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Frustrated Lewis Pair Route to Hydrodesilylation of Silylphosphines

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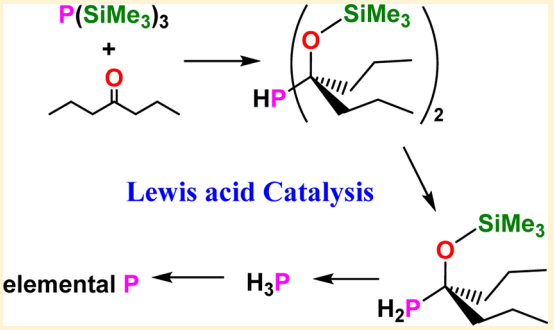
Supporting Information

ABSTRACT: A 1:1 mixture of $P(SiMe_3)_3$ and $B(p\text{-}C_6F_4H)_3$ reacts with 3 equiv of 4-heptanone to afford a 1:2 mixture of $[(Me_3SiO)(n\text{-}Pr)_2C]H_2P{-}B(p\text{-}C_6F_4H)_3$ and the silyl enol ether, 4-trimethylsiloxy-3-heptene. Subsequent thermolysis of the adduct produces $H_3P{-}B(p\text{-}C_6F_4H)_3$ and an additional equiv of silyl enol ether. In the presence of a catalytic quantity of $B(p\text{-}C_6F_4H)_3$, however, $P(SiMe_3)_3$ reacts with 4-heptanone to produce a 1:1 mixture of $[(Me_3SiO)(n\text{-}Pr)_2C]_2PH$ and silyl enol ether. Heating this mixture further produces $[(Me_3SiO)(n\text{-}Pr)_2C]PH_2$, which is eventually converted to elemental phosphorus.

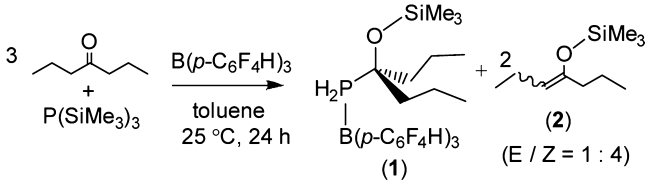


Phosphine ligands are ubiquitous in transition metal chemistry and indeed an enormous variety of mono- and multidentate ligands have been prepared and utilized.[1] While a variety of strategies have been developed to achieve the synthesis of phosphine ligands, principal among the synthons used are secondary and primary phosphines. These precursors are often challenging to handle as a result of their volatility, air-sensitivity, and disagreeable odor. Typically, primary and secondary phosphines are made by treatment of phosphorus-halide or alkoxide species with hydride reagents. Alternatively, alkylation of phosphide such as $NaPH_2$ and reduction of hydroxyl-methylphosphines have been exploited to prepare either primary[2] or secondary[3] phosphines. Nonetheless, the number of synthetic routes to these useful synthons is limited.

The advent of frustrated Lewis pair (FLP) chemistry[4] has seen the unquenched reactivity of sterically encumbered phosphines and boranes applied to activations of various small molecules. FLP chemistry has also been exploited for hydrogenation catalysis.[5] Among the various reductions that have been demonstrated, we have also shown that P−P bonds can be hydrogenated to provide an FLP-mediated approach to secondary or primary phosphines.[6] In more recent work, we reported that the FLP derived from $P(SiMe_3)_3$ and $B(p\text{-}C_6F_4H)_3$ participates in the sequential activation of H_2 and CO_2, with migrations of one or more Me_3Si groups to oxygen.[7] Herein, we report that FLPs derived from silylphosphines and $B(p\text{-}C_6F_4H)_3$[8] react with aliphatic ketone in stoichiometric and catalytic reactions with the elimination of silyl enol ethers. This hydrodesilylation reaction is shown to provide a new synthetic route to secondary and primary phosphines, PH_3 and elemental phosphorus, respectively.

