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Non-Metal Catalysed Heterodehydrocoupling of Phosphines and Hydrosilanes: Mechanistic Studies of B(C₆F₅)₃-Mediated Formation of P-Si Bonds

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ABSTRACT: Non-metal catalysed heterodehydrocoupling of primary and secondary phosphines (R₁R₂PH, R₂ = H or R₁) with hydrosilanes (R₁'R₂'R₃'SiH, R₂', R₃' = H or R₁') to produce synthetically useful silylphosphanes (R₁R₂P-SiR₁'R₂'R₃') has been achieved using B(C₆F₅)₃ as the catalyst (10 mol%, 100 °C). Kinetic studies demonstrated that the reaction is first-order in silane and B(C₆F₅)₃ but zero-order in phosphine. Control experiments, DFT calculations as well as DOSY NMR studies suggest that a R₁R₂HP•B(C₆F₅)₃ adduct is initially formed and which subsequently undergoes partial dissociation to form an "encounter complex" held together *via* weak secondary interactions. The latter mediates Frustrated Lewis Pair-type Si-H bond activation of the silane substrates. We also found that B(C₆F₅)₃ catalyses the homodehydrocoupling of primary phosphines to form cyclic phosphine rings and the first example of catalytic hydrosilylation of P-P bonds to produce silylphosphanes (R₁R₂P-SiR₁'R₂'R₃'). Moreover, the introduction of PhCN to the reactions involving secondary phosphines with hydrosilanes allowed the heterodehydrocoupling reaction to proceed efficiently under much milder conditions (1.0 mol% B(C₆F₅)₃ at 25 °C). Mechanistic studies, as well as DFT calculations, revealed that PhCN plays a key mechanistic role in facilitating the dehydrocoupling reactions rather than simply functioning as H₂-acceptor.

INTRODUCTION

Molecular and macromolecular species containing bonds between main-group elements (E-E') (E = *p*-block element) represent attractive synthetic targets due to their interesting reactivity and useful properties.¹⁻¹⁵ For example, main group polymers containing Si-O,⁸ Si-N,¹⁴ Si-Si,¹⁵ or P=N⁶⁻⁷ bonds in the main chain and related materials have found applications as elastomers, lithographic resists, biomaterials, polyelectrolytes, ceramic precursors and optoelectronics, and several other materials are of exploratory interest.^{3-5, 9-13} As the second most abundant element in the earth's crust, silicon introduces useful functionality and transformations, the construction of Si-E bonds has received considerable attention. However, compared with the large number of well-known species containing Si-O or Si-N bonds, compounds containing P-Si bonds (silylphosphanes) have received much less attention.¹⁶ Silylphosphanes have considerable potential utility in chemical synthesis, for example, as silyl cation equivalents in the silylation of alcohols (Scheme 1, A);¹⁷ through their reaction with acid chlorides to yield acylphosphides (Scheme 1, B)¹⁸ and their palladium-catalysed reaction with aryl halides to produce aryl(diphenyl)phosphines (Scheme 1, C).¹⁹ Very recently, Miura and Hirano reported the diphosphination of alkenes using silylphosphanes to afford dppe-type (dppe = 1,2-bis(diphenylphosphino)ethane) bidentate ligands (Scheme 1, D).²⁰ Complexation of cyclic silylphosphanes with transition metal centers has also been reported (Scheme 1, E).²¹

A. Silylation of alcohols

B. Synthesis of acylphosphides

C. Synthesis of Aryl-diphenylphosphine

D. Diphosphination of alkenes to provide dppe-type ligand

E. Complexation with transition metal species

Scheme 1. Transformations of silylphosphanes and complexation with transition metals species.

Traditionally, silylphosphanes have been prepared by the reaction of chlorosilanes with alkali metal phosphi-

nides, a process that generates at least one equivalent of salt waste and has limited functional group tolerance.^{16,22} The recent expansion in catalytic dehydrocoupling methods has provided a much milder and general route to form E-E' bonds.²³⁻²⁹ Surprisingly, the catalytic heterodehydrocoupling of phosphines (R_1R_2PH) with hydrosilanes ($R_1'R_2'R_3'SiH$) has only been reported using titanocene for secondary phosphines³⁰ (Scheme 2, equation 1) or triamidoamine-supported zirconium complexes for primary phosphines³¹ (Scheme 2, equation 2), and the reactions were limited to primary and secondary silanes. Significantly, the synthetically useful silylphosphanes illustrated in Scheme 1 are all derived from tertiary silanes. As part of our interest in catalytic reactions of main group substrates we have explored the development of new catalytic dehydrocoupling routes to silylphosphanes. Here, we chose the well-known Lewis acid $B(C_6F_5)_3$ (tris(pentafluorophenyl)borane) as the catalyst for this transformation.³²⁻³⁴ The $B(C_6F_5)_3$ -mediated activation of Si-H bonds has been very well-studied in the pioneering work by Piers³⁴⁻⁴¹ and more recently by Ostreich,⁴²⁻⁴⁵ Chang⁴⁶⁻⁴⁸ and others in the context of hydrosilylation of $C=X$ ($X = O$ and NR)^{37,44,49-52} and $C\equiv N$ ⁴⁷⁻⁴⁸ containing substrates as well as in the dehydrocoupling of silanes with $-OH$,^{36,53} $-NHR$ ⁵⁴ and aromatic C-H bonds.⁵⁵ Surprisingly, the related dehydrocoupling of phosphines R_1R_2PH with silanes using $B(C_6F_5)_3$ or any other non-metal species has not been reported. Herein, we report the first non-metal catalysed heterodehydrocoupling of primary and secondary phosphines (R_1R_2PH , $R_2 = H$ or R_1) with primary, secondary, and tertiary silanes ($R_1'R_2'R_3'SiH$, $R_2', R_3' = H$ or R_1').

