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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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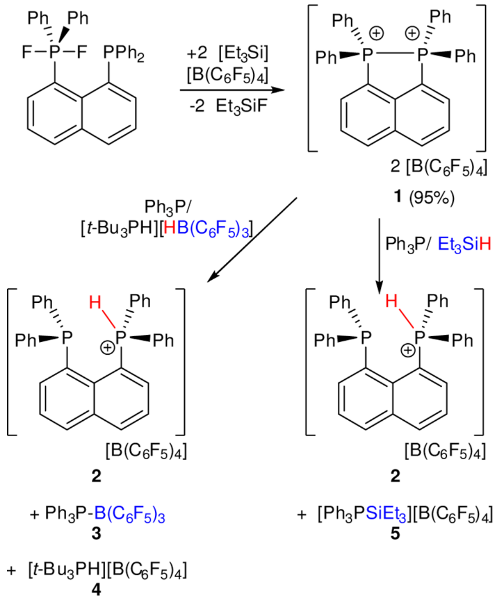
S *Supporting Information*

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 carbon-[4] or silicon-centered[5] 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 fluorophosphonium[7] $[(SIMes)PPh_2F]^{2+}$ (SIMes = 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene) or bidentate *bis*(fluorophosphonium) dications[8] 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] Bi[13]) 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 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]

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



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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 Et_3PO in CD_2Cl_2 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 Et_3PO 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 Et_3PO 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*-Bu_3P, while Ph_3P 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 Ph_3P was reacted with [*t*-Bu_3PH][$HB(C_6F_5)_3$][2b] in CD_2Cl_2 (Scheme 1). The $^{11}B\{^1H\}$ NMR spectrum of the reaction mixture revealed two resonances assigned to the $[B(C_6F_5)_4]^-$ anion ($\delta(^{11}B) = -16.6$ ppm) and the phosphine borane adduct $Ph_3P{-}B(C_6F_5)_3$ (**3**, $\delta(^{11}B) = -0.3$ ppm).[18] Adduct **3** was identified in the $^{31}P\{^1H\}$ NMR spectrum as well, with a resonance at −4.4 ppm. Two additional ^{31}P resonances revealed $^1J_{PH}$ coupling and were assigned to the cations of [*t*-Bu_3PH][$B(C_6F_5)_4$] (**4**, $\delta(^{31}P) = -59.8$ ppm, $^1J_{PH} = 429$ Hz)[2a] and $[(C_{10}H_6)(Ph_2P)_2H][B(C_6F_5)_4]$ (**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 $[N(SO_2CF_3)_2]^-$-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 Ph_3P acts as an FLP, heterolytically cleaving the B–H bond in $[HB(C_6F_5)_3]^-$ yielding **2** and **3**. Interestingly, the combination of **1** and [*t*-Bu_3PH][$HB(C_6F_5)_3$] in the absence of base resulted in the incomplete conversion to **2** (85%). Multinuclear NMR investigations showed evidence of the partial sequestration of the $[HB(C_6F_5)_3]^-$ anion by the liberated $B(C_6F_5)_3$ preventing complete hydride abstraction by **1**.[20] Nonetheless, this reactivity indicates that diphosphonium dication **1** possesses a higher hydridophilicity than the electrophilic Lewis acid $B(C_6F_5)_3$.

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).

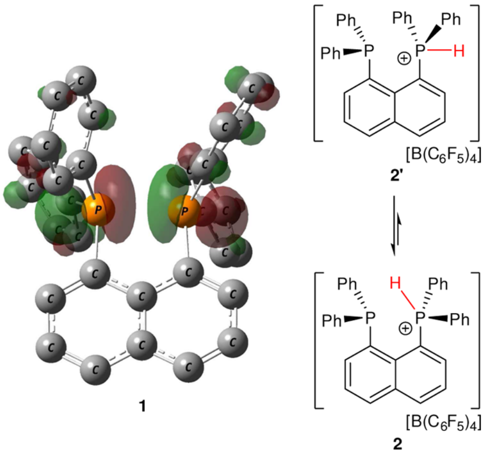

Figure 1. LUMO of the cation of **1** overlaid on its optimized geometry (hydrogens were omitted for clarity) and equilibrium between **2** and **2′**.