While the combination of $P(SiMe_3)_3$ and 4-heptanone shows no evidence of reaction, the stoichiometric combination of a 1:1 ratio of $P(SiMe_3)_3$ and $B(p\text{-}C_6F_4H)_3$ with 3 equivalents of 4-heptanone in toluene at ambient temperature produced the phosphine−borane adduct $[(CH_3CH_2CH_2)_2C(OSiMe_3)]PH_2{-}B(p\text{-}C_6F_4H)_3$ **1** and silyl enol ether $CH_3CH_2CH_2C(OSiMe_3){=}C(H)CH_2CH_3$ **2**[9] (E/Z = 1:4) in a 1:2 ratio (Scheme 1), as

Scheme 1. Stoichiometric Synthesis of 1 and 2



made evident by ^1H nuclear magnetic resonance (NMR) spectroscopy. Following evaporation of the solvent and volatile **2** from the reaction mixture, recrystallization of the residual solid with hexanes produced crystals of **1** in 78% yield. The ^1H NMR spectrum of **1** shows a doublet at δ 5.19 with a large $^1J_{PH}$ = 385 Hz, and the ^{31}P NMR spectrum shows a triplet with the same coupling constant at δ −37.1, consistent with that of the RPH_2 moiety. The $^{11}B\{^1H\}$ NMR spectrum of **1** shows a broad signal at δ −15.4, indicating a 4-coordinate B center. These spectral data are consistent with those reported for the adduct $(Cy)H_2P{-}B(C_6F_5)_3$ (δ_H 4.65, δ_B −17.5, and δ_P −30.0; $^1J_{PH}$ = 393 Hz).[10] The X-ray structure of **1** (Figure 1) shows the *pseudo*-tetrahedral geometries at P and B, with a P−B bond length of 2.042(2) Å and P−H bond lengths of 1.28(2) and 1.29(2) Å,[11] similar to those reported for $(t\text{-}Bu)H_2P{-}B(C_6F_5)_3$ [P−B = 2.015(3) Å, P−H = 1.28(2) and 1.30(3) Å].[12]

The silylphosphine, $P(SiMe_3)_3$, also reacted with 3 equivalents of 4-heptanone in the presence of a catalytic amount of $B(p\text{-}C_6F_4H)_3$ (5 mol %) at ambient temperature. In this case, however, NMR data were consistent with a product that was not a primary phosphine but rather the secondary

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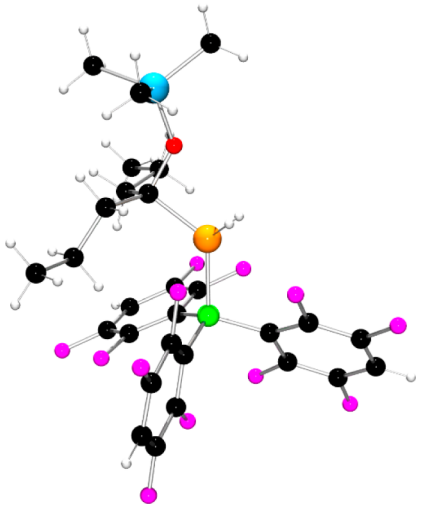
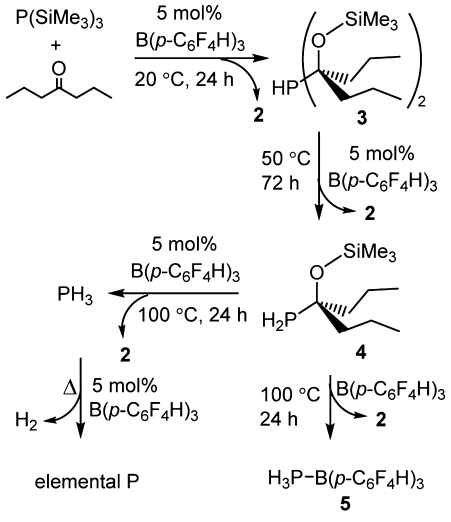


