

1,2-Diphosphonium Dication: A Strong P-Based Lewis Acid in Frustrated Lewis Pair (FLP)-Activations of B–H, Si–H, C–H, and H–H Bonds

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S Supporting Information

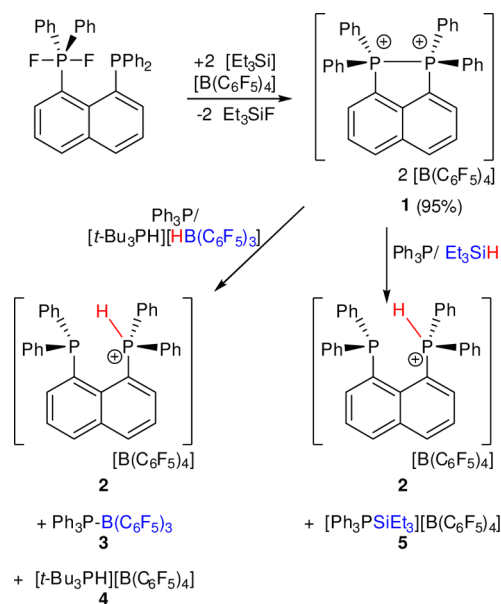
ABSTRACT: A highly Lewis acidic diphosphonium dication $[(C_{10}H_6)(Ph_2P)_2]^{2+}$ (**1**), in combination with a Lewis basic phosphine, acts as a purely phosphorus-based frustrated Lewis pair (FLP) and abstracts hydride from $[HB(C_6F_5)_3]^-$ and Et_3SiH demonstrating the remarkable hydridophilicity of **1**. The P-based FLP is also shown to activate H_2 and C–H bonds.

The past two decades have witnessed fundamental advances in the area of Lewis acid chemistry, particularly due to the development of increasingly electron-deficient molecules. For instance, fluorinated organoboranes have been widely used as Lewis acids in small molecule activation and catalysis.¹ In this context, the heterolytic splitting of dihydrogen (H_2) by sterically frustrated Lewis pairs (FLPs), composed of a Lewis acidic borane and a suitable Lewis base, was a landmark achievement.² In addition to boranes and alanes,³ tricoordinated carbon⁴ or silicon-centered⁵ cations have been used as main-group based Lewis acids in FLP-type small molecule (in particular H_2) activation. Exploring electron-deficient compounds of group 15, we found that $[(C_6F_5)_3PF]^+$ is a highly electrophilic phosphonium cation (EPC) that exhibits remarkable Lewis acidity derived from strongly electron-withdrawing substituents and an energetically accessible LUMO (opposite to P–F bond) acceptor orbital.⁶ Pursuing alternative approaches to EPCs, we showed that carbene-based fluorophosphonium⁷ $[(SIMEs)PPh_2F]^{2+}$ ($SIMEs = 1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{-2-imidazolidinylidene}$) or bidentate *bis*(fluorophosphonium) dications⁸ reveal comparable Lewis acidities, highlighting the impact of an additional positive charge. These EPCs were shown to catalyze a range of Lewis acid mediated transformations including hydrodefluorination,^{6–8} hydrosilylation,^{7–9} dehydrocoupling, and transfer hydrogenation.¹⁰ Strong Lewis acids based on heavier group 15 elements (As,¹¹ Sb,¹² Bi¹³) have been explored recently, and in some cases, the activation of Si–H or Si–Cl bonds was observed. The activation of H_2 in reactions with group 15 Lewis acids is rare. Indeed we reported the direct reaction of H_2 with a triphosphabenzene derivative, and computational studies confirmed the role of phosphorus as a Lewis acid in an FLP-type mechanism.¹⁴ Herein, we present a naphthalene-bridged P–P bonded 1,2-diphosphonium dication which demonstrates high Lewis acidity without a polarized P–F bond. The electrophilicity of the dication is exploited in several

stoichiometric E–H bond activation reactions (E = H, B, C, Si), highlighting its remarkable hydridophilicity.

