.21−30.51	2.18−30.51
total data	38255	41854	39549
unique data (R_{int})	2384 (0.0249)	8626 (0.0385)	8690 (0.0387)
restraints/param	12/128	0/480	0/482
GOF on F^2	1.060	1.041	1.024
R1, wR2 [$I > 2\sigma(I)$]^a	0.0424, 0.1085	0.0371, 0.0841	0.0368, 0.0770
R1, wR2 (all data)	0.0441, 0.1097	0.0486, 0.0899	0.0533, 0.0836
residual electron density (e·Å^{-3})	1.189, −1.057	0.584, −0.242	0.412, −0.336

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

■ RESULTS AND DISCUSSION

Phosphine−Borane Adducts as Precursors. *Compound **2**.* The secondary ferrocenylphosphine−borane adduct **2** was obtained as a yellow powder from **1** and BH_3(THF) in almost quantitative yield (Scheme 2). Compound **1** was synthesized from **1a** and $LiAlH_4$ in 80% yield. Compound **1a** was previously reported by Jung et al. but was not isolated or characterized.[42] We have developed an improved synthesis employing the method of Sanders and Mueller-Westerhoff for monolithiating ferrocene with *t*BuLi/KO*t*Bu,[43] followed by the addition of *t*$BuPCl_2$. Compound **1a** was obtained in about 85% yield as a deep-red oil.

Scheme 2. Synthesis of 1 and 2



Single crystals of **1a** (orange-red), **1** (yellow-orange), and **2** (orange) suitable for X-ray crystallography were obtained from diethyl ether at −16 °C. The molecular structures and selected bond lengths and angles of **1** and **1a** are given in the SI (Figure S2 and Table S1). In **2**, the atoms C1, C4, C7, and Fe1 are located on a crystallographic mirror plane, resulting in disorder of the cyclopentadienyl substituent (Figure 1).

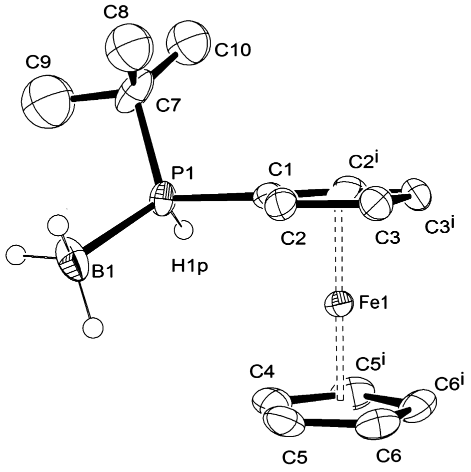


Figure 1. ORTEP of the molecular structure of **2**. Only hydrogen atoms on phosphorus and boron are shown. Disordered fragments of **2** are omitted for clarity. Symmetry operator i: *x*, 0.5 − *y*, *z*. Selected bond lengths [Å] and angles [deg]: P1−C1 1.797(3), P1−C7 1.837(3), P1−H1p 1.32(4), P1−B1 1.928(5); C1−P1−C7 107.2(1), C12−C11−P1 107.7(1), C9−C7−P1 103.1(3).

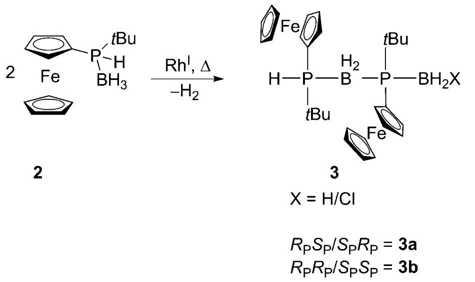
Compounds **1** and **2** were also characterized by ^1H, ^{31}P, ^{11}B, and ^{13}C NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows a broad quartet at 20.5 ppm ($^1J_{P,B}$ = 50 Hz), which is shifted downfield by almost 45 ppm compared to **1** and splits into a broad doublet upon proton coupling ($^1J_{P,H}$ = 366 Hz). The $^{11}B\{^1H\}$ NMR spectrum shows a broad doublet at −42.6 ppm ($^1J_{P,B}$ = 50 Hz). This is typical for a four-coordinate phosphorus atom attached to borane.[44]

Tertiary Phosphine−Borane Adducts. For the cross-dehydrocoupling reactions, the tertiary phosphine−borane adducts P(*t*Bu)(*n*Bu)$_2$(BH_3) (**2a**) and PPh(*n*Bu)$_2$(BH_3) (**2b**) were chosen because of their facile synthesis.[45] Furthermore, **2a** and **2b** are nonchiral, and this makes purification and analysis of NMR spectra of the products easier.