Figure 1. POV–Ray depiction of **1**. P: orange; Si: sky blue; O: red; F: pink; C: black; B: green.

phosphine $[(CH_3CH_2CH_2)_2C(OSiMe_3)]_2PH$ (**3**), accompanied by **2** (E/Z = 1:4) (see the Supporting Information). The ^1H NMR spectrum of **3** shows a doublet at δ 3.44 with $^1J_{PH}$ = 207 Hz, while the ^{31}P NMR spectrum exhibits a doublet with the same coupling constant at δ −18.8, corresponding to a secondary phosphine. Heating the toluene solution of **3** to 50 °C for 72 h in the presence of 5 mol % $B(p\text{-}C_6F_4H)_3$ results in gradual conversion of the resonances at δ_H 3.44 and δ_P −18.8, to a new doublet at δ_H 3.00 and a triplet signal at δ_P −98.4 with $^1J_{PH}$ = 192 Hz, again accompanied by the production of 2 (E/Z = 1:4). The change in chemical shift is indeed consistent with the production of the primary phosphine $(CH_3CH_2CH_2)_2C(OSiMe_3)PH_2$ **4**, which although not isolated, could be converted to adduct **1** upon the addition of $B(p\text{-}C_6F_4H)_3$, enabling its facile spectroscopic identification (Scheme 2). It is also interesting to note that addition of 1 equivalent of $B(p\text{-}C_6F_4H)_3$ to **3** prompted the immediate formation of adduct **1** and silyl enol ether **2** at room temperature.

Compound **3** was stable on heating to 50 °C in the absence of $B(p\text{-}C_6F_4H)_3$, consistent with a borane-catalyzed elimination of silyl enol ether **2** on formation of **1**. Heating the mixture of **4** and **2** to 100 °C in the presence of 5 mol % $B(p\text{-}C_6F_4H)_3$ for an additional 24 h eventually gave rise to an insoluble orange precipitate. At this point, the ^{31}P NMR spectrum of the mother liquor showed a new broad quartet at δ −238.9 with $^1J_{PH}$ = ca. 180 Hz, corresponding to PH_3. However, monitoring the thermal degradation of adduct **1** in solution upon heating to 100 °C for 24 h by NMR spectroscopy again showed the gradual production of a new adduct **5** accompanied by the loss of **2**. Removal of the solvent and **2** in vacuo, followed by recrystallization of the residues in 10:1 *n*-pentane/CH_2Cl_2, afforded colorless crystals of **5** in 35% yield. The ^1H NMR spectrum of **5** shows the characteristic doublet of the PH_3 unit at δ 5.19 ($^1J_{PH}$ = 407 Hz). This signal is similar but shifted downfield from that reported for the adduct $(H_3P)B(C_6F_5)_3$ (δ 3.34, $^1J_{PH}$ = 410 Hz).[6] The ^{31}P NMR spectrum of **5** shows a quartet with the same coupling constant at δ −93.5, consistent with that of the PH_3 moiety, while the $^{11}B\{^1H\}$ NMR spectrum shows a broad signal at δ −16.1, indicating a 4-coordinate B atom. Collectively, these data are consistent with the formulation of **5**, as $(H_3P)B(p\text{-}C_6F_4H)_3$. This assignment was confirmed by an X-ray diffraction analysis (Figure 2),[11] which

Scheme 2. Syntheses of 3-5



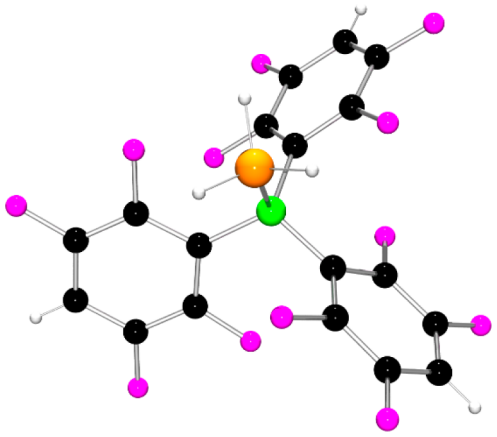


Figure 2. POV–Ray depiction of **5**. P: orange; F: pink; C: black; B: green.