Scheme 2. Previous work on the transition-metal-catalysed heterodehydrocoupling of phosphines with hydrosilanes.

RESULTS AND DISCUSSION

Conditions optimization: We first examined the reaction between $PhPH_2$ (**1a**) and Et_3SiH (**2a**) in the presence of catalytic amounts of various Lewis acids ($[Ph_3C][B(C_6F_5)_4]$, $AgNO_3$, $Zn(OAc)_2$), carbene (IMes) or combinations of $B(C_6F_5)_3$ with different bulky Lewis bases ($P(tBu)_3$, 2,6-di-*tert*-butylpyridine - DTBP) to form typical Frustrated Lewis Pairs (FLPs)⁵⁶ (Table S1). We found that $B(C_6F_5)_3$ alone gave superior results and produced monosilylation product **3a** and bis-silylation product **4a**. It is worth noting that no reaction took place without the addition of $B(C_6F_5)_3$ even at 130°C (Table 1, entry 1). Further experiments showed that this reaction was sensitive to temperature: at 80°C after 16 h only 50% of **1a** was consumed albeit with 100% selectivity to **3a** (Table 1, entry 4). The reaction conditions were optimized with 10 mol%

$B(C_6F_5)_3$, at 100°C for 16 h in benzene to give 95% conversion of **1a** and 98% selectivity for **3a** (Table 1, entry 5). After completion the ^{19}F NMR spectrum of the reaction mixture showed two major species that were identified as being the adducts of $B(C_6F_5)_3$ with either **1a** or **3a**.⁵⁷⁻⁵⁸ No signals due to Piers' borane ($HB(C_6F_5)_2$)⁵⁹ or adducts thereof were observed. Higher temperature (130°C) or catalyst loading (20 mol%) produced more of **4a** (Table 1, entries 6 and 8).

Table 1. $B(C_6F_5)_3$ -catalysed heterodehydrocoupling of $PhPH_2$ with Et_3SiH – effect of catalyst loading and temperature.^a

Entries	x [mol%]	T [°C]	Conversion [%] ^b	Selectivity [%] ^b	
				3a	4a
1	0	130	0	-	-
2	10	25	0	-	-
3	10	50	3	100	0
4	10	80	50	100	0
5	10	100	95	98	2
6	10	130	99	80	20
7	2	100	50	100	0
8	20	100	99	82	7

^a $PhPH_2$ (0.1 mmol, 11 μL), Et_3SiH (0.3 mmol, 48 μL), $B(C_6F_5)_3$ (0.1x mmol), benzene 0.5 mL in J. Young NMR tube, 16 h; ^bdetermined by ^{31}P NMR spectroscopy using PCl_3 as a calibration standard.

Figure 1. Time-dependent $^{31}\text{P}\{H\}$ NMR spectra of the $B(C_6F_5)_3$ (0.01 mmol) catalysed heterodehydrocoupling of $PhPH_2$ (**1a**, 0.1 mmol) with Et_3SiH (**2a**, 0.3 mmol) in 0.5 mL benzene at 100°C .

Although **1a** has two potentially reactive P-H bonds, we found that the reaction did not yield more than 8% of the

Figure 2. Kinetic studies of B(C₆F₅)₃-catalyzed heterodehydrocoupling of PhPH₂ with Et₃SiH: (A) Decay of PhPH₂ during the reaction at 100 °C with the release of H₂ every 20 min; (B) Zero-order reaction rate in PhPH₂, (initial concentration of PhPH₂: blue line 0.05 M, orange line 0.1 M, purple line 0.4 M); (C) First-order reaction rate in Et₃SiH; (D) First-order reaction rate in B(C₆F₅)₃.

bis-silylation product **4a** even after 120 h at 100 °C. Monitoring the reaction by ³¹P NMR spectroscopy showed that **4a** did not appear until 90% of **1a** had been consumed (Figure 1), which implies that the mono-silylation product **3a** is much less reactive than **1a**. This could be attributed to the enhanced steric and/or changed electron density on the phosphorus atom. By heating the reaction to 130 °C for 48 h, we could obtain **4a** with 78% selectivity together with 14% of the homodehydrocoupling product from **1a** and minor amount of an unassigned product. This finding is in agreement with the computed thermodynamics: the formation of **3a** (**1a** + **2a** = **3a** + H₂) is only marginally exergonic ($\Delta G = -0.33$ kcal/mol) and slightly favoured thermodynamically. However, the formation of **4a** (**3a** + **2a** = **4a** + H₂) is endergonic ($\Delta G = 3.73$ kcal/mol) and is not favoured thermodynamically.

Kinetic studies and isotope labelling experiments: While monitoring the B(C₆F₅)₃-mediated reaction of PhPH₂ (**1a**) and Et₃SiH (**2a**) in benzene we found that the reaction rate was constant for the first 100 min (Figure S1), which motivated detailed kinetic studies. The initial reaction rate was recorded to avoid the possible reverse hydrogenation reaction. In fact, we found that the reaction rate did not change with H₂ ventilation every 20 min compared to a closed system and we could still detect the deviation from the constant reaction rate after 100 min (Figure 2A).