To synthesize the diphosphonium dication, 2 equiv of $[Et_3Si][B(C_6F_5)_4] \cdot 2(C_7H_8)$ were added to a C_6H_5F solution of difluorophosphorane $(C_{10}H_6)(Ph_2PF_2)(Ph_2P)$,⁸ resulting in a double fluoride abstraction (Scheme 1). The obtained

Scheme 1. Synthetic Route to Diphosphonium Dication Salt **1 and Reactions of **1** and Ph_3P with B–H and Si–H Bonds**



dicationic species, $[(C_{10}H_6)(Ph_2P)_2]^{2+}$ (**1**), is stabilized by intramolecular coordination of the phosphine moiety to the P(V) atom which renders **1** a rare example of a dicationic, P–P-bonded diphosphonium species.¹⁵ Compound **1** as a $[B(C_6F_5)_4]^-$ salt was isolated in high yields (95%) and fully characterized. The diphosphonium salt **1** is relatively stable and does not decompose in coordinating solvents such as acetonitrile. In the solid state, it can be exposed to air for 24 h without significant decomposition. The ^{31}P NMR spectrum of **1** shows a singlet resonance at 23.2 ppm (CD_2Cl_2) comparable to the related phosphonium center in $[Ph_3P-PPh_2]^+$ ($\delta(^{31}P) = 15$ ppm).¹⁶

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In an effort to probe the Lewis acidity of **1** the Gutmann–Beckett method was employed.¹⁷ Reaction with 1 equiv of Et₃PO in CD₂Cl₂ revealed an acceptor number (AN) of 30 which is significantly higher than that of the corresponding *bis*(fluorophosphonium) dication ($[(C_{10}H_6)(Ph_2PF)_2]^{2+}$; AN = 21).⁸ Mixtures of dicationic fluorophosphonium species and Et₃PO were reported to react rapidly via a fluoride–oxide exchange reaction;^{7,8} however, species **1** exhibits increased stability showing no degradation even in the presence of Et₃PO after 24 h at 50 °C. It is interesting to note that NMR spectroscopic investigations indicated no adduct formation between diphosphonium species **1** and *t*-Bu₃P, while Ph₃P displays only a weak interaction with **1**, inferring the presence of unique all-phosphorus-based FLPs.

To gain insight into the hydridophilicity of **1**, a 1:1 mixture of **1** and Ph₃P was reacted with [*t*-Bu₃PH][HB(C₆F₅)₃]^{2b} in CD₂Cl₂ (Scheme 1). The ¹¹B{¹H} NMR spectrum of the reaction mixture revealed two resonances assigned to the [B(C₆F₅)₄][−] anion ($\delta(^{11}B) = -16.6$ ppm) and the phosphine borane adduct Ph₃P–B(C₆F₅)₃ (**3**, $\delta(^{11}B) = -0.3$ ppm).¹⁸ Adduct **3** was identified in the ³¹P{¹H} NMR spectrum as well, with a resonance at −4.4 ppm. Two additional ³¹P resonances revealed ¹J_{PH} coupling and were assigned to the cations of [*t*-Bu₃PH][B(C₆F₅)₄]⁺ (**4**, $\delta(^{31}P) = -59.8$ ppm, ¹J_{PH} = 429 Hz)^{2a} and [(C₁₀H₆)(Ph₂P)₂H][B(C₆F₅)₄]⁺ (**2**, $\delta(^{31}P) = -4.1$ ppm, ¹J_{PH} = 284 Hz).¹⁹ The ¹H NMR spectrum of the reaction mixture shows a low field triplet resonance at 10.2 ppm corresponding to the P–H fragment of **2**. Collectively, these NMR data indicate a fast exchange of the H atom between the P centers in **2**. The [N(SO₂CF₃)₂][−]-salt of **2** was independently prepared (see Supporting Information (SI)). X-ray crystallography of **2** revealed that in the solid state the H atom is bonded to one P atom with P–H distances of 1.32(3) and 2.76(1) Å. This reactivity demonstrates that the combination of **1** and Ph₃P acts as an FLP, heterolytically cleaving the B–H bond in [HB(C₆F₅)₃][−] yielding **2** and **3**. Interestingly, the combination of **1** and [*t*-Bu₃PH][HB(C₆F₅)₃] in the absence of base resulted in the incomplete conversion to **2** (85%). Multinuclear NMR investigations showed evidence of the partial sequestration of the [HB(C₆F₅)₃][−] anion by the liberated B(C₆F₅)₃ preventing complete hydride abstraction by **1**.²⁰ Nonetheless, this reactivity indicates that diphosphonium dication **1** possesses a higher hydridophilicity than the electrophilic Lewis acid B(C₆F₅)₃.

