

B(C₆F₅)₃-catalyzed formation of B–P bonds by dehydrocoupling of phosphine–boranes†

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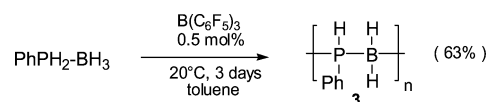
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Tris(pentafluorophenyl)borane was used as a new catalyst in the formation of P–B bonds by dehydrocoupling of phosphine–boranes.

Catalytic heterodehydrocoupling of covalent hydrides represents an interesting route to the formation of element–element bonds. In this way, formation of Si–N and Si–C bonds has been achieved some years ago using group 4 metallocenes as catalysts.¹ The Manners group has recently developed a new route to B–P² and B–N³ bond formation involving catalytic dehydrocoupling of the corresponding phosphine– and amine–boranes with Rh(I) as catalyst. In this preliminary communication we report two selected examples of the use of tris(pentafluorophenyl)borane,^{4†} B(C₆F₅)₃ (BX₃) as a catalyst for the formation of B–P bonds under mild conditions by dehydrocoupling of phosphine–borane adducts. Our results will be compared with those obtained with the transition-metal catalyzed reactions.² A mechanism will be proposed.

Dehydrogenative coupling of H₃B–PPhH₂ **1** has recently been performed by refluxing a toluene solution overnight in the presence of 0.5 mol% Rh(I) as catalyst.² High molecular weight poly(phosphinoboranes) [PhPH–BH₂]_n were thus obtained (Table 1, entry 1). We observed the dehydro-condensation of **1** at 20 °C in a toluene solution containing 0.5 mol% of B(C₆F₅)₃§ (entry 2).¶ Evolution of gas could be observed during the first 2 h. The reaction was completed after 3 days (yield 63% in isolated products). ³¹P- and ¹¹B-NMR displayed two separated groups of signals (≈ 1:1 ratio). The ³¹P NMR (toluene) presented a broad signal at δ –48.9 (d, J_{PH} ≈ 348 Hz) and poorly resolved peaks from δ –52 to –56, respectively. The corresponding ¹¹B NMR spectra revealed a broad peak at δ –35.5 and a shoulder at δ –33.2. All these data are characteristic of four-coordinated boron centres attached to two phosphorus.² Similar results were obtained by performing the reaction at 90 °C for 3 h (entry 2). The ³¹P and ¹¹B values observed at δ –48.9 and –35.8, respectively, are consistent

with the formation of poly(phenylphosphino)boranes **3** recently described in the literature.² The poorly resolved ³¹P signals from δ –52 to –56,² in the PH region suggested the presence of low molecular-weight oligomeric or cyclic structures. The coexistence of two main fractions corresponding roughly to M_w = 3900 and 830 were observed by size exclusion chromatography measurements (according to polystyrene standards) with a polydispersity index of 2.3 and 1.9, respectively. Differential scanning calorimetry confirmed these results and indicated a crystalline structure for **3** (T_m = 215 and 194 °C, respectively). Poly(phenylphosphinoboranes) **3** are air- and moisture-stable in the solid state.



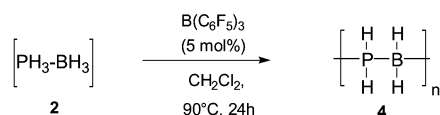
The main problem encountered in extending the dehydrocoupling to the complex H₃B–PH₃ **2** was due the weakness of the P–B bond and its fast dissociation at temperatures as low as –30 °C under atmospheric pressure.⁵ We used for this reaction safety equipment which allowed to bubble at –50 °C PH_{3(g)}⁶ and B₂H_{6(g)}⁷ into a CH₂Cl₂ solution of B(C₆F₅)₃ (≈ 5 mol% with regard to BH₃) and thereafter to heat the solution to the desired temperature. Oligomerisation started around +20 °C and was completed by heating at 70 °C overnight (entry 3). The oligomeric structure H₃P(BH₂PH₂)_nBH₃ was proposed from the ³¹P and ¹¹B spectra [disappearance of the peak at δ_p –119 corresponding to the complex **2** and formation of three broad peaks at δ –104 (t, J_{PH} 362 Hz), –109 (t, J_{PH} 342) (PH₂ groups) and a small peak at δ –115 (q, J_{PH} 356) (terminal PH₃ group)]. The ¹¹B NMR showed complex resonances (main peaks at δ –32 and –35 in good agreement with such a structure).² The material obtained by heating the solution at 90 °C for one day (entry 4) was assigned to **4** on the basis of the ³¹P NMR (very broad peak from δ –95 to –120) and ¹¹B NMR (very broad peak centred at δ –32). The white solid material thus obtained after evacuation of the solvent was very sensitive to air and moisture. Very fast oxidation prevented reliable elemental and HRMS analyses.