Dehydrocoupling and Cross-dehydrocoupling Reactions of 2. Because electron-withdrawing groups on phosphorus promote the dehydrocoupling reaction of phosphine−borane adducts by increasing the acidic nature of the hydrogen atoms on phosphorus,[46] dehydrocoupling of **2**, which contains an electron-donating *t*Bu group on phosphorus, should require harsh reaction conditions. The reaction conditions (time and temperature) were varied, and the reactions were monitored by TLC [silica, *n*-hexane/diethyl ether, 7/1, v/v]. It was found that heating of neat **2** with 3 mol % of rhodium(I) catalyst [{Rh(*μ*-Cl)(1,5-cod)}$_2$] (cod = cyclooctadiene) at 160 °C for 3 h gave the best result, with almost 70% conversion to **3** (Scheme 3) calculated from the ^{31}P NMR spectra. Lower temperatures resulted in no conversion, while prolonged heating led to decomposition of the dehydrocoupled product **3**.

Both four-coordinate phosphorus atoms in **3** are chiral and give rise to two pairs of stereoisomers [R_P,S_P/S_P,R_P (**3a**) and

Scheme 3. Dehydrocoupling of 2 in the Presence of Rhodium(I) Catalyst [{Rh(μ-Cl)(1,5-cod)}$_2$]



$R_P,R_P/S_P,S_P$ (**3b**); ratio of ca. 1:2.5; Figure S1 in the SI]. These diastereomers can be separated by column chromatography on silica gel with *n*-hexane/diethyl ether (6/1) as the eluent. Needle-shaped orange crystals obtained from the first fraction were found to be the $R_P,S_P/S_P,R_P$ diastereomer (minor) (**3a**), and cube-shaped orange crystals obtained from the second fraction were found to be the $R_P,R_P/S_P,S_P$ diastereomer (major) (**3b**). The configuration was determined by X-ray crystallography.

Partial H/Cl exchange between the terminal BH_3 group and a chlorine atom of the catalyst [{Rh(μ-Cl)(1,5-cod)}$_2$] was observed in the single-crystal X-ray diffraction measurements of **3a** and **3b** [H/Cl occupancy = 0.741(6)/0.259(6) for **3a** and 0.871(3)/0.129(3) for **3b**]. H/Cl exchange in the dehydrocoupling reaction was also reported by Manners et al.[47] Molecular structures of **3a** and **3b** are given in the SI (Figure S3). Compounds **3a** and **3b** were further characterized by ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectroscopy, elemental analysis, and mass spectrometry.

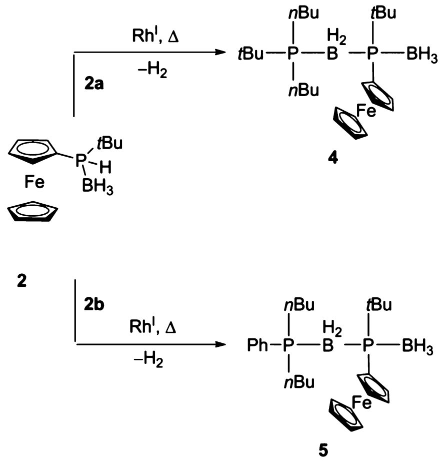
Dehydrocoupling reactions between **2** and **2a** or **2b** were also performed in the presence of [{Rh(μ-Cl)(1,5-cod)}$_2$] as the catalyst (Figure S4 in the SI). We have named this type of reaction, which involves two different phosphine–borane adducts in the metal-catalyzed dehydrocoupling reaction, a cross-dehydrocoupling reaction. As in **3**, partial H/Cl exchange between the terminal BH_3 group and a chlorine atom of the catalyst [{Rh(μ-Cl)(1,5-cod)}$_2$] was observed here as well. The products were obtained as single crystals from *n*-hexane at 0 °C. Molecular structures of **4′** [X = H/Cl (ca. 0.96/0.04)] and **5′** [X = H/Cl (ca. 0.907/0.093)] are shown in Figure S5 in the SI.

To avoid H/Cl exchange, a chlorine-free catalyst, namely, [Rh(1,5-cod)$_2$]OTf, was employed.

Optimal conditions were elucidated for the reaction of **2** with the tertiary phosphine–borane adducts **2a** and **2b** in the presence of [Rh(1,5-cod)$_2$]OTf as the catalyst to give the cross-dehydrocoupled products **4** and **5**. Thus, heating a mixture of **2**, tertiary phosphine–borane adduct **2a** or **2b**, and 4 mol % rhodium(I) catalyst without solvent at 160 °C for 3–5 h gave the products **4** and **5** in moderate yield (Scheme 4).

