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Non-Metal Catalysed Heterodehydrocoupling of Phosphines and Hydrosilanes: Mechanistic Studies of $B(C_6F_5)_3$-Mediated Formation of P-Si Bonds

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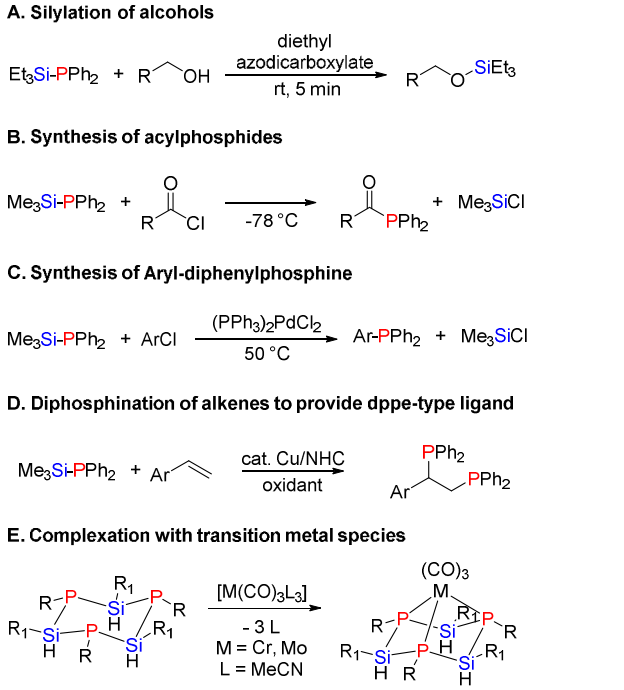
ABSTRACT: Non-metal catalysed heterodehydrocoupling of primary and secondary phosphines (R^1R^2PH, R^2 = H or R^1) with hydrosilanes ($R^3R^4R^5SiH$, R^4, R^5 = H or R^3) to produce synthetically useful silylphosphanes (R^1R^2P-$SiR^3R^4R^5$) has been achieved using $B(C_6F_5)_3$ as the catalyst (10 mol%, 100 °C). Kinetic studies demonstrated that the reaction is first-order in hydrosilane and $B(C_6F_5)_3$ but zero-order in phosphine. Control experiments, DFT calculations as well as DOSY NMR studies suggest that a $R^1R^2HP{\bullet}B(C_6F_5)_3$ adduct is initially formed and which subsequently undergoes partial dissociation to form an "encounter complex". The latter mediates Frustrated Lewis Pair-type Si-H bond activation of the silane substrates. We also found that $B(C_6F_5)_3$ catalyses the homodehydrocoupling of primary phosphines to form cyclic phosphine rings and the first example of a non-metal catalysed hydrosilylation of P-P bonds to produce silylphosphanes (R^1R^2P-$SiR^3R^4R^5$). 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% $B(C_6F_5)_3$ 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 H_2-acceptor.

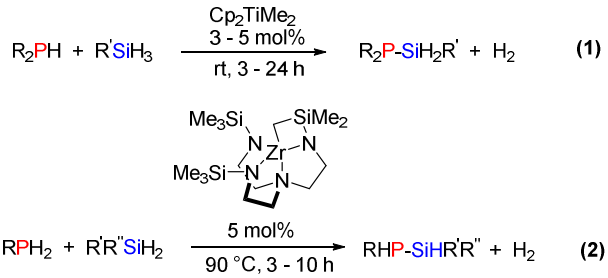
INTRODUCTION

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=N[6-7] bonds in the main chain and related materials have found applications as elastomers, lithographic resists, biomaterials, polyelectrolytes, ceramic precursors, 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]



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

Traditionally, silylphosphanes have been prepared by the reaction of chlorosilanes with alkali metal phosphanides, 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 ($R^3R^4R^5SiH$, R^4, R^5 = H or R^3) has only been reported using titanocene for secondary phosphines[30] (Scheme 2, equation 1) or triamidoamine-supported zirconium complexes for primary phosphines[31] (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 well-studied in the pioneering work by Piers[34-41] and more recently by Ostreich,[42-45] Chang[46-48] and others in the context of hydrosilylation of C=X (X = O and NR)[37, 44, 49-52] and C≡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 hydrosilanes 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 hydrosilanes ($R^3R^4R^5SiH$, R^4, R^5 = H or R^3).

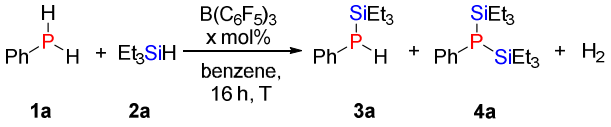


Scheme 2. Previous work on the transition-metal-catalysed heterodehydrocoupling of phosphines with hydrosilanes.

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]



1a **2a** **3a** **4a**

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; [b] determined by ^{31}P NMR spectroscopy using a sealed capillary of PCl_3 as an integration standard.

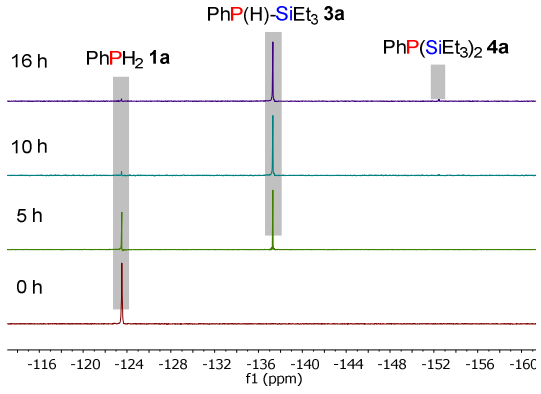


Figure 1. Time-dependent $^{31}P\{^1H\}$ NMR spectra of the $B(C_6F_5)_3$ (0.01 mmol) catalysed heterodehydrocoupling of $PhPH_2$ (**1a**, 0.1 mmol) with Et_3SiH (**2a**, 0.3 mmol) in 0.5 mL benzene at 100 °C.