Under pseudo-first order conditions generated using excess **2a** (8-60 fold), we varied the concentration of **1a** from 0.05 M to 0.1 M and 0.4 M and obtained same k_{obs} which indicated a zero-order reaction rate in **1a** (Figure 2B). This implied that **1a** was not involved in the rate determining step. The reaction order in **2a** was determined using 1.5 –

12 equivalents of **2a** with respect to **1a**, with the concentration of **1a** = 0.1 M, and that of B(C₆F₅)₃ = 0.01 M at 100 °C. A linear correlation between k_{obs} and [**2a**] ($R^2 = 0.9924$) revealed a first-order dependence of the reaction on the concentration of **2a** (Figure 2C). Changing the concentration of B(C₆F₅)₃ and keeping the concentration of **1a** at 0.2 M and **2a** at 0.6 M, a plot of k_{obs} versus the concentration of B(C₆F₅)₃ also yielded a straight line ($R^2 = 0.9986$) that passed through the origin, in accordance with a first-order reaction in B(C₆F₅)₃ (Figure 2D).

As the reaction was found to be first-order in silane, deuterium-labelling experiments using Et₃SiD (**2a'**) were performed to gain further insight into the reaction mechanism. Using standard reaction conditions determined in Table 1, entry 5 (0.2 M **1a** and 0.6 M **2a'** with 0.02 M B(C₆F₅)₃, in benzene at 100 °C), we were surprised to find that H/D-scrambling was detected by ³¹P NMR spectroscopy (characterized by the appearance of the PhPHD triplet at -124.7 ppm with a $J(P-D)$ spin-spin coupling constant of 31.8 Hz and PhPD₂ quintet at -125.8 ppm) (Figure 3A). In addition, we could also observe H₂ and HD (characterized by the appearance of the HD triplet at 4.44 ppm with a $J(H-D)$ spin-spin coupling constant of 42.7 Hz in the ¹H NMR spectrum) (Figure 3B). Nevertheless, we were able to run the deuterium-labelling experiments at a lower catalyst loading (0.01 M, 5 mol%) while keeping the concentration of other reactants the same and halting the reaction before the H/D-scrambling was observed (100 min). This led to the determination of a kinetic isotope effect 1.5. Isotope effects of 1.4-1.9 have been reported for the hydrosilylation of carbonyl compounds and

Figure 3. Deuterium labelling experiments: (A) $^{31}\text{P}\{\text{H}\}$ NMR spectrum of the reaction PhPH_2 0.2 M, Et_3SiD 0.6 M, and 0.02 M $\text{B}(\text{C}_6\text{F}_5)_3$ in 0.5 mL benzene after 4 h at 100 °C; (B) ^1H NMR spectrum of the reaction PhPH_2 0.2 M, Et_3SiD 0.6 M, and 0.02 M $\text{B}(\text{C}_6\text{F}_5)_3$ in 0.5 mL benzene after 10 h at 100 °C; (C) ^{11}B NMR spectrum of the reaction PhPH_2 0.2 M, Et_3SiH 0.6 M, and 0.02 M $\text{B}(\text{C}_6\text{F}_5)_3$ in 0.5 mL benzene before heating; (D) ^{11}B NMR spectrum of the reaction PhPH_2 0.2 M, Et_3SiD 0.6 M, and 0.02 M $\text{B}(\text{C}_6\text{F}_5)_3$ in 0.5 mL benzene before heating.

were interpreted in terms of hydride transfer.^{37, 60} Additional experiments showed that the H/D-scrambling did not take place in the absence of $\text{B}(\text{C}_6\text{F}_5)_3$ or when the temperature was reduced to 25 °C. This observation together with the fact that we could detect $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ and $[\text{DB}(\text{C}_6\text{F}_5)_3]^-$ at room temperature (Figure 3C-D) support the assertion that hydride transfer was involved in the rate determining step. Based on these observations we propose that both **1a** and **2a'** are each activated by $\text{B}(\text{C}_6\text{F}_5)_3$ at high temperature to generate $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ and $[\text{DB}(\text{C}_6\text{F}_5)_3]^-$ (Scheme 3, equations 1-2), followed by anion exchange (Scheme 3, equation 3) which eventually gave the H/D-scrambling products PhPHD and Et_3SiH (Scheme 3, equation 4).

Scheme 3. Proposed reaction pathway for the H/D-scrambling of PhPH_2 with Et_3SiD .

$\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed homodehydrocoupling of PhPH_2 and hydrosilylation of P-P bonds. As our kinetic studies and deuterium labelling experiments suggested that PhPH_2 (**1a**) was activated by $\text{B}(\text{C}_6\text{F}_5)_3$, and that previous work by Stephan and co-workers has demonstrated the catalytic homodehydrocoupling of **1a** with $\text{B}(p\text{-C}_6\text{F}_4\text{H})_3$ at 130 °C to give cyclophosphines, $(\text{PhP})_5$,⁶¹ we considered the possibility that homodehydrocoupling products from **1a** were formed initially, followed by $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed hydrosilylation of the skeletal P-P bonds⁶² to produce the silylphosphane (Scheme 4). To test our hypothesis, the reaction was repeated without **2a** but under otherwise identical conditions (0.2 M **1a** and 0.02 M $\text{B}(\text{C}_6\text{F}_5)_3$ in 0.5 mL benzene), we found that no reaction took place at 100 °C after 16 h. However on raising the reaction temperature to 130 °C we observed the homodehydrocoupling of **1a**. Monitoring the reaction

Scheme 4. Proposed reaction pathway involving homodehydrocoupling of **1a** with subsequent hydrosilylation of the P-P bonds.

showed that the (PhPH)₂ and a mixture of cyclic phosphine products (PhP)_x (x = 4-6) were produced initially and eventually all converted to the cyclic products, predominantly (PhP)₅ (89% selectivity) (Figure 4). The computed homodehydrocoupling of PhPH₂ [2PhPH₂ = PhPH-PhPH + H₂] is slightly endergonic ($\Delta G = 0.84$ kcal/mol) and such endergonic characteristics explain the need of higher temperature experimentally.