Compound **4** was purified by column chromatography (silica gel) with *n*-hexane/diethyl ether (10/1) as the eluent and obtained as yellow crystals. Almost pure compound **5** was obtained by heating at 75 °C in a vacuum (10^{-1} Pa) to remove impurities (starting materials and free phosphines) by sublimation and purified by recrystallization from *n*-hexane. Like **4**, **5** can also be purified by column chromatography (silica gel) with *n*-hexane/diethyl ether (10/1) as the eluent. Both compounds were characterized by multinuclear NMR spectroscopy ($^{31}P\{^1H\}$, $^{11}B\{^1H\}$, ^1H, and $^{13}C\{^1H\}$), elemental analysis, and mass spectrometry.

Scheme 4. Cross-dehydrocoupling of 2 with 2a and 2b in the Presence of the Rhodium(I) Catalyst [Rh(1,5-cod)$_2$]OTf to Give 4 and 5, Respectively



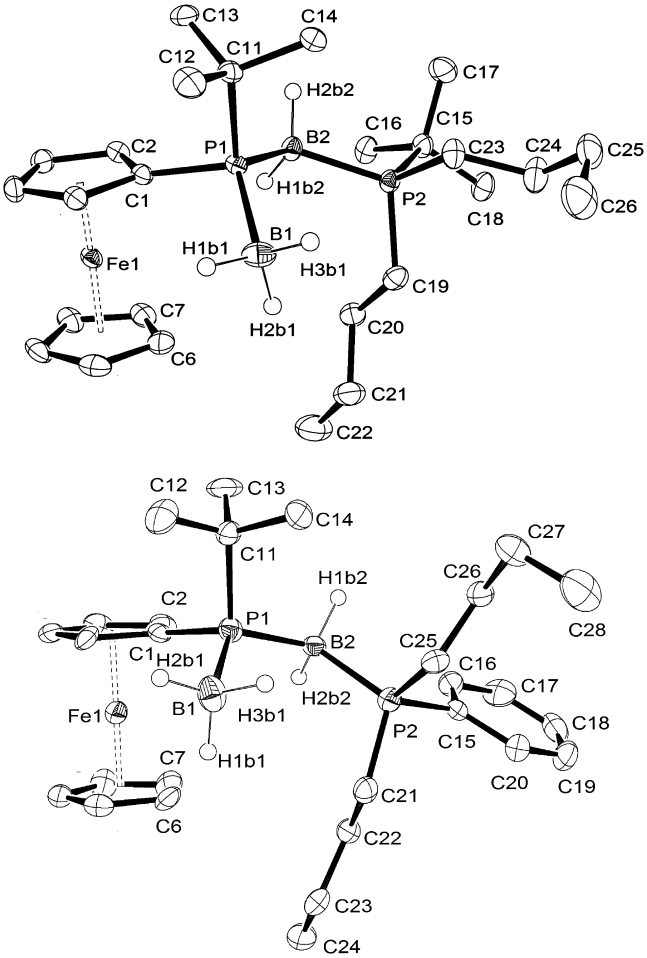


Figure 2. ORTEPs of the molecular structures of **4** (top) and **5** (bottom) with selected atoms labeled. Only hydrogen atoms of borane are shown for clarity.

Single crystals of **4** and **5** suitable for X-ray crystallography were obtained from *n*-hexane at 0 °C. Both compounds crystallize in the monoclinic space group $P2_1/n$ with four molecules in the unit cell; selected bond lengths and angles are listed in Table 2, and the molecular structures are depicted in Figure 2.

Table 2. Selected Bond Lengths [Å] and Bond Angles [deg] of 4 and 5

bond lengths (Å)	4	5	bond angles (deg)	4	5
P1−C1	1.805(1)	1.805(1)	C1−P1−C11	100.8(1)	101.9(1)
P1−C11	1.874(1)	1.876(2)	C1−P1−B1	112.1(1)	110.4(1)
P1−B1	1.943(2)	1.938(2)	B2−P1−B1	118.9(1)	118.5(1)
P1−B2	1.957(2)	1.965(2)	C1−P1−B2	103.6(1)	106.4(1)
P2−B2	1.951(2)	1.936(2)	C11−P1−B2	109.1(1)	109.0(1)
P2−C19	1.817(2)		C21−P2−C15		103.7(1)
			C19−P2−C15	109.9(1)	
			C25−P2−B2	116.1(1)	
P2−C15	1.855(2)	1.802(2)	C23−P2−B2		113.1(1)
P2−C23	1.826(2)		C15−P2−B2	108.8(1)	111.1(1)
P2−C21		1.815(2)	P2−B2−P1	118.3(1)	115.4(1)
P2−C25		1.816(2)	P2−B2−H1b2	104(1)	105(1)
			P1−B1−H3b1	108(1)	104(1)