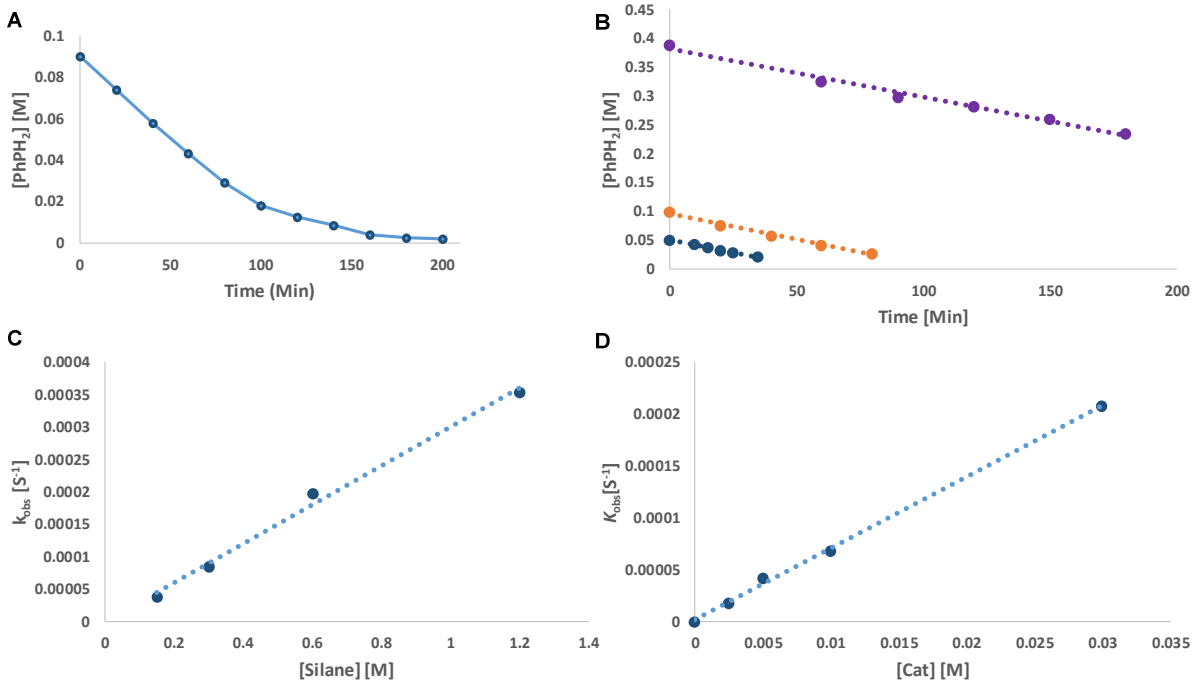


Figure 2. Kinetic studies of $B(C_6F_5)_3$-catalyzed heterodehydrocoupling of $PhPH_2$ with Et_3SiH: (A) Decay of $PhPH_2$ during the reaction at 100 °C with the release of H_2 every 20 min; (B) Zero-order reaction rate in $PhPH_2$, (initial concentration of $PhPH_2$: blue line 0.05 M, orange line 0.1 M, purple line 0.4 M); (C) First-order reaction rate in Et_3SiH; (D) First-order reaction rate in $B(C_6F_5)_3$.

Although **1a** has two potentially reactive P-H bonds, we found that the reaction did not yield more than 8% of the bis-silylation product **4a** even after 120 h at 100 °C. Monitoring the reaction by ^{31}P 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** + H_2) is only marginally exergonic (ΔG = -0.33 kcal/mol) and slightly favoured thermodynamically. However, the formation of **4a** (**3a** + **2a** = **4a** + H_2) is endergonic (ΔG = 3.73 kcal/mol) and is not favoured thermodynamically.

Kinetic studies and isotope labelling experiments: While monitoring the $B(C_6F_5)_3$-mediated reaction of $PhPH_2$ (**1a**) and Et_3SiH (**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 H_2 ventilation every 20 mins compared to a closed system and we could still detect the deviation from the constant reaction rate after 100 mins (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 $B(C_6F_5)_3$ = 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 $B(C_6F_5)_3$ 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 $B(C_6F_5)_3$ also yielded a straight line (R^2 = 0.9986) that passed through the origin, in accordance with a first-order reaction in $B(C_6F_5)_3$ (Figure 2D).

As the reaction was found to be first-order in silane, deuterium-labelling experiments using Et_3SiD (**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 $B(C_6F_5)_3$, in benzene at 100 °C), we were surprised to find that H/D-scrambling was detected by ^{31}P 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 $PhPD_2$ quintet at -125.8 ppm) (Figure 3A). In addition, we could also observe H_2 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