Figure 4. Time-dependent ³¹P{H} NMR spectra of B(C₆F₅)₃-catalyzed homodehydrocoupling of **1a**: B(C₆F₅)₃ (0.01 mmol), **1a** (0.1 mmol) in 0.5 mL benzene at 130 °C.

Figure 5. Time-dependent ³¹P{H} NMR spectra of B(C₆F₅)₃-catalysed hydrosilylation of phosphine rings: (PhP)₄₋₆ (0.02 mmol, cal. 10.8 mg), Et₃SiH (0.3 mmol, 48 μ l), B(C₆F₅)₃ (0.01 mmol) in 0.5 mL benzene in a J. Young NMR tube at 130 °C. ^a Selectivity was calculated as a sum of **4a** + **5a** (where **5a** is the adduct PhP(SiEt₃)₂•B(C₆F₅)₃).

Next, we explored the catalytic hydrosilylation of the isolated phosphine rings (91% (PhP)₅) with 3 equivalents **2a** and 10 mol% B(C₆F₅)₃. Once again, under our catalytic conditions (100 °C, 16 h) no reaction was detected and heating to 130 °C was necessary for the hydrosilylation of P-P bonds to take place. After 200 h, 96% conversion was achieved, with the mono-silylation product **3a** formed with

43% and the bis-silylation product **4a** with 45% selectivity (Figure 5). We also found that the reaction worked as well for the isolated (P_nHex)₅ rings (Figure S5). In contrast, catalytic hydrosilylation of the bulkier cyclic phosphines (P^tBu)₄ or (P^tBu)₃ was unsuccessful. The hydrosilylation of tetraphenyldiphosphine (**6a**), on the other hand, gave rise to 45% silylation product **8a** together with 14% diphenylphosphine (**7a**) and other unidentified side products which indicated that some of the silylation product arises from the dehydrocoupling of the silane with **7a** generated by the hydrosilylation (Figure 6).

Figure 6. Time-dependent ³¹P{H} NMR spectra of B(C₆F₅)₃-catalysed hydrosilylation of tetraphenylbiphosphine **6a**: (Ph₂P)₂ (0.05 mmol, 18.5 mg), Et₃SiH (0.3 mmol, 48 μ l), B(C₆F₅)₃ (0.01 mmol), benzene 0.5 mL in a J. Young NMR tube, 130 °C.

From these experiments, we concluded that although the reaction pathway described in Scheme 4 is feasible, it is not operative in our catalytic reaction since the B(C₆F₅)₃-catalysed homodehydrocoupling of **1a** requires a higher temperature (130 °C vs 100 °C) and a longer reaction time (120 h vs 16 h). In addition, the similar distribution of mono- and bis-silylphosphane products **3a** (43%) and **4a** (45%) observed in the catalytic hydrosilylation of the skeletal P-P bonds of the (PhP)_x rings and the higher temperature required (130 °C) further ruled out the pathway in Scheme 4 as a possibility in our catalytic experiments. Nevertheless, our experiments represent the first examples of B(C₆F₅)₃-catalyzed homodehydrocoupling of phenylphosphine as well as the first catalytic hydrosilylation of P-P bonds (Scheme 4).

The phosphine-borane adduct PhH₂P•B(C₆F₅)₃ as a thermally generated FLP catalyst: The observed zero-order reaction in PhPH₂ prompted us to investigate another possible reaction pathway involving an intermediate adduct derived from PhPH₂ and B(C₆F₅)₃. DFT calculations show that PhPH₂ (**1a**) and B(C₆F₅)₃ can form a stable complex PhH₂P•B(C₆F₅)₃ (**9a**) based on the computed exergonic ($\Delta G = -7.53$ kcal/mol). In contrast, the formation of the complex Et₃Si-H•B(C₆F₅)₃ between Et₃SiH (**2a**) and B(C₆F₅)₃ is endergonic ($\Delta G = 5.85$ kcal/mol) and not favoured thermodynamically. Furthermore, we failed to optimize a stable complex Et₃Si-H•Ph₂P between **1a** and **2a**.

This shows that **9a** should be one of the principal intermediates in the reaction. Since the loading of $\text{B}(\text{C}_6\text{F}_5)_3$ is only 10% of the concentration of **1a**, the formation **9a** explains the zero-order dependence of $[\mathbf{1a}]$ and the first order dependence of $[\text{B}(\text{C}_6\text{F}_5)_3]$. That **2a** cannot form stable complexes with $\text{B}(\text{C}_6\text{F}_5)_3$ and **1a** also explains the first order dependence of **2a**. In addition, we computed the adducts of **3a** and **4a** with $\text{B}(\text{C}_6\text{F}_5)_3$. It was found that that formation of **3a**• $\text{B}(\text{C}_6\text{F}_5)_3$ and **4a**• $\text{B}(\text{C}_6\text{F}_5)_3$ is exergonic by 10.64 and 3.90 kcal/mol, respectively. **3a** Coordinates more strongly to $\text{B}(\text{C}_6\text{F}_5)_3$ than **1a** is consistent with the kinetic behaviour in Figure 2A after 100 min, where **1a** is liberated from $\text{B}(\text{C}_6\text{F}_5)_3$ by the subsequently formed **3a**.