Species **1** also reacts with Ph_3P and Et_3SiH in C_6D_5Br (Scheme 1). After 24 h of reaction time at ambient temperature, almost quantitative conversion to **2** was observed by means of $^{31}P\{^1H\}$ NMR spectroscopy. A singlet resonance at −3.3 ppm was assigned to the cation of $[Ph_3PSiEt_3][B(C_6F_5)_4]$ (**5**), and its formulation was subsequently confirmed by independent synthesis (see SI). The stronger Lewis base *t*-Bu_3P (2 equiv) reacts with **1** to give **2** and [*t*-Bu_3PSiEt_3][$B(C_6F_5)_4$] (**6**). Afterward, deprotonation of **2** by the phosphine yields [*t*-$Bu_3PH]^+$ and 1,8-diphenylphosphinonaphthalene (1,8-dppn). Indeed, reaction of the $[N(SO_2CF_3)_2]^-$-salt of **2** with *t*-Bu_3P revealed quantitative formation of 1,8-dppn and [*t*-Bu_3PH][$N(SO_2CF_3)_2$] (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]

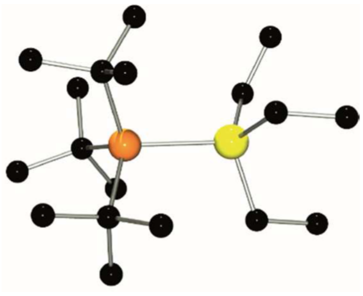

Figure 2. POV-ray depiction of the cation in **6**. P, orange; Si, yellow; C, black. Hydrogen atoms are omitted for clarity.

It is noteworthy that a mixture of **1** and Et_3SiH in CD_2Cl_2 in the absence of base shows only slow conversion to **2** and the products of degradation of the transient $[Et_3Si]^+$ cation (65% after 48 h). In CD_3CN **1** reacts with excess Et_3SiH to give complete conversion to 1,8-dppn and H_2 as observed by ^{31}P and ^1H NMR spectroscopy. In addition, the solvated $[Et_3Si]^+$-species was detected via a $^{29}Si\{^1H\}$ NMR experiment (see SI).[22] The species **2** is formed by hydride abstraction from Et_3SiH, while a second equivalent of silane yields H_2 giving 1,8-dppn. Collectively, these observations demonstrate the hydridophilicity of **1** as it competes with the strong Lewis acid $[Et_3Si]^+$.

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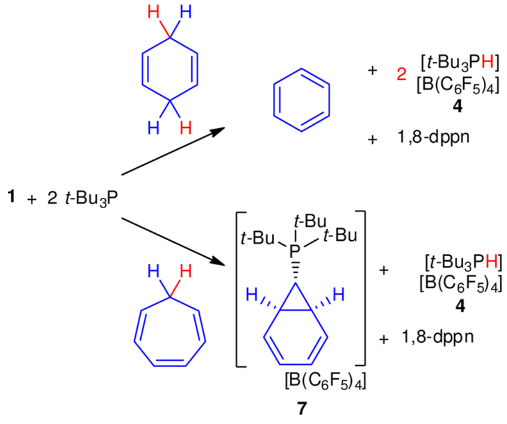
This remarkable hydridophilicity of **1** prompted an exploration of stoichiometric C−H bond activation reactions. Mixtures of **1** and phosphine were reacted with 1,4-cyclohexadiene (CHD) in C_6D_5Br as the solvent. While use of PPh_3 showed no reaction even upon heating to 100 °C for several days, use of the more basic phosphine *t*-Bu_3P resulted in complete consumption of **1** after 24 h at 90 °C (Scheme 2). A 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.

Scheme 2. C−H Activations by 1 and *t*-Bu$_3$P



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*-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.

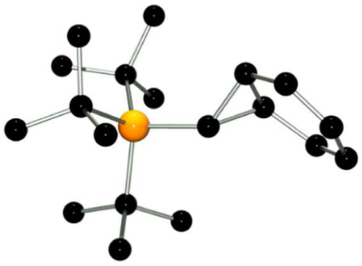
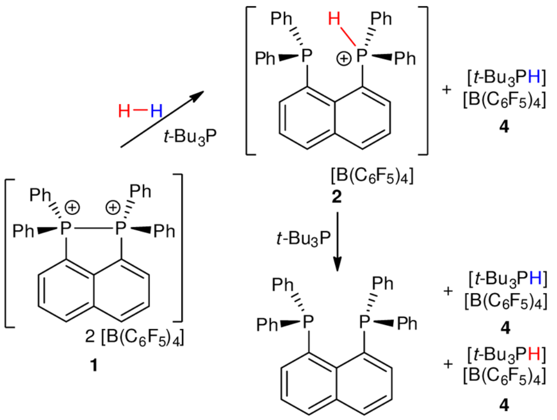


Figure 3. POV-ray depiction of the cation of **7**. P, orange; C, black. Hydrogen atoms are omitted for clarity.

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*-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*-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 phosphenium 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*-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, 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*-Bu_3P. As observed previously, **2** is deprotonated by the second equivalent of *t*-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 $[t\text{-}Bu_3PD][(C_6F_5)_4]$ (**4**-d^1).[5c] In the presence of HD gas, a mixture of the salts **4** and **4**-d^1 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*-$Bu_3P/B(C_6F_5)_3$.[28] The present system is also an example of an all-phosphorus based FLP effecting stoichiometric H_2 activation.[14]

Scheme 3. H$_2$ Activation by 1 and *t*-Bu$_3$P



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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