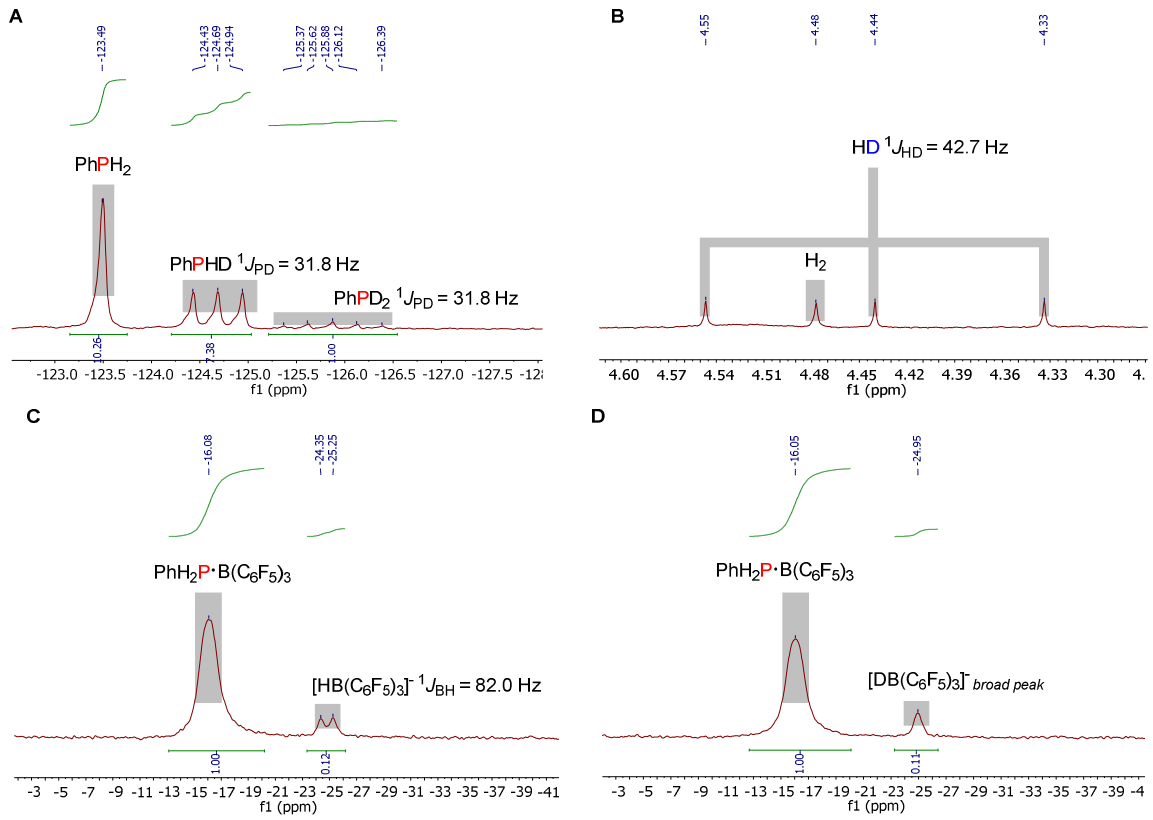


Figure 3. Deuterium labelling experiments: (A) $^{31}P\{^{1}H\}$ NMR spectrum of the reaction $PhPH_2$ 0.2 M, Et_3SiD 0.6 M, and 0.02 M $B(C_6F_5)_3$ in 0.5 mL benzene after 4 h at 100 °C; (B) ^{1}H NMR spectrum of the reaction $PhPH_2$ 0.2 M, Et_3SiD 0.6 M, and 0.02 M $B(C_6F_5)_3$ in 0.5 mL benzene 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 $B(C_6F_5)_3$ 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 $B(C_6F_5)_3$ in 0.5 mL benzene before heating.

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 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 $B(C_6F_5)_3$ or when the temperature was reduced to 25 °C. This observation together with the fact that we could detect $[HB(C_6F_5)_3]^-$ and $[DB(C_6F_5)_3]^-$ at room temperature (Figure 3C-D) support the assertion that hydride transfer was involved in the rate determining step. Based on these observations, and that formation of $[HB(C_6F_5)_3]^-$ only occurs in the presence of phosphine **1a**, we propose that both **1a** and deuterated hydrosilane **2a'** are each activated by $B(C_6F_5)_3$ with the assistance of Lewis base (**1a**) at high temperature to generate $[HB(C_6F_5)_3]^-$ and $[DB(C_6F_5)_3]^-$ (Scheme 3, equations 1-3), followed by anion exchange (Scheme 3, equation 4) which eventually gives the H/D-scrambling products PhPHD and Et_3SiH (Scheme 3, equation 5). We discuss further evidence to support $B(C_6F_5)_3$–mediated activation of **1a** in the following section.

$$PhPH_2 + B(C_6F_5)_3 \rightleftharpoons PhH_2P{\cdot}B(C_6F_5)_3 \quad (1)$$

$$PhH_2P{\cdot}B(C_6F_5)_3 + Et_3SiD \rightleftharpoons [PhH_2P\text{-}SiEt_3]^+[DB(C_6F_5)_3]^- \quad (2)$$

$$PhH_2P{\cdot}B(C_6F_5)_3 + PhPH_2 \rightleftharpoons [PhH_2P\text{-}PHPh]^+[HB(C_6F_5)_3]^- \quad (3)$$

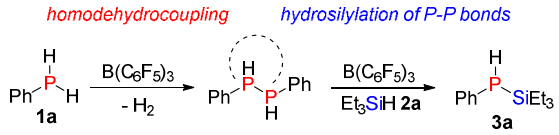
$$[PhH_2P\text{-}SiEt_3]^+[DB(C_6F_5)_3]^- + [PhH_2P\text{-}PHPh]^+[HB(C_6F_5)_3]^- \rightleftharpoons [PhH_2P\text{-}PHPh]^+[DB(C_6F_5)_3]^- + [PhH_2P\text{-}SiEt_3]^+[HB(C_6F_5)_3]^- \quad (4)$$

$$[PhH_2P\text{-}PHPh]^+[DB(C_6F_5)_3]^- \rightleftharpoons PhPH_2 + PhPHD + B(C_6F_5)_3 \quad (5)$$

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

$B(C_6F_5)_3$-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 $B(C_6F_5)_3$, and since previous work by Stephan and co-workers has demonstrated the catalytic homodehydrocoupling of **1a** with $B(p\text{-}C_6F_4H)_3$ at 130 °C to give cyclophosphines, $(PhP)_5$,[61] we considered the possibility that homodehydrocoupling products from **1a** were formed initially, followed by $B(C_6F_5)_3$-catalyzed

hydrosilylation of the skeletal P-P bonds[62] 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 $B(C_6F_5)_3$ 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 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 $PhPH_2$ [$2PhPH_2$ = PhPH-PHPh + H_2] is slightly endergonic (ΔG = 0.84 kcal/mol) and such endergonic characteristics explain the need of higher temperature experimentally.