In further probing the Lewis acidic nature of **1**, DFT computations were performed. The geometry of the cation was optimized at the wB97XD/def2-TZV level of theory (see SI).²¹ The major component of the lowest unoccupied molecular orbital (LUMO) of **1** is the antibonding σ^* orbital of the P–P bond (Figure 1, left). Thus, the reaction of **1** with hydride is expected to yield **2'**. The donation of electron density from the hydride into the LUMO of **1** cleaves the P–P bond and significantly increases the computed distances between the P atoms (**1**: 2.31 Å, **2'**: 3.08 Å). Interestingly, adduct formation between **1** and a fluoride anion does not initiate a P–P bond cleavage resulting in a phosphorane species with fluoro- and phosphonium-substituents in axial positions (P–P: 2.530(1) Å).⁸ Moreover, compound **2'** and its isomer **2** are in equilibrium with each other, with **2'** being the minor component. This equilibrium was previously observed by NMR spectroscopy for other salts of the cation in **2**.¹⁹ The transformation of **2'** to **2** was computed to be slightly exergonic ($\Delta G_R^{298} = -1.2$ kcal/mol).

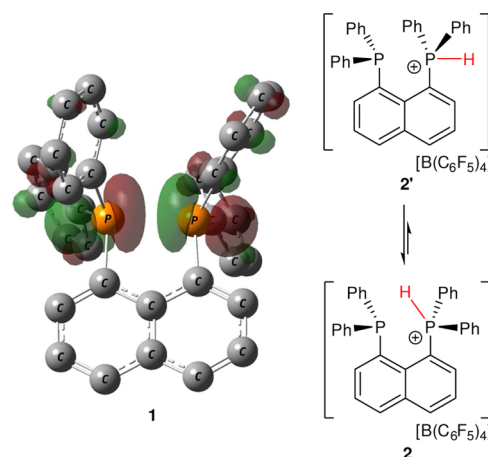


Figure 1. LUMO of the cation of **1** overlaid on its optimized geometry (hydrogens were omitted for clarity) and equilibrium between **2** and **2'**.

Species **1** also reacts with Ph₃P and Et₃SiH in C₆D₃Br (Scheme 1). After 24 h of reaction time at ambient temperature, almost quantitative conversion to **2** was observed by means of ³¹P{¹H} NMR spectroscopy. A singlet resonance at −3.3 ppm was assigned to the cation of [Ph₃PSiEt₃][B(C₆F₅)₄]⁺ (**5**), and its formulation was subsequently confirmed by independent synthesis (see SI). The stronger Lewis base *t*-Bu₃P (2 equiv) reacts with **1** to give **2** and [*t*-Bu₃PSiEt₃][B(C₆F₅)₄][−] (**6**). Afterward, deprotonation of **2** by the phosphine yields [*t*-Bu₃PH]⁺ and 1,8-diphenylphosphinonaphthalene (1,8-dppn). Indeed, reaction of the [N(SO₂CF₃)₂][−]-salt of **2** with *t*-Bu₃P revealed quantitative formation of 1,8-dppn and [*t*-Bu₃PH][N(SO₂CF₃)₂]⁺ (see SI). The formation of **6** was affirmed crystallographically (Figure 2), and the comparably large P–Si bond length (2.388 Å) is likely a result of steric congestion.^{5c}

