P Dication

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The Highly Lewis Acidic Dicationic Phosphonium Salt: $[(SIMes)PFPh_2][B(C_6F_5)_4]_2$**

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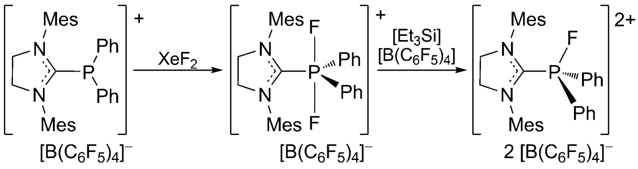
Abstract: *The dicationic imidazolium-phosphonium salt $[(SIMes)PFPh_2][B(C_6F_5)_4]_2$ has been prepared and shown to exhibit remarkable Lewis acidity in stoichiometric reactions and acting as an effective Lewis acid catalyst for the hydrodefluorination of fluoroalkanes and the hydrosilylation of olefins.*

Historically, P-compounds have been widely exploited as Lewis donor ligands in transition metal and organometallic chemistry. Such ancillary roles have been critical to a number of landmark advances in catalysis. While studied to a lesser extent, P-based compounds have also been shown to exhibit Lewis acidity.[1] For example, P^{III} di-coordinated phosphenium ions have been shown to be ambiphiles and the Lewis acidity[2] of these species has been shown to prompt activation of C–C/H[3] or P–P[4] bonds. Similarly, the Lewis acidity of tetra-coordinated P^{V}-phosphonium cations has been exploited to capture fluoride ions in sensor applications[5] and to act as catalysts for additions to polar unsaturates[6] and in Diels–Alder reactions.[7] In a similar manner, the classical addition of P-based ylides to ketones is facilitated by the electrophilicity of the phosphorus center.[8] More recently, we have reported the preparation and Lewis acidity of the fluorophosphonium cations $[(C_6F_5)_2PhPF]^+$ (**1**) and $[(C_6F_5)_3PF]^+$ (**2**) and the application of these species in the hydrodefluorination of fluoroalkanes, the isomerization of terminal olefins and the hydrosilylation of alkenes and alkynes.[9] This reactivity has been attributed to their energetically accessible σ*(P–F) acceptor orbitals.

The discovery of these electrophilic phosphonium cations provides a new avenue to Lewis acid catalysts. However, the initial systems described above, require strongly electron-withdrawing substituents, thus limiting potential structural variations. Herein, we report a new strategy that avoids the use of fluoroarene substituents by enhancing the Lewis acidity by targeting an electrophilic fluorophosphonium dication. Oxidation of an N-heterocyclic carbene (NHC) derived cationic phosphine[10] provides a cationic difluorophosphorane, while subsequent fluoride abstraction affords a phosphonium dication salt. This latter species is shown to be more electrophilic than **1** or **2** in stoichiometric reactions and exhibits Lewis acidity in catalytic reactions.

The reaction of Ph_2PCl, 1,3-dimesitylimidazolidin-2-ylidene (SIMes) and $[Et_3Si][B(C_6F_5)_4]\cdot 2(C_7H_8)$ afforded the cationic phosphine $[(SIMes)PPh_2][B(C_6F_5)_4]$ (**3**) in almost quantitative yield (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **3** in CD_2Cl_2 shows a singlet resonance at −1.5 ppm. This compares with a shift of −12.9 ppm observed for the related carbene-phosphine salt $[(IDipp)PPh_2]^+$.[11] The molecular structure of **3** was confirmed crystallographically, revealing a $P{-}C_{carbene}$ bond length of 1.861(4) Å. The remaining metric parameters were unexceptional (see Supporting Information).



3 **4** **5**

Scheme 1. Preparative route to **5**.