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

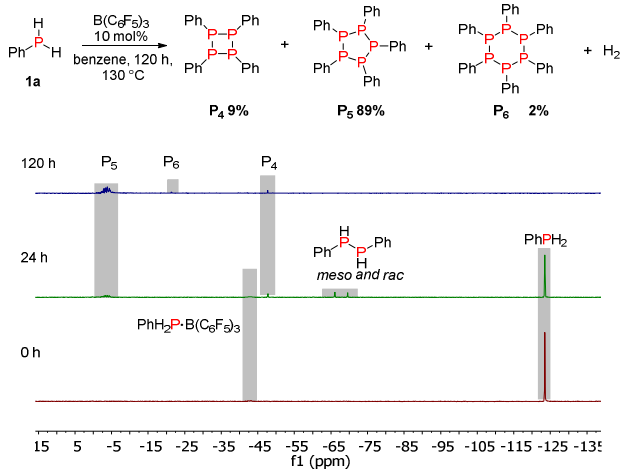


Figure 4. Time-dependent $^{31}P\{^1H\}$ NMR spectra of $B(C_6F_5)_3$-catalyzed homodehydrocoupling of **1a**: $B(C_6F_5)_3$ (0.01 mmol), **1a** (0.1 mmol) in 0.5 mL benzene at 130 °C.

Next, we explored the catalytic hydrosilylation of the isolated phosphine rings (91% $(PhP)_5$) with 3 equivalents **2a** and 10 mol% $B(C_6F_5)_3$. 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

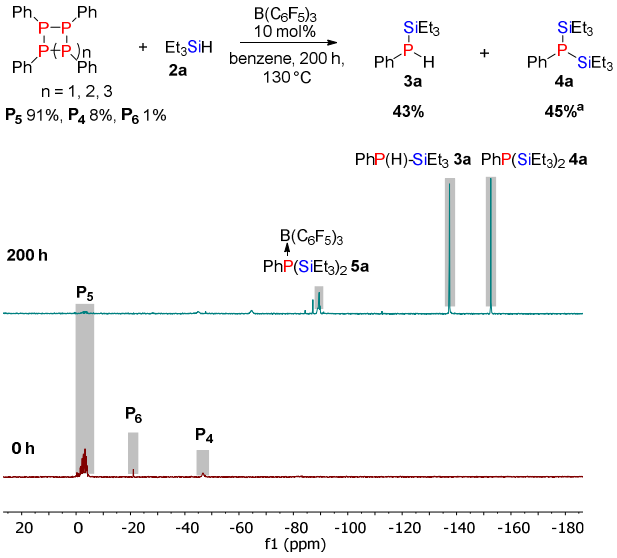


Figure 5. Time-dependent $^{31}P\{^1H\}$ NMR spectra of $B(C_6F_5)_3$-catalysed hydrosilylation of phosphine rings: $(PhP)_{4\text{-}6}$ (0.02 mmol, cal. 10.8 mg), Et_3SiH (0.3 mmol, 48 µl), $B(C_6F_5)_3$ (0.01 mmol) in 0.5 mL benzene in a J. Young NMR tube at 130 °C. [a] Selectivity was calculated as a sum of **4a** + **5a** (where **5a** is the adduct $PhP(SiEt_3)_2 \cdot B(C_6F_5)_3$).

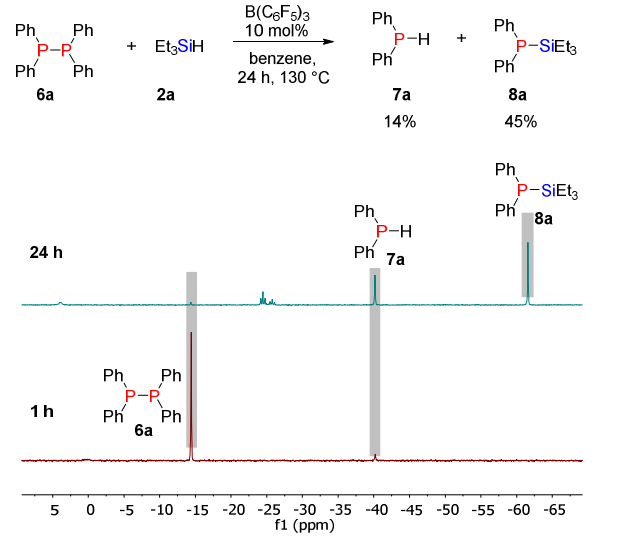


Figure 6. Time-dependent $^{31}P\{^1H\}$ NMR spectra of $B(C_6F_5)_3$-catalysed hydrosilylation of tetraphenylbiphosphine **6a**: $(Ph_2P)_2$ (0.05 mmol, 18.5 mg), Et_3SiH (0.3 mmol, 48 µl), $B(C_6F_5)_3$ (0.01 mmol), benzene 0.5 mL in a J. Young NMR tube, 130 °C.

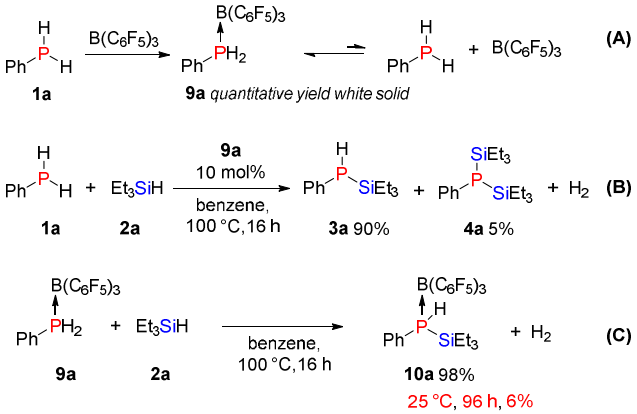
14% diphenylphosphine (**7a**) and other unidentified side products which indicated that some of the silylation product arises from the dehydrocoupling of the silane with **7a** generated by the hydrosilylation (Figure 6).

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 $B(C_6F_5)_3$-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 distribu-

tion 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 $B(C_6F_5)_3$-catalyzed homodehydrocoupling of phenylphosphine as well as the first catalytic hydrosilylation of P-P bonds (Scheme 4).