† Electronic supplementary information (ESI) available: experimental section. See <http://www.rsc.org/suppdata/cc/b2/b206559b/>

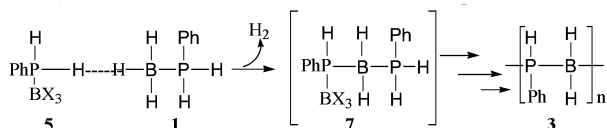
Table 1 B(C₆F₅)₃-catalysed formation of B–P bonds by dehydrocoupling of the phosphine–boranes **1** and **2**

Entry	Starting material	Catalyst (reagent)	Conditions	Conv. ^a (%)	Product(s)	³¹ P NMR δ (J _{PH})	¹¹ B NMR δ
1	1 ^b	RhI (0.5 mol%)	110 °C, 15 h (toluene)	100	3	–48.9 (360)	–34.7
2	1	(C ₆ F ₅) ₃ B (0.5 mol%)	20 °C, 3 days (toluene) or 90 °C, 3 h (toluene)	100	3	–48.9 (348) –52 to –56	–35.8 –33 ^c
3	2	(C ₆ F ₅) ₃ B (5 mol%)	Bubbling PH ₃ and BH ₃ into CH ₂ Cl ₂ /(C ₆ F ₅) ₃ B then 70 °C overnight	100	H ₃ P(BH ₂ PH ₂) _n BH ₃ oligomers	–104 (t, 362) –109 (t, 342) –115 (q, 356)	Main peaks at –32 and –35
4	2	(C ₆ F ₅) ₃ B (5 mol%)	Bubbling PH ₃ and BH ₃ into CH ₂ Cl ₂ /(C ₆ F ₅) ₃ B then 90 °C for 24 h	100	[PH ₂ BH ₂] _n 4	Broad peak centred at –107	Broad peak centred at –32

^a Progress of the reaction was monitored by ³¹P NMR. ^b See ref. 2. ^c Shoulder.



These results prove the efficiency of $\text{B}(\text{C}_6\text{F}_5)_3$ as a new catalyst for the preparation of poly(phosphinoboranes) by dehydrocoupling of phosphine–boranes (Table 1). In order to get a better understanding of the mechanism, a stoichiometric experiment between **5**†† and **1** was performed. Attempts to isolate the primary product **7** resulting from dehydrocoupling reaction were unsuccessful, even at -10°C . The poly(phosphinoborane) **3** was in all the cases the main observed product.



We suppose from this experiment that complex **5** (Fig. 1)†† formed by ligand exchange was probably the reactive intermediate in the catalytic dehydrocoupling. The acceptor strength of Lewis-acidic perfluorinated triarylborane compounds is well established.^{8,9} This effect should contribute to activate the P–H bond by withdrawing electron density from the phosphorus, making dehydrocoupling easier. Polymerisation presumably followed a process involving iterative dehydrocoupling reactions and BX_3/BH_3 exchanges.

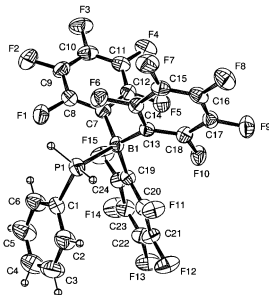


Fig. 1 Molecular structure of **5**. Selected bond length (Å): P(1)–B(1) 2.039.

Poly(phosphinoboranes) **3**, **4** were also formed by another route involving in the first step the formation of the complexes **8**, **9** (Fig. 2)†† respectively and slow decomposition of these intermediates (20°C for **8** and 110°C , 3 h for **9**) To explain the formation of the complex $\text{BX}_3\text{-SMe}_2$ **10**, a transient three-coordinate complex $\text{R}(\text{H})\text{P-BH}_2$ was suggested as intermediate.¹⁰

In conclusion, we have presented a new and efficient route to poly(phosphinoboranes) by using the strong Lewis acid

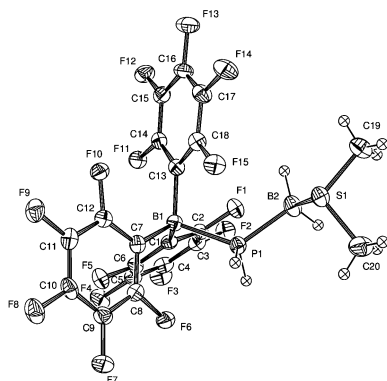
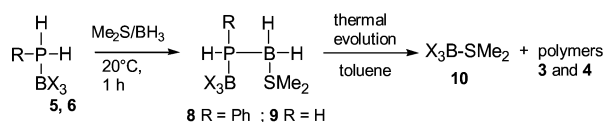


Fig. 2 Molecular structure of **9**. Selected bond length (Å): P(1)–B(1) 2.049.



$\text{B}(\text{C}_6\text{F}_5)_3$ as catalyst. The ease of the dehydrocoupling of **1** and **2** is attributed to the strong acidic character of the P–H bond of complexes **5** and **6**. The polymerisation presumably followed a process involving iterative dehydrocoupling reactions and BX_3/BH_3 exchanges. This work addresses mechanistic questions. Extension of this dehydrocoupling route to other element–element bond formation is in progress.

