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analysis using unit weights (heavy atoms anisotropic. H atoms fixed, whereby H positions are based on stereochemical considerations). Final R(F) = 0.0368, wR(F) = 0.038 for 596 variables and 4864 observed reflections with $F > 5\sigma(F)$. Further details of the crystal structure investigations may be obtained from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation.

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Bis(pentafluorophenyl)borane: Synthesis, Properties, and Hydroboration Chemistry of a Highly Electrophilic Borane Reagent**

Daniel J. Parks, Rupert E. von H. Spence, and Warren E. Piers*

Hydroboration is one of the most widely used reactions in organic synthesis.^{[11} A wide variety of borane reagents have been reported such that a library of reagents exists tailored to many different chemical situations. We were interested in the electrophilic and potentially very reactive borane $HB(C_6F_5)_2$ for possible applications in generation of soluble Ziegler–Natta-type olefin polymerization catalysts. These studies revealed this borane to be an exceptionally active hydroboration reagent. In this communication we describe its synthesis, characterization, and a preliminary survey of its activity towards alkenes and alkynes.

Bis(pentafluorophenyl)borane (1) was prepared from the known chloroborane $(C_6F_5)_2BCl^{[2]}$ in the absence of Lewis bases by reaction with hydride sources such as $[Cp_2Zr(Cl)H]_n$, Bu₃SnH, and Me₂Si(Cl)H (Scheme 1). Traditional metathetical methods for transformations of this type^[3] were not advisable because they necessitated the use of donor solvents which were difficult to remove completely (if at all) owing to the high Lewis acidity^[4] of 1.^[5] The most convenient hydride transfer agent proved to be Me₂Si(Cl)H since it also served as solvent for the reaction and the by-product Me₂SiCl₂ was easily removed; 1 was observed to precipitate over the course of one hour and was isolated in high yield by filtration. The overall yield of 1 from bromopentafluorobenzene was 52%.

Borane 1 is a white, microcrystalline, oxygen- and moisturesensitive solid which was found to be to stable (i.e. it retained 100% of its activity) for at least three months when stored under an inert atmosphere at room temperature. Spectroscopic evidence indicated that the solid material is dimeric in structure. The infrared spectrum of the solid showed a strong band at 1550 cm⁻¹ characteristic¹⁶¹ of the v_{asym} in-phase mode for a B-(μ -H)₂-B unit, and no bands corresponding to stretching vibrations of terminal B–H bonds were evident.^[7] Solution NMR data were, however, consistent with the presence of monomeric



Scheme 1. Synthesis of $(C_6F_5)_2BH$ (1). In the last step the reagent Me₂Si(Cl)H also serves as the solvent.

 $(C_6F_5)_2$ BH. Most convincingly, the ¹¹B NMR spectrum revealed the presence of a minor species ($\approx 10\%$) with a signal at $\delta = 60.1$ ppm in addition to a major species giving rise to a signal at $\delta = 18.0$. The downfield resonance appears in the region associated with monomeric dialkylboranes,^[8] while the signal due to the major species is more typical of a dimeric borane.^[9] Thus, although borane 1 is a dimer in the solid state, dissociation into a monomeric borane is facile in aromatic solvents.

Bis(pentafluorophenyl)borane is a highly active hydroboration reagent towards a range of simple alkenes and alkynes (Table 1). Addition of the olefin or alkyne to a suspension of the borane in benzene led to the rapid dissolution of the solid, and the reaction was complete within two minutes.^[10] Even sterically demanding olefins (Table 1, entry 1) were hydroborated very rapidly, and the rates of hydroboration of methylcyclohexene and methylcyclopentene were almost identical.[11, 12] These observations are in contrast with those seen in reactions employing the common hydroboration reagent 9-borabicyclo[3.3.1]nonane (9-BBN) which, under identical conditions, required several hours to go to completion with these substrates. The only substrates that do not react rapidly with 1 are those having a $B(C_6F_5)_2$ functionality attached, in other words those formed upon monohydroboration of alkynes (entries 6-8). Not only are these alkenes more sterically encumbered, the electron-withdrawing effect of the $B(C_6F_5)_2$ substituent likely deactivates the double bond towards subsequent hydroboration. By comparison, hydroborations of alkynes with 9-BBN generally proceed more rapidly for the second hydroboration, often precluding isolation of the singly hydroborated product unless excess substrate is employed.[13]

Entries 2–4 in Table 1 demonstrate that 1 hydroborates the substrates by the commonly accepted *cis* addition mechanism.^[14] Regioselectivity was found to be excellent for substrates for which multiple products were possible. For example, styrene was hydroborated to give the isomer shown with >98% selectivity (as shown by ¹H NMR spectroscopy and oxidation to 2-phenyl-ethanol, vide infra). In some instances (entries 1–3) facile isomerization by means of a retrohydroboration–rehydroboration sequence was observed over the course of a few hours at room temperature. This behavior is typical for substrates with thexyl substituents,^[15] but for other substrates elevated temperatures are usually required to induce these rearrangements.^[16] Fortu-

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Table 1. Hydroboration of simple alkenes and alkynes with bis(pentafluoro-phenyl)borane (1) [a].