The phosphine-borane adduct $PhH_2P{\bullet}B(C_6F_5)_3$ as a thermally generated FLP catalyst: The observed zero-order reaction in $PhPH_2$ prompted us to investigate another possible reaction pathway involving an intermediate adduct derived from $PhPH_2$ and $B(C_6F_5)_3$. DFT calculations show that $PhPH_2$ (**1a**) and $B(C_6F_5)_3$ can form a stable complex $PhH_2P{\bullet}B(C_6F_5)_3$ (**9a**) based on the computed exergonic (ΔG = -7.53 kcal/mol). In contrast, the formation of the complex $Et_3Si\text{-}H{\bullet}B(C_6F_5)_3$ between Et_3SiH (**2a**) and $B(C_6F_5)_3$ is endergonic (ΔG = 5.85 kcal/mol) and not favoured thermodynamically. Furthermore, we failed to optimize a stable complex $Et_3Si\text{-}H{\bullet}PH_2Ph$ between **1a** and **2a**. This shows that **9a** should be one of the principal intermediates in the reaction. Since the loading of $B(C_6F_5)_3$ is only 10% of the concentration of **1a**, the formation **9a** explains the zero-order dependence of [**1a**] and the first order dependence of $[B(C_6F_5)_3]$. That **2a** cannot form stable complexes with $B(C_6F_5)_3$ and **1a** also explains the first order dependence of **2a**. In addition, we computed the adducts of **3a** and **4a** with $B(C_6F_5)_3$. It was found that that formation of $\mathbf{3a}{\bullet}B(C_6F_5)_3$ and $\mathbf{4a}{\bullet}B(C_6F_5)_3$ is exergonic by 10.64 and 3.90 kcal/mol, respectively. **3a** Coordinates more strongly to $B(C_6F_5)_3$ than **1a** is consistent with the kinetic behaviour in Figure 2A after 100 min, where **1a** is liberated from $B(C_6F_5)_3$ by the subsequently formed **3a**.

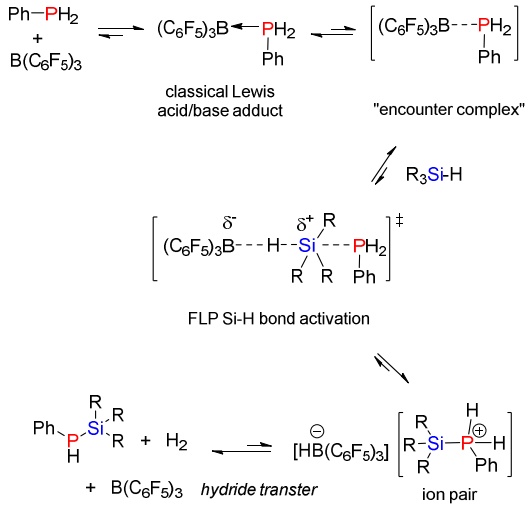
To obtain more insights into the reaction mechanism, a series of stoichiometric reactions were carried out. Upon mixing equimolar amounts of **1a** and $B(C_6F_5)_3$ in benzene we found the formation of **9a** in quantitative yield (triplet at -48.0 ppm with a J(P–H) = 423 Hz).[57] Furthermore, we found that **9a** is very stable even at 100 °C, and neither free phenylphosphine (**1a**) nor $B(C_6F_5)_3$ 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 $PhP(H)SiEt_3{\bullet}B(C_6F_5)_3$ (**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. We propose that the process involves an "encounter complex" generated from the **9a** *via* secondary



Scheme 5. Synthesis of $PhH_2P{\bullet}B(C_6F_5)_3$ adduct and its catalytic and stoichiometric reaction with Et_3SiH: (A) $PhPH_2$ (1 mmol, 110 µl), $B(C_6F_5)_3$ (1 mmol, 510 mg), benzene 10 mL 25 °C; (B) $PhPH_2$ (0.1 mmol, 11 µl), Et_3SiH (0.3 mmol, 48 µl), $PhH_2P{\bullet}B(C_6F_5)_3$ (0.01 mmol, 6.22 mg), benzene 0.5 mL in J. Young NMR tube, 100 °C, 16 h; (C) $PhH_2P{\bullet}B(C_6F_5)_3$ (0.02 mmol, 12.4 mg), Et_3SiH (0.06 mmol, 9.6 µl), benzene 0.5 mL in J. Young NMR tube, 16 h.

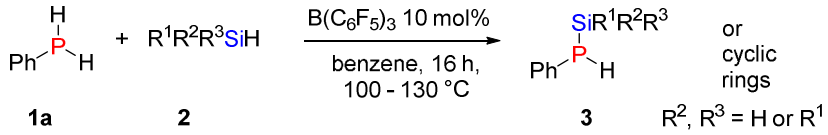
interactions that activates the Si-H before dissociation to form free $PhPH_2$ and $B(C_6F_5)_3$ (Scheme 6).[34, 63-64]

Diffusion-Ordered Spectroscopy (DOSY) NMR studies were conducted to detect the potential dissociation of $PhH_2P{\bullet}B(C_6F_5)_3$ 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 x 10^{-10} m^2 s^{-1} and for $B(C_6F_5)_3$ a value of 7.1 x 10^{-10} m^2 s^{-1}. DOSY NMR analysis of a solution of 0.04 M **9a** in benzene gave values of D = 6.3 x 10^{-10} m^2 s^{-1} and 5.1 x 10^{-10} m^2 s^{-1} for $PhPH_2$ and $B(C_6F_5)_3$, 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).

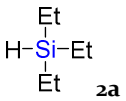
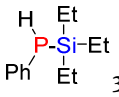
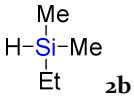
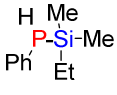
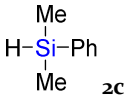
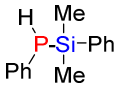
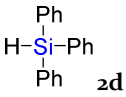
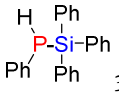
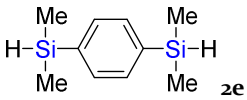
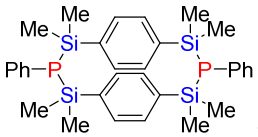
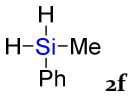
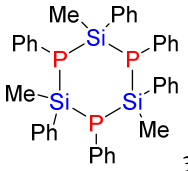
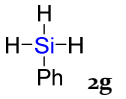
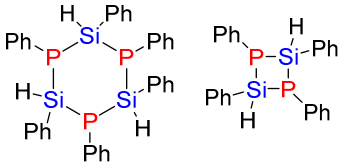


Scheme 6. Formation of a classical Lewis acid/base adduct and dissociation to form the "encounter complex" and activatation of the Si-H bond.