Notes and references

‡ $\text{B}(\text{C}_6\text{F}_5)_3$ is a Lewis acid of comparable strength to BF_3 . Application of this water-tolerant reagent as a catalyst in organic synthesis is rapidly growing.⁴

§ The use of anhydrous grade $\text{B}(\text{C}_6\text{F}_5)_3$ was critical. For each experiment, the product was sublimed by plunging the flask maintained under vacuum (0.02 mbar) into an oil-bath previously heated at 105°C . All the manipulations should be carried out under neutral gas in dry solvents and reagents.

¶ Typical experiment: 2.5×10^{-4} mol of the borane complex $\text{PhPH}_2\text{-BH}_3$ in toluene (400 μL) was slowly added into a toluene solution (100 μL) of the freshly sublimated BX_3 (6.0×10^{-4} g; 1.2×10^{-6} mol, 0.5 mol%) and the solution was maintained at the considered temperature. Progress of the reaction was monitored by ^{31}P NMR. Traces of free phosphine or phosphine oxide were sometimes detected by ^{31}P .

|| An authentic sample of **5** was easily prepared and fully characterised by ^{11}B and ^1H NMR, HRMS, and single crystal X-ray diffraction.

** An authentic sample of **10** was easily prepared and characterised by NMR and X-ray diffraction. CCDC 189752. (ESI†).

†† Crystal data for **5**: $\text{C}_{24}\text{H}_7\text{BF}_{15}\text{P}$, $M = 622.8$, $T = 293(2)$ K, $\lambda = 0.71069$, triclinic, space group $P\bar{1}$, unit cell dimensions: $a = 8.070(5)$, $b = 11.337(9)$, $c = 12.992(9)$ Å, $\alpha = 86.66(9)^\circ$, $\beta = 77.22(7)^\circ$, $\gamma = 87.560(8)^\circ$, $V = 1156.7(14)$ Å³, $Z = 2$, $D_c = 1.786$ g cm⁻³, $\mu = 0.254$ mm⁻¹, $F(000) = 612$, crystal size: $0.32 \times 0.24 \times 0.16$ mm, θ Range for data collection $1.61\text{--}24.97^\circ$, index range, $0 < h < 9$, $-13 < k < 13$, $-15 < l < 15$, reflections collected: 4389, independent reflections: 4070 [$R_{\text{int}} = 0.0156$], reflections observed ($> 2\sigma$): 2495, refinement method, full-matrix least-squares on F^2 , data/restraints/parameters, 4070/0/377, goodness-on-fit on $F^2 = 1.009$, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0422$, $wR2 = 0.0788$, R indices (all data): $R = 0.0989$, $wR = 0.0918$, largest diff. peak and hole, 0.196 and -0.209 e Å⁻³. CCDC 189751.

Crystal data for **9**: $\text{C}_{20}\text{H}_{10}\text{B}_2\text{F}_{15}\text{PS}$, $M = 619.93$, $T = 293(2)$ K, $\lambda = 0.71069$, triclinic, space group $P\bar{1}$, unit cell dimensions: $a = 9.6926(4)$, $b = 10.6562(5)$, $c = 12.3789(7)$ Å, $\alpha = 64.353(2)^\circ$, $\beta = 86.081(2)^\circ$, $\gamma = 84.137(3)^\circ$, $V = 1146.16(10)$ Å³, $Z = 2$, $D_c = 1.796$ g cm⁻³, $\mu = 0.343$ mm⁻¹, $F(000) = 612$, crystal size: $0.12 \times 0.10 \times 0.03$ mm, θ Range for data collection $1.83\text{--}27.61^\circ$, index range, $0 < h < 12$, $-13 < k < 13$, $-15 < l < 16$, reflections collected: 5270, reflections observed: 5270, goodness of fit: 1.029, final R indices: $R = 0.0478$, $wR = 0.1320$. CCDC 189752.

See <http://www.rsc.org/suppdata/cc/b2/b206559b/> for crystallographic data in CIF or other electronic format.

- For a review: F. Gauvin, J. F. Harrod and H. G. Woo, *Adv. Organomet. Chem.*, 1998, **42**, 463.
- H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 2000, **122**, 6669.
- C. A. Jaska, K. Temple, A. J. Lough and I. Manners, *Chem. Commun.*, 2001, 962.
- Reviews: (a) W. E. Piers and T. Chivers, *Chem. Soc. Rev.*, 1997, **26**, 345–354; (b) K. Ishihara and H. Yamamoto, *Eur. J. Chem.*, 1999, 527–538.
- H. Schmidbauer, T. Wimmer, J. Lachmann and G. Muller, *Chem. Ber.*, 1991, **124**, 275.
- D. Semenzin, G. Etemad-Moghadam, D. Albouy and M. Koenig, *Tetrahedron Lett.*, 1994, **35**, 3297.
- J. V. B. Kanth and H. C. Brown, *Inorg. Chem.*, 2000, **39**, 1795.
- D. C. Bradley, I. S. Harding, A. D. Keefe, M. Motevalli and D. H. Zheng, *J. Chem. Soc., Dalton Trans.*, 1996, 3931.
- D. C. Bradley, M. B. Hursthouse, M. Motevalli and D. H. Zheng, *J. Chem. Soc., Chem. Commun.*, 1991, 7.
- Review: P. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 449.