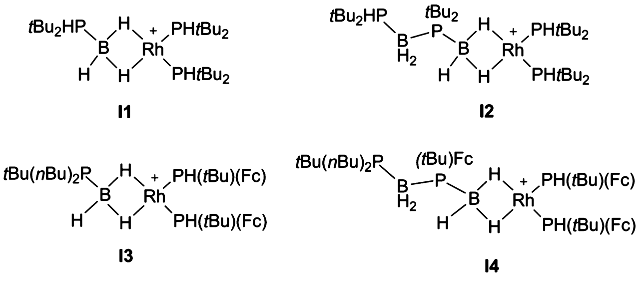
The phosphorus and boron atoms in **4** and **5** are coordinated in a distorted tetrahedral fashion with small C1−P1−C11 [100.8(1) and 101.9(1)°] and P−B−H [104(1) and 105(1)°] and large B2−P1−B1 [118.5(1)−118.9(2)°] and P−B−P [115.4(1)−118.3(1)°] bond angles.[48] The P−B bond lengths in **4** and **5** [1.936(2)−1.965(2) Å] indicate single bonds and are in good agreement with other reported P−B−P−B-type compounds (1.90−2.0 Å).[24,46,49]

Huertos and Weller reported the dehydrocoupling reaction of $t\mathrm{Bu_2PH{-}BH_3}$[50] with 5 mol % $[\mathrm{Rh(1,5\text{-}cod)_2}][\mathrm{BAr^F{}_4}]$ ($\mathrm{BAr^F{}_4} = [\mathrm{B\{C_6H_3(CF_3)_2\}_4}]^-$) at 140 °C for 20 h under melt conditions. The product $t\mathrm{Bu_2PH{-}BH_2{-}P}t\mathrm{Bu_2{-}BH_3}$ was obtained in about 65% yield. Furthermore, compounds **I1** and **I2** (Figure 3) were isolated and assumed to be intermediates in the dehydrocoupling reaction. Cleavage of the P−B bond in the dehydrocoupling reaction was also proposed earlier.[51]

The ^{31}P NMR spectrum of the reaction mixture of **2** and **2a** always showed the signal of the free phosphine [FcP(tBu)H] at −25 ppm but not that of P(tBu)(nBu)$_2$ at −2 ppm. Therefore, similar intermediates, namely, **I3** and **I4** (Figure 3), can also be expected in the cross-dehydrocoupling reaction between **2** and **2a** or **2b**, although these intermediates were not directly observed.

■ CONCLUSION

Transition-metal-catalyzed dehydrocoupling of **2** gave the homocoupled product **3** (diastereomers **3a** and **3b**), whereas cross-dehydrocoupling with tertiary phosphine−boranes **2a** and **2b** gave the corresponding heterocoupled products **4** and **5**. It can be concluded that, for cross-dehydrocoupling of two different phosphine−borane adducts, one of them must have a stronger P−B bond than the other. The phosphine−borane adduct with the stronger P−B bond is less prone to P−B bond cleavage and thus forms a complex with the rhodium catalyst via the $\mathrm{BH_3}$ hydrogen atoms. In the adduct with the weaker P−B bond, this bond is cleaved and the resulting phosphine acts as a ligand to form an intermediate rhodium(I) complex similar to that observed by Huertos and Weller.[50] This results exclusively in a single dehydrocoupled product. The electron-donating substituents on the phosphorus atom of the tertiary phosphine−borane adduct (**2a** and **2b**) strengthen the P−B dative bond compared to **2** and result in successive dehydrocoupling. Compounds **4** and **5** are the first cross-dehydrocoupled products reported to date. Because the terminal phosphorus atom has no hydrogen atoms and is thus essentially blocked, further dehydrocoupling can only occur at the terminal $\mathrm{BH_3}$ group, so that chain growth is allowed in only one direction. Thus, controlled formation of oligomers starting from **4** and **5** should be possible. These studies are presently underway.



Fc = $(\mathrm{C_5H_5})\mathrm{Fe}(\mathrm{C_5H_4})$, anions are omitted

Figure 3. Intermediates **I1** and **I2** reported by Huertos and Weller[50] and the proposed intermediates **I3** and **I4** for the cross-dehydrocoupling reaction between **2** and **2a**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, dehydrocoupling of **2**, stereoisomers of **3**, molecular structures of **1a**, **1**, **3a**, **3b**, **4′**, and **5′**, bond lengths and angles of **1a** and **1**, cross-dehydrocoupling of **2** with **2a** and **2b**, crystallographic data, details of data collection, and structure refinement parameters, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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