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



1a **2** **3**

Entries	hydrosilanes	Time [h]	T [°C]	Products	Yields [%][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:3g' = 4:1**	62 (55)

[a]$PhPH_2$ (0.1 mmol, 11 µl), hydrosilanes (0.3 mmol, 48 µl), $B(C_6F_5)_3$ (0.01 mmol), benzene 0.5 mL in J. Young NMR tube, 100-130 °C; [b]determined by ^{31}P NMR spectroscopy using a sealed capillary of PCl_3 as an integration standard; [c]isolated yields.

On the other hand, the different values for the two species (6.3 x 10^{-10} m^2 s^{-1} vs 5.1 x 10^{-10} m^2 s^{-1}) using **9a** indicated that the P-B interaction is dynamic with the equilibrium highly favouring **9a**.

The activation of E-H bonds using $B(C_6F_5)_3$/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 a classical adduct.[56, 65] When $B(C_6F_5)_3$ 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 $PhH_2P{\bullet}B(C_6F_5)_3$ 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.* $B(C_6F_5)_3/Mes_3P$) (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 different substituents were applied to study the generality of our strategy (Table 2). We found that hydrosilanes **2b** and **2c** with small 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 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 single-crystal X-ray diffraction as shown in Figure 7.

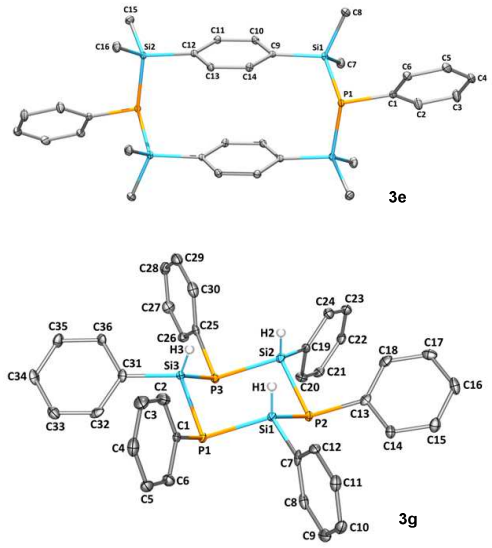
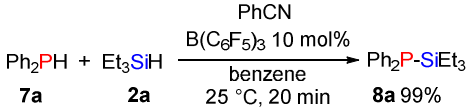


Figure 7. Molecular structures of **3e** and **3g** determined by single-crystal X-ray Diffraction. For **3e** non-hydrogen atoms shown as 30% probability ellipsoids and all H-atoms are omitted for clarity, the molecule possesses a crystallographically imposed inversion centre in the middle of the ring. 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 $[Si\text{-}P]_3$ ring are omitted for clarity.

$B(C_6F_5)_3$-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, Ph_2PH (**7a**) with Et_3SiH (**2a**) in benzene, we found that the reaction proceeded very slowly. Even with 20 mol% $B(C_6F_5)_3$ 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 ^{31}P NMR spectroscopy revealed the appearance of multiple peaks around -24.4 ppm which might arise from the thermal rearrangement of the adduct $Ph_2HP{\bullet}B(C_6F_5)_3$.[68] This was further confirmed via the independent reaction of equimolar amounts of Ph_2PH and $B(C_6F_5)_3$ at 130 °C for 24 h (Figure S13). Compared with the formation of $PhH_2P{\bullet}B(C_6F_5)_3$ (ΔG = -7.53 kcal/mol), the formation of $Ph_2HP{\bullet}B(C_6F_5)_3$ is even more exergonic (ΔG = -9.38 kcal/mol), indicating that $Ph_2HP{\bullet}B(C_6F_5)_3$ is more stable than $PhH_2P{\bullet}B(C_6F_5)_3$ by 1.85 kcal/mol. In addition, the formation of **8a** [**7a** + **2a** = **8a** + H_2] 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 $Ph_2HP{\bullet}B(C_6F_5)_3$ by lowering the reaction temperature. Stephan[69] and Oestreich[70] have previously introduced alkenes as H_2-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 H_2-acceptors to the reaction of **7a** with **2a**. Initially, we added different alkenes, unfortunately, cyclohexene, 1-octene, and 1, 1-diphenylethylene all failed to affect the reaction rate. Other types of H_2-acceptor such as phenylacetylene, benzophenone, nitrobenzene, azobenzene also failed as H_2-acceptors (Table S2). Remarkably, we found that by using PhCN as the H_2-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 $B(C_6F_5)_3$-catalyzed heterodehydrocoupling of Ph_2PH with Et_3SiH: Ph_2PH (0.1 mmol, 17.4 µl), Et_3SiH (0.3 mmol, 48 µl), PhCN (0.1 mmol, 10.3 µl), $B(C_6F_5)_3$ (0.01 mmol), 0.5 mL benzene in a J. Young NMR tube, 20 min, 25 °C.

The dramatic acceleration effect of PhCN suggested that rather than simply functioning as an H_2-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 $B(C_6F_5)_3$ gave rise to the classical adduct. Addition of 1 equiv. of PhCN to the adduct and monitoring the reaction by ^{31}P NMR spectroscopy after 1 h showed 40% free Ph_2PH which indicated 60% $Ph_2HP{\bullet}B(C_6F_5)_3$ adduct and 40% $PhCN{\bullet}B(C_6F_5)_3$ adduct (^{11}B NMR, -12.6 ppm) existed(Figure 8 and S14). These ratios give a K_{eq} of 0.44 for the displacement of the phosphine from $Ph_2HP{\bullet}B(C_6F_5)_3$ by PhCN, indicating that the binding of the phosphine to $B(C_6F_5)_3$ is 0.5 kcal mol^{-1} more favorable. Indeed, this value is in excellent agreement with our calculation that Ph_2PH binding to $B(C_6F_5)_3$ is 0.6 kcal mol^{-1} more favorable than PhCN (Scheme 8).