The phosphine salt **3** is cleanly oxidized with XeF_2 to the cationic difluorophosphorane $[(SIMes)PF_2Ph_2][B(C_6F_5)_4]$ (**4**) and was isolated in 81% yield (Scheme 1) This species gives rise to a $^{31}P\{^1H\}$ NMR signal at −62.9 ppm with a $^1J_{PF}$ coupling constant of 733 Hz consistent with the presence of two equivalent F atoms. This chemical shift is downfield of that observed for the neutral phosphorane $(C_6F_5)_3PF_2$ at −48.0 ppm ($^1J_{PF} = 694$ Hz).[9b]

The molecular structure of **4** shows a distorted trigonal bipyramidal arrangement at the P atom (Figure 1). The fluoro-substituents occupy the axial positions with a F-P-F angle of 168.8(2)° while the carbene and the phenyl-substituents occupy equatorial positions. While carbenes have been exploited to stabilize low valent phosphorus species,[10c,12] compound **4** is the first cationic halophosphorane derivative to be structurally characterized.[13]

One of the fluoro-substituents on the cation of **4** is removed upon treatment with $Et_3Si[B(C_6F_5)_4]\cdot 2(C_7H_8)$ giving rise to the dication $[(SIMes)PFPh_2][B(C_6F_5)_4]_2$ (**5**) and the expected by-product Et_3SiF. While Burford and co-workers have recently described dicationic Sb and Bi species,[14] **5** is

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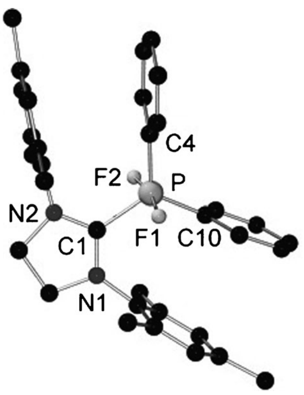


Figure 1. POV-ray depiction of the cation of **4**. Hydrogen atoms have been omitted for clarity. Selected bond distances and angles: C1–N1 1.322(6), C1–N2 1-325(6), P–C1 1.866(5), P–C4 1.799(6), P–C10 1.815(5), P–F1 1.628(4), P–F2 1.660(4); N1-C1-N2 111.5(5), C1-P-C4 121.2(2), C1-P-C10 121.2(2), C4-P-C10 117.6(3), F1-P-F2 168.8(2), F1-P-C1 85.0(2), F1-P-C4 92.8(3), F1-P-C10 93.4(2), F2-P-C1 83.8(2), F2-P-C4 93.0(3), F2-P-C10 92.4(2).

a rare example of an isolable dicationic phosphonium salt (Scheme 1).[15] Compound **5** exhibits a dramatic ^{31}P downfield shift to 78.1 ppm with a P–F coupling of 1040 Hz. The corresponding ^{19}F resonance is observed at −131.7 ppm. Interestingly, the ^{31}P and ^{19}F chemical shifts are reminiscent of those observed for the very Lewis acidic phosphonium ions **1** ($\delta(^{31}\mathrm{P}) = 78$ ppm, $\delta(^{19}\mathrm{F}) = -122$ ppm) and **2** ($\delta(^{31}\mathrm{P}) = 68$ ppm, $\delta(^{19}\mathrm{F}) = -121$ ppm) inferring similar P-environments and thus perhaps comparable Lewis acidities. The formulation of **5** was further confirmed crystallographically (Figure 2). The P–F bond length (1.532(2) Å) is substantially shorter than those observed in phosphorane **4** (1.628(4) and 1.660(4) Å). Similarly the P–C bonds to the phenyl-substituents are shortened to 1.753(3) and 1.756(3) Å in **5** in comparison to those in **3** and **4** which range from 1.799(6) Å to 1.866(5) Å).