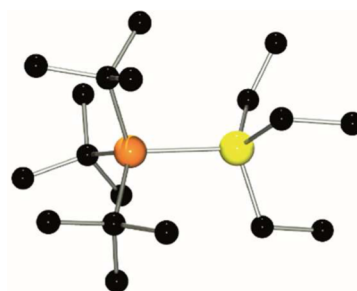
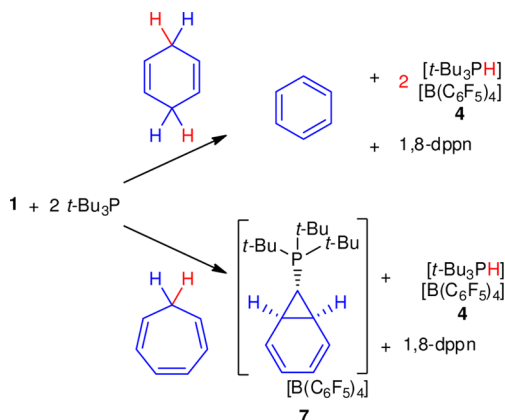


Figure 2. POV-ray depiction of the cation in **6**. P, orange; Si, yellow; C, black. Hydrogen atoms are omitted for clarity.

It is noteworthy that a mixture of **1** and Et₃SiH in CD₂Cl₂ in the absence of base shows only slow conversion to **2** and the products of degradation of the transient [Et₃Si]⁺ cation (65% after 48 h). In CD₃CN **1** reacts with excess Et₃SiH to give complete conversion to 1,8-dppn and H₂ as observed by ³¹P and ¹H NMR spectroscopy. In addition, the solvated [Et₃Si]⁺-species was detected via a ²⁹Si{¹H} NMR experiment (see SI).²² The species **2** is formed by hydride abstraction from Et₃SiH, while a second equivalent of silane yields H₂ giving 1,8-dppn. Collectively, these observations demonstrate the hydridophilicity of **1** as it competes with the strong Lewis acid [Et₃Si]⁺.

This remarkable hydridophilicity of **1** prompted an exploration of stoichiometric C–H bond activation reactions. Mixtures of **1** and phosphine were reacted with 1,4-cyclohexadiene (CHD) in C_6D_5Br as the solvent. While use of PPh_3 showed no reaction even upon heating to 100 °C for several days, use of the more basic phosphine $t\text{-Bu}_3P$ resulted in complete consumption of **1** after 24 h at 90 °C (Scheme 2). A

Scheme 2. C–H Activations by **1** and $t\text{-Bu}_3P$



singlet resonance was observed at 7.21 ppm in the 1H NMR spectrum of the reaction mixture, which indicates the formation of benzene. This is consistent with dehydrogenation of CHD and formation of **4** and 1,8-dppn.

The corresponding reaction of 1,3,5-cycloheptatriene (CHT) gave rise to a $^{31}P\{^1H\}$ NMR spectrum exhibiting three singlet resonances which were assigned to the cation of **4**, 1,8-dppn, and a new phosphonium ion species **7** ($\delta(^{31}P) = 45.1$ ppm). 1H NMR data for **7** suggest a *cyclo*-propanyl motif based on the observation of a CH resonance adjacent to the P atom ($\delta(^1H) = 0.09$ ppm).²³ These data indicate the formulation of **7** as $[C_7H_7Pt\text{-}Bu_3][B(C_6F_5)_4]$. To support this view, the tropylium ion salt $[C_7H_7][BF_4]$ was independently reacted with $t\text{-Bu}_3P$ to give the $[BF_4]^-$ salt of **7**. This salt was characterized by X-ray crystallography confirming **7** as the diastereomer in which the phosphonium substituent adopts the *exo*-position to the bicyclo[4.1.0]heptane framework (Figure 3). The remaining metric parameters are unexceptional.