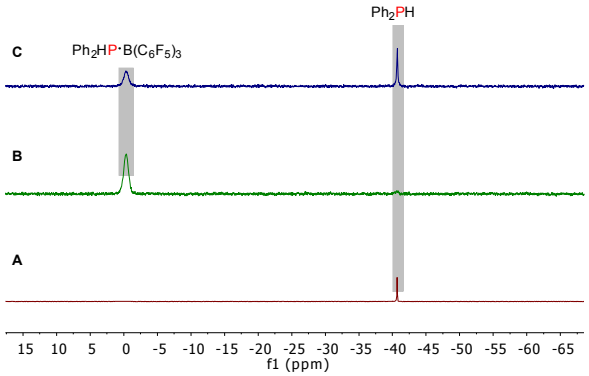


Figure 8. $^{31}P\{^1H\}$ NMR spectra of competitive binding experiments of Ph_2PH and PhCN with $B(C_6F_5)_3$: (A) Ph_2PH (0.01 mmol, 1.7 µl), benzene 0.5 mL in a J. Young NMR tube, 25 °C; (B) after addition of $B(C_6F_5)_3$ (0.01 mmol, 5.1 mg); (C) 1 h after addition of PhCN (0.01 mmol, 1.1 µl).

$Ph_2PH + B(C_6F_5)_3 \rightleftharpoons Ph_2HP{\cdot}B(C_6F_5)_3$

$\Delta G = -9.38$ kcal/mol

$PhCN + B(C_6F_5)_3 \rightleftharpoons PhCN{\cdot}B(C_6F_5)_3$

$\Delta G = -8.78$ kcal/mol

$Ph_2PH + PhCN{\cdot}B(C_6F_5)_3 \rightleftharpoons Ph_2HP{\cdot}B(C_6F_5)_3 + PhCN$

$\Delta G = -0.6$ kcal/mol

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

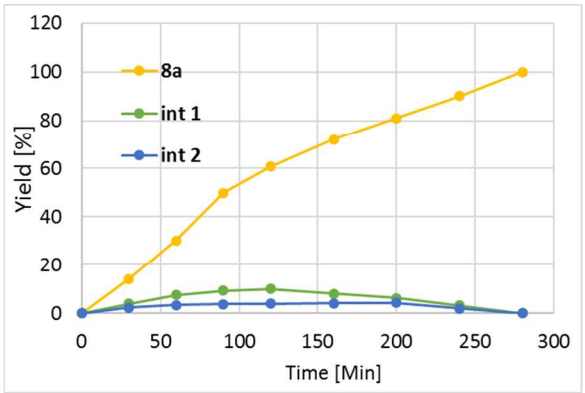
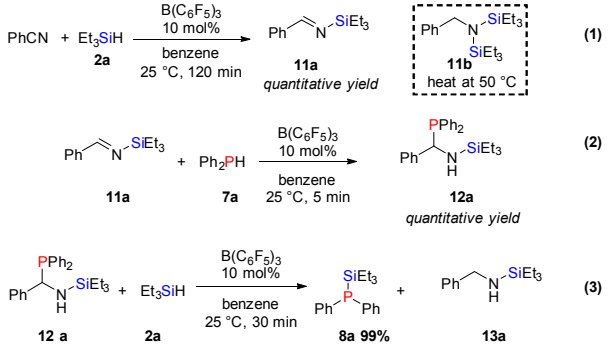


Figure 9. Reaction profile of $B(C_6F_5)_3$-catalyzed heterodehydrocoupling of Ph_2PH with Et_3SiH in the presence of PhCN: Ph_2PH (0.1 mmol, 17.4 µl), Et_3SiH (0.3 mmol, 48 µl), $B(C_6F_5)_3$ (0.0025 mmol), PhCN (0.1 mmol, 10.3 µl), benzene 0.5 mL in J. Young NMR tube, 25 °C.

We then carried out a kinetic study by monitoring the reaction of 0.1 mmol **7a**, 0.3 mmol **2a** and 0.1 mmol PhCN with 2.5 mol% $B(C_6F_5)_3$ at 25 °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 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 °C. Only after heating at above 50 °C, the saturated silylamine (**11b**) could be detected (Scheme 9, equation 1). As a control experiment no hydrosilylation occured 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 **12a** with **2a** gave rise to the dehydrocoupling product **8a** (Scheme 9, equation 3). These stepwise experiments confirmed our hypothesis that PhCN functions as a precursor to **11a** which undergoes hydrophosphination with **7a** to produce **12a**, the latter species subsequently reacts with **2a** to give the final 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 µl), Et_3SiH (0.3 mmol, 48 µl), $B(C_6F_5)_3$ (0.01 mmol), benzene 0.5 mL in J. Young NMR tube, 25 °C; (2) **11a** (0.1 mmol, 22 µl), Ph_2PH (0.1 mmol, 17.4 µl), $B(C_6F_5)_3$ (0.01 mmol), benzene 0.5 mL in J. Young NMR tube, 25 °C; (3) **12a** (0.1 mmol, 40.5 mg), Et_3SiH (0.2 mmol, 32 µl), $B(C_6F_5)_3$ (0.01 mmol), benzene 0.5 mL in J. Young NMR tube, 25 °C.

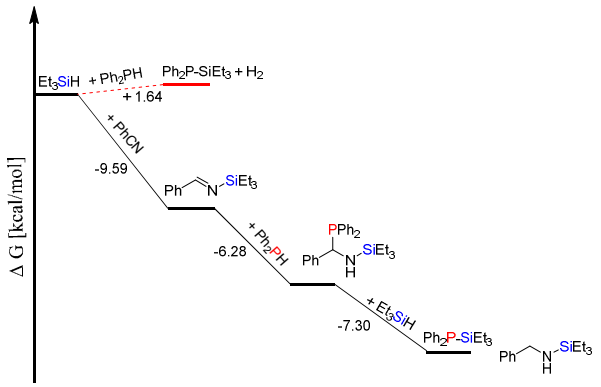


Figure 10. Energy profile (kcal/mol) for the $B(C_6F_5)_3$-catalyzed heterodehydrocoupling of Ph_2PH with Et_3SiH with and without PhCN.