In order to obtain more insights into the reaction mechanism, a series of stoichiometric reactions were carried out. Upon mixing equimolar amounts of **1a** and $\text{B}(\text{C}_6\text{F}_5)_3$ in benzene we found the formation of **9a** in quantitative yield (triplet at δ 48.0 ppm with a $J(\text{P-H}) = 423 \text{ Hz}$).⁵⁷ Furthermore, we found that **9a** is very stable even at 100 °C, and neither free phenylphosphine (**1a**) nor $\text{B}(\text{C}_6\text{F}_5)_3$ was observed in a high temperature NMR experiment (Figure S7). We thus considered whether **9a** is directly involved in the catalytic cycle. To explore this possibility, **9a** was isolated as a white solid and used as the catalyst (10 mol%) for the heterodehydrocoupling of **1a** and **2a** at 100 °C. Significantly, we observed a similar reaction yield and selectivity to **3a** (Scheme 5B). We were also interested to explore whether **9a** was reactive towards Et_3SiH in the absence of **1a**. Our experiments indeed demonstrated that **9a** reacts readily with Et_3SiH in benzene and that this yields $\text{PhP}(\text{H})\text{SiEt}_3 \cdot \text{B}(\text{C}_6\text{F}_5)_3$ (**10a**) in high yield at 100 °C over 16 h (Scheme 5C, Figure S8). Furthermore, the reaction also worked at 25 °C, albeit with a significantly reduced reaction rate (Scheme 5C). These results suggest that **9a** is involved in the Si-H bond activation in our catalytic reaction. Based on the mechanism of H-H bond activation with $\text{B}(\text{C}_6\text{F}_5)_3$, we propose that the process involves an “encounter complex” generated from the **9a** via secondary interactions that activates the Si-H before dissociation to form free PhPH_2 and $\text{B}(\text{C}_6\text{F}_5)_3$.^{34, 63-64}

Scheme 5. Synthesis of $\text{PhH}_2\text{P}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ adduct and its catalytic and stoichiometric reaction with Et_3SiH : (A) PhPH_2 (1 mmol, 110 μL), $\text{B}(\text{C}_6\text{F}_5)_3$ (1 mmol, 510 mg), benzene 10 mL 25 $^\circ\text{C}$; (B) PhPH_2 (0.1 mmol, 11 μL), Et_3SiH (0.3 mmol, 48 μL), $\text{PhH}_2\text{P}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ (0.01 mmol, 6.22 mg), benzene 0.5 mL in J. Young NMR tube, 100 $^\circ\text{C}$, 16 h; (C)

PhPH₂•B(C₆F₅)₃ (0.02 mmol, 12.4 mg), Et₃SiH (0.06 mmol, 9.6 μl), benzene 0.5 mL in J. Young NMR tube, 16 h.

Diffusion-Ordered Spectroscopy (DOSY) NMR studies were conducted to detect the potential dissociation of $\text{PhH}_2\text{P}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ adduct (**9a**) and further understand the nature of the interactions (Figure S9-12).⁶³ At a concentration of 0.04 M in benzene at 25 °C, we found that **1a** possesses a diffusion coefficient (D) of $17.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and for $\text{B}(\text{C}_6\text{F}_5)_3$ a value of $7.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. DOSY NMR analysis of a solution of 0.04 M **9a** in benzene gave values of $D = 6.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $5.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for PhPH_2 and $\text{B}(\text{C}_6\text{F}_5)_3$, respectively. The smaller diffusion coefficients in both cases compared to the separate species indicated an interaction in solution consistent with our variable temperature ^{31}P NMR spectroscopy studies (Scheme S7). On the other hand, the different values for the two species ($6.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ vs $5.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) using **9a** indicated that the P-B interaction is dynamic with the equilibrium highly favouring **9a**.

Scheme 6. Formation of a classical Lewis acid/base adduct and dissociation to form the “encounter complex” and activation of the Si-H bond.

The activation of E-H bonds using $\text{B}(\text{C}_6\text{F}_5)_3$ /bulky phosphine *via* FLP-type combinations has been well-studied over the past decade in cases where the Lewis acid and base do not form an adduct.^{56, 65} When $\text{B}(\text{C}_6\text{F}_5)_3$ is used with oxygen- or nitrogen-containing compounds (*e.g.* alcohols, amines, imines) as bases and reactants, labile Lewis acid/base adduct formation is generally observed prior to subsequent reactivity (*e.g.* imine reduction with H_2 , dehydrocoupling of hydrosilanes with alcohols).^{36, 64, 66} Our system represents the first case for phosphines where a classical Lewis acid/base adduct (**9a**) is observed and can be isolated prior to its thermally-induced concerted reaction with a third substrate (Et_3SiH). The observed reaction of the thermally stable adduct $\text{PhH}_2\text{P}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ with Et_3SiH , the zero-order reaction in PhPH_2 , and DOSY NMR studies indicate that the rupture of the P-B dative bond to form an “encounter complex” is responsible for the Si-H activation and in this manner is analogous to the activations of H-H and Sn-H bonds using FLPs (*e.g.* $\text{B}(\text{C}_6\text{F}_5)_3/\text{Mes}_3\text{P}$) (Scheme 6).^{34, 67}