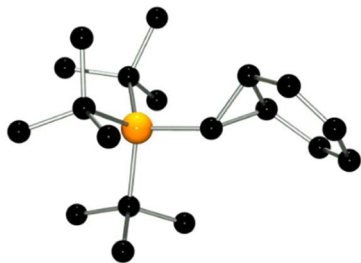


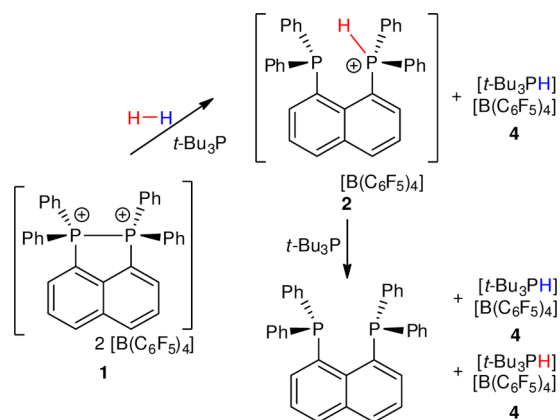
Figure 3. POV-ray depiction of the cation of **7**. P, orange; C, black. Hydrogen atoms are omitted for clarity.

The above reactions of the diphosphonium dication **1** with CHD and CHT are thought to proceed via hydride abstraction generating **2**. In the case of CHD, $t\text{-Bu}_3P$ sequesters the proton affording benzene while, for CHT, the transient tropylium cation is in equilibrium with its isomeric, bicyclic norcaradiene derivative.²⁴ Capture by $t\text{-Bu}_3P$ yields **7**.²⁵ In both cases, the

generated **2** reacts with a second equivalent of phosphine to liberate 1,8-dppn and the cation $[t\text{-Bu}_3PH]^+$. Although several C–H bond activations by ambiphilic phosphonium cations have been reported previously,²⁶ the present examples are, to the best of our knowledge, the first examples of FLP-type C–H activations^{4b,27} involving a phosphorus-based Lewis acid.

Finally, the FLP-type heterolytic splitting of H_2 utilizing **1** as a Lewis acid was probed as a mixture of diphosphonium species **1** and $t\text{-Bu}_3P$ in 1:2 stoichiometry in C_6D_5Br was exposed to a pressure of 4 atm of H_2 at 100 °C (Scheme 3). Within 48 h,

Scheme 3. H_2 Activation by **1** and $t\text{-Bu}_3P$



complete conversion to 1,8-dppn and 2 equiv of **4** was observed by NMR spectroscopy. This is indicative of heterolytic H_2 splitting by **1** and $t\text{-Bu}_3P$. As observed previously, **2** is deprotonated by the second equivalent of $t\text{-Bu}_3P$. Performing the same reaction under an atmosphere of D_2 (4 atm) resulted in the observation of a triplet resonance ($\delta(^{31}P) = 58.9$ ppm, $^1J_{PD} = 65$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum. This is consistent with the formation of $[t\text{-Bu}_3PD][B(C_6F_5)_4]$ (**4-d**).^{5c} In the presence of HD gas, a mixture of the salts **4** and **4-d** was obtained and scrambling of HD to D_2 and H_2 was not observed. This indicates that heterolytic cleavage of hydrogen is not reversible and is directly analogous to the irreversible cleavage of H_2 by the FLP $t\text{-Bu}_3P/B(C_6F_5)_3$.²⁸ The present system is also an example of an all-phosphorus based FLP effecting stoichiometric H_2 activation.¹⁴

In conclusion, we have presented the facile and high-yielding synthesis of robust but highly Lewis acidic diphosphonium dication **1**. While previously reported strong Lewis acids based on EPCs contain reactive P–F bonds, the present diphosphonium dication **1** achieves similar Lewis acidity as a result of the accumulation of positive charge on two adjacent P atoms. This phosphorus-based Lewis acid combined with phosphines generates the first examples of purely phosphorus-based FLP systems. The hydridophilicity of compound **1** was exploited in the stoichiometric FLP-type activation of B–H, Si–H, C–H, and H–H bonds. These unique examples of FLP reactivity with an EPC creates a new avenue for phosphorus-based Lewis acids, thus providing new strategies to FLP chemistry and Lewis acid catalysis. The application of related dications is the subject of ongoing studies in our laboratories.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthetic details and spectroscopic data for all reactions and new compounds; crystallographic details for **2**, **5**, and **7**. CIF

files for 2, 5, and 7 are also available free of charge from the Cambridge Crystallographic Data Centre under reference CCDC-1060485–1060487. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b04109.

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Notes

The authors declare no competing financial interest.

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