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 Et_3SiH is exergonic with ΔG = -9.59 kcal·mol^{-1} and further hydrophosphination with Ph_2PH is also exergonic with ΔG = –6.28 kcal·mol^{-1}, this are consistent with our experimental results (Scheme 9, equations 1-2). The final step, surprisingly, is even more exergonic with a value of ΔG = –7.30 kcal·mol^{-1} and confirms again that 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 ^{11}B NMR spectroscopy in order to further understand the mechanism and the fate of $B(C_6F_5)_3$ (Figure 11). We found that by adding Et_3SiH to a solution containing Ph_2PH, PhCN, and $B(C_6F_5)_3$ the anion $[HB(C_6F_5)_3]^-$ was formed and persisted throughout the reaction (Figure 11C). After the reaction was complete, we could also observe the accumulation of the $[HB(C_6F_5)_3]^-$ (Figure 11D), which might arise from the activation of excess amount of Et_3SiH in the presence of phosphines or amines.

Compound **12a** could interact with Et_3SiH to yield product **8a** *via* two different mechanisms: a) σ-bond metathesis of the Si-H bond with the C-P bond from **12a**, which has previously been proposed[30,31] or b) coordination of **12a** with $B(C_6F_5)_3$ 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 σ-bond exchange mechanism features a symmetry forbidden metathesis reaction and the fact that we could observe $[HB(C_6F_5)_3]^-$

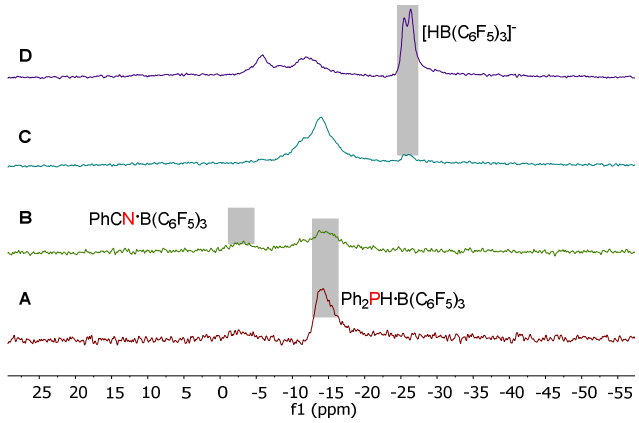


Figure 11. ^{11}B NMR spectra of the reactions: (A) Ph_2PH 0.1 mmol, $B(C_6F_5)_3$ 0.025 mmol in 0.5 mL benzene at 25 °C; (B) after addition of 0.1 mmol PhCN to A at 25 °C; (C) addition of 0.3 mmol Et_3SiH to B and monitor after 30 min; (D) addition of 0.3 mmol Et_3SiH to B and monitor after 12 h.

by ^{11}B NMR throughout the reaction (Figure 11) supports the FLP mechanism.

CONCLUSION

The first non-metal catalysed heterodehydrocouplings of phosphines (R^1R^2PH, R^2 = H or R^1) with primary, secondary, and tertiary hydrosilanes ($R^3R^4R^5SiH$, R^4, R^5 = H or R^3) to produce synthetically useful silylphosphanes (R^1R^2P-$SiR^3R^4R^5$) has been achieved using $B(C_6F_5)_3$. Detailed mechanistic studies (kinetic studies, variable temperature NMR spectroscopy) have shown that the reaction relies on the key Lewis acid/base adduct, $R^1R^2HP{\bullet}B(C_6F_5)_3$. 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 $B(C_6F_5)_3$ is dynamic and leads to the formation of an "encounter complex" which is responsible for the reactivity. We have also demonstrated the $B(C_6F_5)_3$-catalysed homodehydrocoupling of phosphines to produce cyclic phosphine rings and the first non-metal catalytic hydrosilylation of P-P bonds. Moreover, we have successfully introduced PhCN in the reaction of secondary phosphines Ph_2PH with Et_3SiH to avoid the thermal rearrangement side products from the $Ph_2HP{\bullet}B(C_6F_5)_3$ 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 hydrosilanes 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.

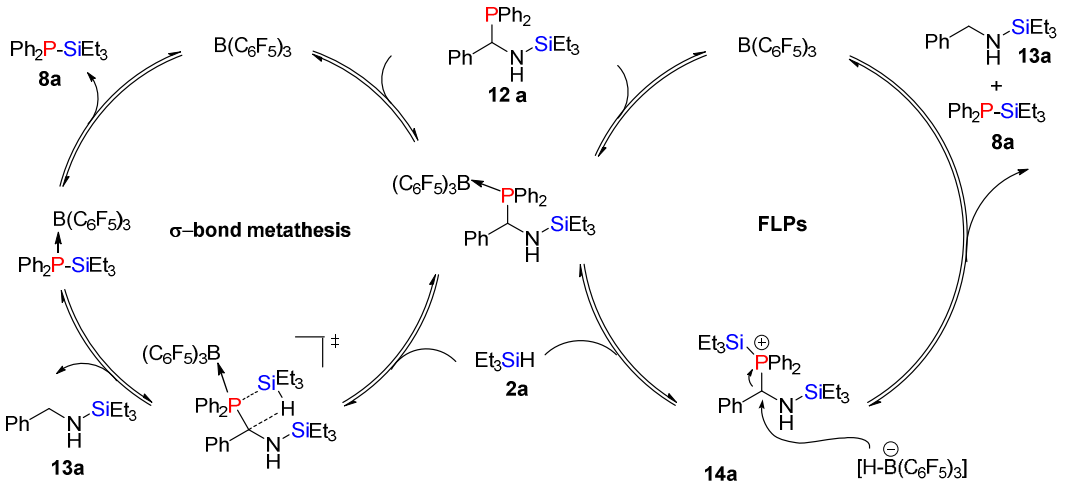


Figure 12. Proposed reaction mechanism for the reaction of **12a** to **8a**: left, sigma-bond metathesis route; right, FLP route.

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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