Entry	Substrate	Product (1 equiv. 1)	Product (2 equiv. 1)
1	\succ	H B(C ₆ F ₅₎₂	0.
2 ^[b]	\bigcirc	$\square_{B(C_6F_5)_2}^{H}$	
3161	\bigcirc	B(C ₆ F ₅) ₂	
4101		$(C_6F_5)_2B$	
5 ^[d]	\bigtriangledown		
6	<u></u>	H B(C ₆ F ₅) ₂	no reaction
7 ^[b]			$(C_6F_5)_2B \to B(C_6F_5)_2$
8161, I	el Si-	SiB(C ₆ F ₅) ₂	(C ₆ F ₅) ₂ B B(C ₆ F ₅) ₂
9 ^[f]	۲ / _ ^{Si}	, Si (C ₆ F ₅) ₂ B	

[a] 100% yield by ¹H NMR (see ref. [10]). [b] Regioselectivity >98%. [c] [D₁]-1 was used. [d] Small amounts ($\approx 4\%$) of the other regioisomer were also detected. [e] The second hydroboration initially produced a mixture of regioisomers which converted quantitatively into the thermodynamic product shown (see text). [f] A thermodynamic mixture of isomers was observed (85:15); the major isomer is shown (see text).

nately, the difference in the rates of initial hydroboration and rearrangement in these systems allows for good control in obtaining either the kinetic or thermodynamic products.

Selective monohydroboration of terminal alkynes was effected by reaction of substrates with a single equivalent of 1 (entries 7, 8). Although slower, double hydroboration occurred upon addition of a second equivalent of the borane. In the reaction of 1 with phenylacetylene, the product was the 1,1 isomer in accord with the normal selectivity observed with other borane reagents.^[10] In contrast, the thermodynamic product for trimethylsilylacetylene was the 1,2 isomer. Initially, a mixture of the two possible products of double hydroboration was observed (ratio of 1,1:1,2 = 2.5:1, Scheme 2), which converted to the 1,2 regioisomer quantitatively. A similar phenomenon was observed for trimethyl(vinyl)silane (entry 9). The kinetic product in this reaction was that with the expected selectivity, 1-trimethylsilyl-2bis(pentafluorophenyl)borylethane. Upon heating to 100 °C this compound isomerized to a mixture (ratio = 85:15) of the two possible regioisomers; the primary isomer was that with



Scheme 2. Hydroboration of trimethylsilylacetylene using 1.

boron attached to the α -carbon atom (see structural formula in Table 1). In the products arising from reaction of silylated substrates with BH₃ boron has been observed to occupy the α -position for electronic reasons, when steric repulsions between the Me₃Si group and boron substituents are at a minimum. Similarly, hydroboration of substrates with the general formula RC≡CSiMe₃ is selective: in the products boron is attached to the carbon atom α to silicon in the monohydroborated product.^[17] These observations suggest that there is a thermodynamic preference for silicon to occupy a position β to a boron center in analogy to the well-known " β -silicon effect"^[18] in the stabilization of carbocations. Instead of stabilizing a carbocation-like transition state structure, the boron migrates to form a more

stable ground state structure **A**. The generality of this phenomenon and its possible applications are being explored further.

Oxidation of the hydroborated products $RB(C_6F_5)_2$ could not be effected cleanly with



aqueous methods or with *meta*-chloroperbenzoic acid (MCP-BA) owing to the proteolytic instability of the $B(C_6F_5)_2$ group (loss of HC_6F_5). We have found that anhydrous $Me_3NO^{[19]}$ is a mild and efficient reagent for oxidizing alkylboranes to provide alcohols in good yields. For example 3,3-dimethyl-1-butanol was isolated in 58% yield (unoptimized) from the hydroboration of *tert*-butylethylene. We are exploring other methods for functionalizing these boranes. We are also interested in the properties of the boranes, particularly the dihydroborated products shown in entries 7 and 8, which should be excellent chelating Lewis acid activators for a variety of organic reactions and Ziegler–Natta olefin polymerization systems.^[20]