showed the expected pseudo-tetrahedral geometries of the P and B centers, with a P–B bond length of 2.042(2) Å and P–H bond lengths of 1.29(2), 1.30(2), and 1.33(2) Å, similar to those of $H_3P–B(C_6F_5)_3$ [P–B = 2.044(8) Å, P–H = 1.24(3) to 1.36(3) Å].[13]

Further heating of **5** at 100 °C resulted in its gradual decomposition with increased production of the isolable orange precipitate. The solid was identified as elemental phosphorus (>90 wt %) by elemental analysis, ICP-AES, and DART-MS data. The air-stable nature of this red-orange solid is also consistent with its characterization as elemental (red) phosphorus.

In consideration of the mechanisms of the above reactions, it is important to note that the use of $B(p\text{-}C_6F_4H)_3$ is critical because this borane does not undergo *para*-attack by silylphosphine, as is seen with $B(C_6F_5)_3$.[14] This combination therefore represents a stable FLP. As shown in Scheme 3, a plausible mechanism for the catalytic reaction of ketone and $P(SiMe_3)_3$ in the presence of $B(p\text{-}C_6F_4H)_3$ is thought to be initiated by activation of the carbonyl group by coordination of O to B. This prompts nucleophilic attack of $P(SiMe_3)_3$ at C to give the proposed zwitterionic intermediate **Int1**. Migration of

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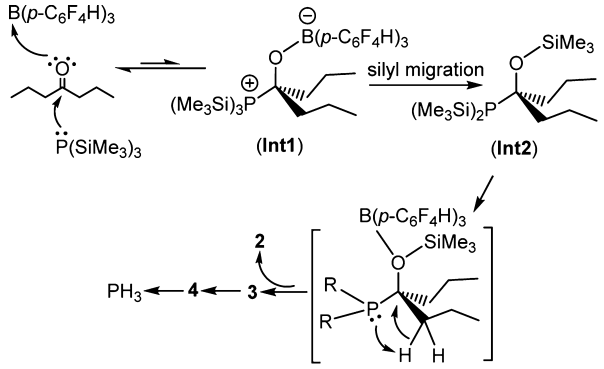
Scheme 3. Proposed Reaction Mechanism for Desilylation of $P(SiMe_3)_3$