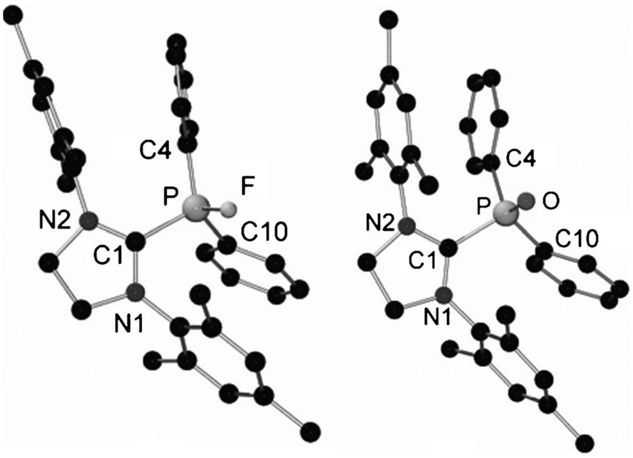
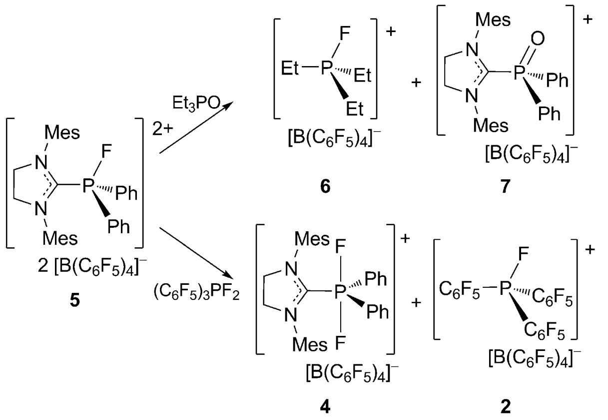


Figure 2. POV-ray depiction of the dication of **5** (left) and the cation of **7** (right). Hydrogen atoms have been omitted for clarity. Selected bond distances and angles: **5**: C1–N1 1.329(3), C1–N2 1.316(4), P–C1 1.852(3), P–C4 1.753(3), P–C10 1.756(3), P–F 1.532(2); N1-C1-N2 112.8(3), C1-P-C4 113.4(1), C1-P-C10 109.2(1), C4-P-C10 116.6(1), F-P-C1 101.8(1), F-P-C4 106.4(1), F-P-C10 108.2(1); **7**: C1–N1 1.328(3), C1–N2 1-328(2), P–C1 1.881(2), P–C4 1.798(2), P–C10 1.796(2), P–O 1.480(2); N1-C1-N2 111.8(2), C1-P-C4 106.7(1), C1-P-C10 106.9(1), C4-P-C10 109.0(1), O-P-C1 107.2(1), O-P-C4 113.7(1), O-P-C10 112.9(1).

To probe the Lewis acidity of **5** the Gutmann–Beckett method was employed.[16] Compound **5** was combined with Et_3PO in CD_2Cl_2. ^{31}P NMR spectroscopy revealed the formation of a mixture containing fluorophosphonium **6** and oxophosphorane **7** salts (Scheme 2). This was evidenced by the ^{31}P NMR spectrum which reveals a doublet resonance at comparably low field ($\delta(^{31}\mathrm{P}) = 147.2$ ppm) with a typical $^{1}J_{PF}$ coupling constant of 989 Hz[9] attributed to **6** whereas a singlet resonance observed at 14.0 ppm was attributed to **7**.[13] These data infer that simple coordination of Et_3PO to the phosphonium P atom of **5** does not occur but rather an oxide–fluoride exchange reaction takes place affording $[Et_3PF][B(C_6F_5)_4]$ (**6**) and $[(SIMes)POPh_2][B(C_6F_5)_4]$ (**7**). The salts **6** or **7** could not be separated from the reaction mixture, however, these species were independently synthesized and fully characterized. The formulation of the cationic oxophosphorane derivative featuring an imidazolium-based substituent **7** was further confirmed by X-ray crystallography (Figure 2).[13] Similar to **5**, the cation of **7** shows a distorted tetrahedral environment at the P atom. However, the cation of **7** exhibits longer P–C bonds (P–C1 1.881(2) Å, av. P–C_{aryl} 1.797(2) Å) consistent with the formal mono-cationic charge.



Scheme 2. Reactions of **5** with Et_3PO and $(C_6F_5)_3PF_2$.