Synthesis of different silylphosphanes. After establishing the mechanism for the $B(C_6F_5)_3$ -catalysed heterodehydrocoupling between **1a** with **2a**, hydrosilanes with

Table 2. $B(C_6F_5)_3$ -catalysed heterodehydrocoupling of $PhPH_2$ with different hydrosilanes.^a

Entries	Silane	Time [h]	T [°C]	Product	Yield [%] ^b
1	 2a	16	100	 3a	93 (89) ^c
2	 2b	16	100	 3b	76
3	 2c	16	100	 3c	77
4	 2d	16	130	 3d	91
5	 2e	36	100	 3e	92 (85)
6	 2f	4	130	 3f	54
7	 2g	8	130	 3g	62 (55)

3g:3g' = 4:1

^a $PhPH_2$ (0.1 mmol, 11 μ l), silanes (0.3 mmol, 48 μ l), $B(C_6F_5)_3$ (0.01 mmol), benzene 0.5 mL in J. Young NMR tube, 100-130 °C; ^bdetermined by ^{31}P NMR spectroscopy using PCl_3 as a calibration standard; ^cnumbers in bracket are isolated yields.

substituents on silicon gave the products **3b** and **3c** with yields 76% and 77%, respectively. Bulky silanes such as triphenylsilane **2d** led to a much lower reaction rate and required higher temperature (130 °C) to produce the corresponding silylphosphane **3d** in good yield (91%). 1,4-Bis(dimethylsilyl)benzene **2e** reacted with **1a** at 100 °C after 36 h produce the cyclic product **3e** in very good yield (92%). Moreover, when using secondary silanes **2f** or

different substituents were applied to study the generality of our strategy. We found that hydrosilanes **2b** and **2c** with small

primary silane **2g**, 6 and 4-membered rings **3f-3g** were obtained at 130 °C with moderate yield (54-62%). The structures of **3e** and **3g** were confirmed by X-ray diffraction as shown in Figure 7.

$B(C_6F_5)_3$ -catalyzed heterodehydrocoupling of secondary phosphines with Et_3SiH in the presence of $PhCN$. When we attempted to extend the $B(C_6F_5)_3$ -

catalysed heterodehydrocoupling chemistry to the secondary phosphine,

Figure 7. Molecular structure of **3e** and **3g** determined by Single-crystal X-ray Diffraction: For **3e** non-hydrogen atoms shown as 30% probability ellipsoids and all H-atoms are omitted for clarity. The molecule possesses a crystallographically imposed inversion centre in the middle of the ring; for **3g** non-hydrogen atoms are shown as 30% probability ellipsoids, and H atoms bound to Si are shown as spheres of arbitrary radius. All other H atoms, and the second component of the disordered central 6-membered [Si-P]₃ ring are omitted for clarity.

Ph₂PH (**7a**) with Et₃SiH (**2a**) in benzene, we found that the reaction proceeded very slowly. Even with 20 mol% B(C₆F₅)₃ at 100 °C, only 10% of the heterodehydrocoupling product **8a** was produced after 16 h. Heating the reaction to 130 °C for 48 h increased the yield of **8a** to ca. 60%. Analysis of the reaction mixture by ³¹P NMR spectroscopy revealed the appearance of multiple peaks around -24.4 ppm which might arise from the thermal rearrangement of the adduct Ph₂HP•B(C₆F₅)₃.⁶⁸ This was further confirmed via the independent reaction of equimolar amounts of Ph₂PH and B(C₆F₅)₃ at 130 °C for 24 h (Figure S13). Compared with the formation of PhH₂P•B(C₆F₅)₃ (ΔG = -7.53 kcal/mol), the formation of Ph₂HP•B(C₆F₅)₃ is even more exergonic (ΔG = -9.38 kcal/mol), indicating that Ph₂HP•B(C₆F₅)₃ is more stable than PhH₂P•B(C₆F₅)₃ by 1.85 kcal/mol. In addition, the formation of **8a** [7a + 2a = 8a + H₂] is computed to be endergonic by 1.64 kcal/mol and therefore thermodynamically not favoured thus rationalizing the need of high temperature.

In order to obtain a higher yield of **8a**, we attempted to avoid the side reaction involved Ph₂HP•B(C₆F₅)₃ by lowering the reaction temperature. Stephan⁶⁹ and Oestreich⁷⁰ have previously introduced alkenes as H₂-acceptors to allow the homodehydrocoupling reactions of phosphines and heterodehydrocoupling of aromatic C-H and B-H bonds to take place under milder conditions. Adopting this

strategy, we explored the addition of different potential H₂-acceptors to the reaction of **7a** with **2a**. Initially, we added different alkenes, unfortunately, cyclohexene, octene, and 1, 1-diphenylethylene all failed to affect the reaction rate. Other types of H₂-acceptor such as phenylacetylene, benzophenone, nitrobenzene, azobenzene also failed as H₂-acceptors (Table S2). Remarkably, we found that by using PhCN as the H₂-acceptor we could obtain **8a** in 99% yield within 20 min at 25 °C (Scheme 7). This is a dramatic acceleration effect and allowed the reaction to be performed with only 1 mol% catalyst loading and still gave 99% yield at 25 °C, furthermore, with even 0.5 mol% catalyst loading at 50 °C the reaction was essentially complete in 3 h with 99% yield (Table S3).