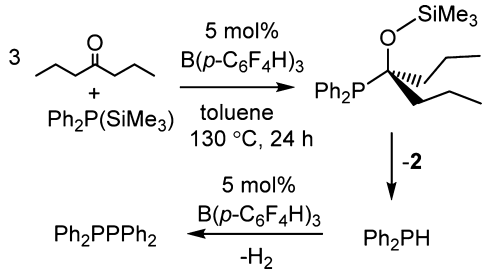


a silyl group from phosphorus to oxygen is concurrent with liberation of the borane catalyst, affording the intermediate phosphine, $(Me_3Si)_2PC(CH_2CH_2CH_3)_2(OSiMe_3)$ **Int2**. Steric crowding and coordination of the borane, $B(p\text{-}C_6F_4H)_3$, is thought to prompt 1,3-migration of proton from C to P, producing **3** with concurrent β-elimination of silyl enol ether **2**. Conversely, one can envision a mechanism whereby each silaphosphination step is followed by an elimination step (rather than three silylphosphination steps followed by three elimination steps). To the best of our knowledge, reactions between $P(SiMe_3)_3$ and ketones in the absence of a Lewis acid catalyst have not been reported. It is noteworthy that the combination of $P(SiMe_3)_3/B(p\text{-}C_6F_4H)_3$ did not react with the nonenolizable ketones such as benzophenone or di-*tert*-butylketone, even upon heating to 100 °C for 24 h, suggesting that the elimination of silyl enol ether drives these reactions to completion. Nonetheless, in a related sense, the silylphosphine, Me_3SiPEt_2, has been previously reported to react with α-diketones to give $Me_3SiOC(Me)PR_2C(O)Me$.[14] Products **4** and PH_3 are thought to be produced by successive borane-catalyzed β-eliminations from **3** and **4**. In these catalytic reactions, formation of the secondary phosphine **3** at ambient conditions presumably occurs because this species retains significant steric congestion about phosphorus and thus requires additional energy to prompt further borane-catalyzed β-elimination to give **4** and PH_3. Binding the toxic PH_3 gas to $B(p\text{-}C_6F_4H)_3$ affords the isolable adduct **5**.

In order to probe the generality of this FLP-mediated hydrodesilylation reaction, the monosilylphosphine, Ph_2PSiMe_3, was used as a precursor. Heating a 0.06 M C_6D_5Br solution of 1:1 Ph_2PSiMe_3/4-heptanone with 5 mol % $B(p\text{-}C_6F_4H)_3$ to 130 °C resulted in the complete consumption of the starting material Ph_2PSiMe_3 and the generation of Ph_2PH (δ_P −40.3) as the major product (Scheme 4). The yield of the secondary phosphine was 80%, as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy. Interestingly, a minor product that was formed in this reaction in 12% yield was identified as the biphosphine product of homodehydrocoupling Ph_2PPPh_2 (δ_P −15.2). Increasing the reaction concentration under otherwise identical reaction conditions resulted in >95% conversion to Ph_2PPPh_2.

In summary, the stoichiometric and catalytic reactions of silylphosphines in the presence of the borane, $B(p\text{-}C_6F_4H)_3$, and the ketone, 4-heptanone, provide a synthetic route to secondary and primary phosphines with liberation of the silyl enol ether **2** via $SiMe_3$ group migration from phosphorus to oxygen. In stoichiometric reactions the phosphine−borane

Scheme 4. Reactions of $Ph_2P(SiMe_3)$ with Ketone and Catalytic Borane



adducts are isolated, whereas in catalytic reactions, the free phosphines are generated. These reactions result from the generation of a phosphine/borane FLP, allowing activation of the ketone by borane, which then undergoes nucleophilic attack by phosphine. Subsequent silyl-migration to O and β-elimination generates the P−H bond. To the best of our knowledge, this report describes the first reactions of an unactivated dialkylketone with an FLP. Nonetheless, it is noteworthy that Erker et al. have recently reported FLP activations of conjugated ketones, such as ynones and enediones, affording addition products.[15] The utility of the current FLP-catalyzed reactivity in the synthesis of unique phosphine products and the mechanism of Lewis acid-catalyzed P−P dehydrocoupling continues to be the subject of current investigations.

■ ASSOCIATED CONTENT

Supporting Information

Preparations of compounds, reaction procedures, spectra, and experimental crystallographic details. 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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(11) X-ray crystallographic data for **1**: triclinic, $P\bar{1}$, a = 9.9406(8) Å, b = 11.7049(8) Å, c = 13.254(1) Å, α = 95.840(4)°, β = 97.626(4)°, γ = 102.456(4)°, V = 1478.89(19) Å^3, Z = 2, data (>2σ) = 26289, variables = 7239, R_1(>2σ) = 0.0348, wR_2(all) = 0.1270, GOF = 0.923. **5**: Orthorhombic, *Pbca*, a = 10.1556(3) Å, b = 17.4865(5) Å, c = 20.2840(5) Å, V = 3602.2(2) Å^3, Z = 8, data (>2σ) = 16575, variables = 4140, R_1(>2σ) = 0.0328, wR_2(all) = 0.0819, GOF = 1.017.
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