Experimental Procedure

1: Into an evacuated flask containing (C_6F_3)₂BCl (7.00 g, 18.4 mmol) at -78 °C was condensed Me₂Si(Cl)H (10.2 g, 108 mmol). The flask was warmed to room temperature, upon which the chloroborane dissolved and a new white precipitate formed. The reaction mixture was stirred for 1 h and then filtered to give 6.14 g (17.7 mmol, 96%) of the borane as a white crystalline powder. ¹H NMR (C_6D_6): $\delta = 4.2$ (br, full width at half maximum ≈ 25 Hz); ¹¹B NMR (C_6D_6 , 25 °C): major component $\delta = 60.1$; ¹⁹F{¹H} NMR (C_6D_6 , 10 mM, 25 °C): major component (90%) $\delta = -134.8$ (2F), -148.0 (1F), -160.7 (2F); minor component (10%) $\delta = -130.5$ (2F), -143.4 (1F), -161.7 (2F); IR (Nujol, NaCl): $\nu = 1652$ s, 1550 m (B-H), 1521 m, 1406 w, 1395 w, 1315 s, 1307 w, 1149 s, 1111 s, 1050 w, 1018 m, 975 s, 949 m, 937 w, 767 m, 661 m, 634 w, 624 w: MS (CC : 7.0 eV): miz = 346 (M^+); anal. calcd for $C_{12}F_{10}$ BH: C 41.67, H 0.29; found: C 41.87, H 0.33.

Deuteriobis(pentafluorophenyl)borane $[D_1]$ -1: To a solution of $(C_6F_5)_2BCl$ (1.45 g, 3.8 mmol) in hexane (6 mL) was added a solution of tributyltin deuteride (1.11 g, 3.8 mmol) in hexane (2 mL) over 5 min. This led to the immediate precipitation of a white solid. After 1 h the reaction mixture was filtered; the solid was washed with

a little cold hexane to give [D₁]-1 (1.07 g, 3.1 mmol, 81%). ²H{¹H} NMR (C₆H₆): $\delta = 4.2$ (br, full width at half maximum = 6 Hz).

General hydroboration procedure: To a suspension of $HB(C_6F_5)_2$ (0.1 mmol) in dry benzene (0.6 mL) under an argon atmosphere was added the dried alkene or alkyne substrate (1 equiv) by syringe. The mixture was sonicated for 30–60 s and then shaken. The reaction progress was monitored by ¹H NMR spectroscopy.

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New Process for the Sulfonation of Phosphane Ligands for Catalysts**

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Two-phase procedures have opened a new perspective for organometallic homogeneous catalysis as exemplified in hydroformylation.^[1] Sulfonated phosphane ligands have proved themselves in the Ruhrchemie/Rhône–Poulenc process^[1, 2] and suggest that a large potential may be anticipated for other C–C coupling reactions, too.^[3] Fuming sulfuric acid (oleum), often the only effective sulfonating agent for arylphosphanes is not always satisfactory as a reagent for synthesis:^[3d] parallel to the

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[**] Water-Soluble Metal Complexes and Catalysts, Part 8. This work was supported by the Bundesministerium für Forschung und Technologie. Part 7: W. A. Herrmann, C. W. Kohlpaintner, R. B. Manetsberger, H. Bahrmann, H. Kottmann, J. Mol. Catal., in press. sulfonation of the aryl groups it also causes the formation of undesirable phosphane oxides, which, according to our present understanding, are useless for catalytic purposes and, in addition, are laborious to separate.^[4]

These side reactions can be suppressed with low concentrations of SO_3 and short reaction times, but then mixtures of products with different degrees of sulfonation are formed. Phosphanes with a low degree of sulfonation, on the other hand, lead to an increased loss of the catalytically active (noble metal) complexes through extraction into the organic phase because of their poor water-solubility.^[1a] Both disadvantages—phosphane formation and low, nonuniform degree of sulfonation—frequently militate against the industrial use of sulfonated phosphanes. In the following we show how these problems can be avoided.

Treating the standard ligand triphenylphosphane (TPP) according to the previous standard procedure at 20 °C with 30% oleum (30 wt% SO₃) under laboratory conditions yields, after 24 hours, a mixture of sulfonated products containing 12.4 mol% of phosphane oxides (Fig. 1a; ³¹P NMR: $\delta = 36.45$), which must be separated from the sulfonated derivatives by a multistage extraction.^[4]

We have now discovered that the addition of orthoboric acid to the sulfonation charges lessens the phosphane oxidation or suppresses it completely. The boric acid is initially dissolved in



Fig. 1. a) ³¹P NMR spectrum of triply sulfonated triphenylphosphane 2 (TPPTS; $\delta = 2.88$, 53.8 mol%), prepared according to the conventional procedures of ref. [4], crude hydrolysis mixture with 33.8 mol% of 1. b) ³¹P NMR spectrum of doubly sulfonated triphenylphosphane 1 (TPPDS), prepared with H₂SO₄/B(OH)₃/ oleum; see text. The spectrum shows a very small amount of phosphane oxide ($\delta = 37.68$).