Scheme 7. PhCN accelerated B(C₆F₅)₃-catalyzed heterodehydrocoupling of Ph₂PH with Et₃SiH: Ph₂PH (0.1 mmol, 17.4 μl), Et₃SiH (0.3 mmol, 48 μl), PhCN (0.1 mmol, 10.3 μl), B(C₆F₅)₃ (0.01 mmol), 0.5 mL benzene in a J. Young NMR tube, 20 min, 25 °C.

The dramatic effect of PhCN suggested that rather than simply functioning as an H₂-acceptor, a new reaction pathway may be operative. We therefore carried out competitive binding experiments to explore the role of PhCN. As shown in Figure 8, combining **7a** and B(C₆F₅)₃ gave rise to the adduct. Addition of 1 equiv. of PhCN to the adduct and monitoring the reaction by ³¹P NMR spectrum after 1 h showed 40% free Ph₂PH, 60% Ph₂HP•B(C₆F₅)₃ adduct and 40% PhCN•B(C₆F₅)₃ adduct (¹¹B NMR, -12.6 ppm) (Figure 8 and S14). These ratios give a K_{eq} of 0.44 for the displacement of the phosphine from Ph₂P•B(C₆F₅)₃ by PhCN, indicating that the binding of the phosphine to B(C₆F₅)₃ is 0.5 kcal mol⁻¹ more favourable. Indeed, this value is in excellent agreement with our calculation that Ph₂PH binding to B(C₆F₅)₃ is 0.6 kcal mol⁻¹ more favourable than PhCN (Scheme 8).

Figure 8. ³¹P NMR spectrum of competitive binding experiments of Ph₂PH and PhCN with B(C₆F₅)₃: (A) Ph₂PH (0.01 mmol, 1.7 μl), benzene 0.5 mL in a J. Young NMR tube, 25 °C;

(B) after addition of $B(C_6F_5)_3$ (0.01 mmol, 5.1 mg); (C) 1 h after addition of PhCN (0.01 mmol, 1.1 μ l).

Scheme 8. Thermodynamic of Ph_2PH and PhCN binding to $B(C_6F_5)_3$.

Figure 9. Reaction profile of $B(C_6F_5)_3$ -catalyzed heterodehydrocoupling of Ph_2PH with Et_3SiH in the presence of PhCN: Ph_2PH (0.1 mmol, 17.4 μ l), Et_3SiH (0.3 mmol, 48 μ l), $B(C_6F_5)_3$ (0.0025 mmol), PhCN (0.1 mmol, 10.3 μ l), benzene 0.5 mL in J. Young NMR tube, 25 $^\circ\text{C}$.

We then carried out a kinetic study by monitoring the reaction of 2.5 mol% $B(C_6F_5)_3$, 0.1 mmol **7a**, 0.3 mmol **2a** and 0.1 mmol PhCN at 25 $^\circ\text{C}$ using ^{31}P NMR spectroscopy. We observed two new peaks at 15.7 ppm (int1) and 7.7 ppm (int2) after 30 min. The intensity of these peaks increased initially and decreased after 120 min before complete conversion to **8a** (Figure 9). The absence of those two peaks when no PhCN is present and the reaction profile of the reaction with PhCN is added suggested that they represent intermediates arising from reactions involving PhCN. As we have demonstrated binding of both Ph_2PH and PhCN to $B(C_6F_5)_3$ and since it is known that hydrosilylation of PhCN can produce imines or amines (Scheme 9, equation 1),⁴⁸ we proposed that one of the intermediates might be a silylimine that undergoes hydrophosphination with **7a** (Scheme 9, equation 2).

To test our hypothesis, the corresponding stepwise reactions were conducted (Scheme 9). First, the hydrosilylation of PhCN by Et_3SiH in the presence of $B(C_6F_5)_3$ was conducted yielding the imine **11a** as the only product at 25 $^\circ\text{C}$. Only after heating at above 50 $^\circ\text{C}$, the saturated silylamine (**11b**) could be detected (Scheme 9, equation 1). As a control experiment no hydrosilylation occurred without $B(C_6F_5)_3$. Then the reaction between **11a** and **7a** was tested and again we found no reaction in the absence of $B(C_6F_5)_3$. However, upon addition of 10 mol% $B(C_6F_5)_3$ a new peak appeared at 7.7 ppm (int2 in catalytic experiments) in the ^{31}P NMR spectrum within 5 min. The species giving rise to this signal was isolated and identified as the silylimine

hydrophosphination product **12a** (Scheme 9, equation 2). Finally, reaction of the **12a** with **2a** gave rise to the dehydrocoupling product

Scheme 9. The stepwise reaction of the $B(C_6F_5)_3$ -catalyzed heterodehydrocoupling of Ph_2PH with Et_3SiH in the presence of PhCN: (1) PhCN (0.1 mmol, 10.3 μ l), Et_3SiH (0.3 mmol, 48 μ l), $B(C_6F_5)_3$ (0.01 mmol), benzene 0.5 mL in J. Young NMR tube, 25 $^\circ\text{C}$; (2) **11a** (0.1 mmol, 22 μ l), Ph_2PH (0.1 mmol, 17.4 μ l), $B(C_6F_5)_3$ (0.01 mmol), benzene 0.5 mL in J. Young NMR tube, 25 $^\circ\text{C}$; (3) **12a** (0.1 mmol, 40.5 mg), Et_3SiH (0.2 mmol, 32 μ l), $B(C_6F_5)_3$ (0.01 mmol), benzene 0.5 mL in J. Young NMR tube, 25 $^\circ\text{C}$.

Figure 10. Energy profile (kcal/mol) for the $B(C_6F_5)_3$ -catalyzed heterodehydrocoupling of Ph_2PH with Et_3SiH with and without PhCN.

Figure 11. ^{11}B NMR spectra of the reactions: (A) Ph_2PH 0.1 mmol, $B(C_6F_5)_3$ 0.025 mmol in 0.5 mL benzene- d_6 at 25 $^\circ\text{C}$; (B)

addition of 0.1 mmol PhCN to A at 25 °C; (C) addition of 0.3 mmol Et₃SiH to B and monitor after 30 min; (D) addition of 0.3 mmol Et₃SiH to B and monitor after 12 h.

Figure 12. Proposed reaction mechanism for the reaction of **12a** to **8a**: left, sigma-bond metathesis route; right, FLP route.

8a (Scheme 9, equation 3). These stepwise experiments confirmed our hypothesis that PhCN functions as **11a** precursor and undergoes hydrosilylation with **7a** to produce **12a**, which subsequently reacts with **2a** to give the final product. Although no peak at 15.7 ppm (int 1) was observed in these control experiments, we tentatively assign it to be the further dehydrocoupling product from the -NH of **12a** with **2a**.

We performed DFT calculations to assess the viability of the proposed reaction pathway (Figure 10). Hydrosilylation of the PhCN with Et₃SiH is exergonic with $\Delta G = -9.59$ kcal·mol⁻¹ and further hydrophosphination with Ph₂PH is also exergonic with $\Delta G = -6.28$ kcal·mol⁻¹, these are consistent with our experimental results (Scheme 9, equations 1-2). The final step, surprisingly, is even more exergonic with a value of $\Delta G = -7.30$ kcal·mol⁻¹ and confirms again that in the presence of PhCN allows the reaction to be performed under substantially milder conditions and with shorter reaction times. The PhCN free system, on the other hand, is endergonic by 1.64 kcal·mol⁻¹ (Figure 10). This calculation is in line with our experimental findings that without PhCN higher temperatures are needed for the dehydrocoupling of phosphine with hydrosilane to take place.

We also followed the reaction using ¹¹B NMR spectroscopy in order to further understand the mechanism and the fate of B(C₆F₅)₃ (Figure 11). We found that by adding Et₃SiH to a solution containing Ph₂PH, PhCN, and B(C₆F₅)₃ the anion [HB(C₆F₅)₃]⁻ was formed and persisted throughout the reaction (Figure 11C). After the reaction was complete, we could also observe the accumulation of the [HB(C₆F₅)₃]⁻ (Figure 11D), which might arise from the activation of excess amount of Et₃SiH in the presence of phosphines or amines.

Compound **12a** could interact with Et₃SiH to yield product **8a** via two different mechanisms: a) sigma-bond metathesis of the Si-H bond with the C-P bond from **12a**; or b)

coordination of **12a** with B(C₆F₅)₃ either through the P or N atom or both to form a frustrated “encounter complex” capable of activating the Si-H bond and forming an ionic intermediate **14a**. The latter species could undergo hydride attack at the carbon of the C-P bond of **12a** to form the product **8a** and release amine **13a** (Figure 12). The detection of [HB(C₆F₅)₃]⁻ by ¹¹B NMR throughout the reaction (Figure 11) supports the FLP mechanism.

CONCLUSION

The first non-metal catalysed heterodehydrocouplings of phosphines (R₁R₂PH, R₂ = H or R₁) with primary, secondary, and tertiary silanes (R₁'R₂'R₃'SiH, R₂', R₃' = H or R₁') to produce synthetically useful silylphosphanes (R₁R₂P-SiR₁'R₂'R₃') has been achieved using B(C₆F₅)₃. Detailed mechanistic studies (kinetic studies, variable temperature NMR spectroscopy) have shown that the reaction relies on the key Lewis acid/base adduct, R₁R₂HP•B(C₆F₅)₃. Under the reaction conditions this classical Lewis adduct functions as a precursor to a thermally generated FLP to activate Si-H bonds and enable heterodehydrogenative P-Si coupling. Through DOSY NMR spectroscopy experiments we have shown that the interaction of phosphines with B(C₆F₅)₃ is dynamic and leads to the formation of an “encounter complex” which is responsible for the reactivity. We have also demonstrated the B(C₆F₅)₃-catalysed homodehydrocoupling of phosphines to produce cyclic phosphine rings and the first catalytic hydrosilylation of P-P bonds. Moreover, we have successfully introduced PhCN in the reaction of secondary phosphines Ph₂PH with Et₃SiH to avoid the thermal rearrangement side products from the Ph₂HP•B(C₆F₅)₃ adduct and this allows the reaction to take place under much milder conditions (100 °C reduced to 25 °C and catalyst loading from 10 mol% to 0.5 mol%). Control experiments have revealed that PhCN is involved in the formation of key intermediate (**12a**), which will react with silanes to give the final heterodehydrocoupling

products via an FLP-type activation. The excellent agreement between calculated and experimental thermodynamics provides a convincing rationalization of the experimental results.

ASSOCIATED CONTENT

Supporting Information. Experimental details, products characterizations, computational chemistry, crystallographic data for **3e** and **3g**; 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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