Efforts to apply the Child's protocol to assess the Lewis acidity[17] involved combination of **5** with excess crotonaldehyde at −20 °C in CD_2Cl_2. NMR data suggest a complex mixture with formation of **7** and **4** in addition to other organic products. While these Lewis acidity tests do not permit comparison to other Lewis acids, the observed reactivity suggests that the dication **5** is highly electrophilic. This notion is supported by the fact that exposure of 1 mg of **5** to $[D_8]$THF leads to polymerization as GPC after 2 h reveals a molecular weight of the polymer of 8.6×10^4 Da with a polydispersity of 2.6. Similar evidence of Lewis acidity is seen with the addition of 2 mol % of **5** to a solution of 1,1-diphenylethylene in CD_2Cl_2 as this effects complete Friedel–Crafts dimerization of the olefin in less than 30 min yielding the indene product in 97 % isolated yield.[18]

In order to get insights into the fluorophilicity, **5** was reacted with phosphorane $(C_6F_5)_3PF_2$ in CD_2Cl_2 (Scheme 2). This led to the clean and complete conversion to fluorophosphonium salt **2** and difluorophosphorane **4** as revealed by ^{31}P and ^{19}F NMR spectroscopy. This infers that **5** is more fluorophilic than **2**. The fluorophilicity of **5** was further demonstrated in the 1:1 reaction of **5** with Ph_3CF. This led to the conversion of **5** to **4** and trityl cation as evidenced by ^{31}P, ^{19}F and ^{13}C NMR spectra.

This evidence of Lewis acidity and fluorophilicity suggests that **5** could act as an effective Lewis acid catalyst. This prompted an investigation of **5** as a catalyst for hydrodefluorination reactions. A series of fluoroalkanes was combined with Et_3SiH in the presence of **5** as a catalyst (Table 1).

Table 1: Catalytic hydrodefluorination of fluoroalkanes.

$$\text{F–R} + Et_3SiH \xrightarrow[\substack{CD_2Cl_2 \\ 25\,^\circ C}]{\mathbf{5}} \text{H–R} + Et_3SiF$$

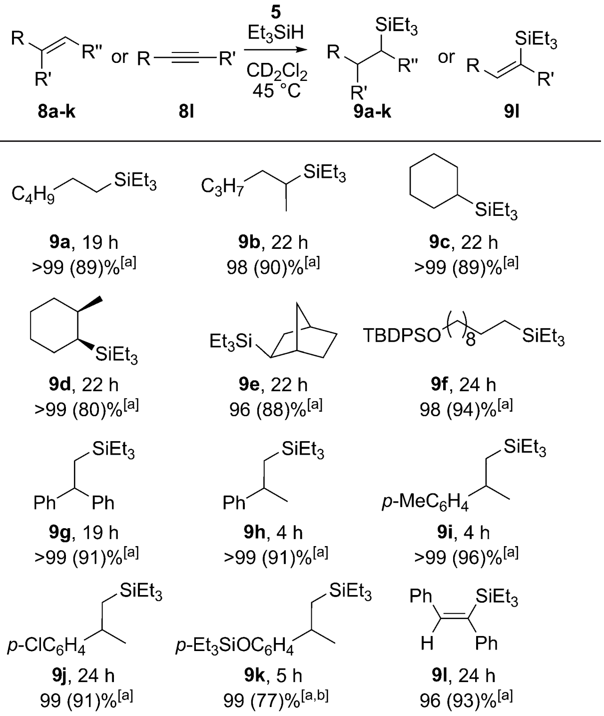
Substrate	Cat. (mol %)[a]	*t* [h]	%Si–F[b,c]	%C–F[b,d]	TON
1-fluoroadamantane	1	1	> 99	100	100
fluorocyclohexane	1	1	92	99	100
1-fluoropentane	5	1	> 99	100	100
$(CF_3)C_6H_5$	1	24	53	88	88
1,4-$C_6H_4(CHF_2)_2$	5	24	31	44	8.8
	10	24	66	72	7.2
perfluorotoluene	5	24	14	20	4.0
	10	24	29	28	2.8

[a] Relative to fluoroalkane substrate. [b] Conversions were determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard. [c] Calculated from the proportion of C–F bonds originally present relative to Si–F bonds formed. [d] Calculated from the proportion of C–F bonds consumed after time *t* (h).

At ambient temperature, almost complete conversion of 1-fluoroadamantane, 1-fluorocyclohexane and 1-fluoropentane was observed within one hour. The consumption of substrate and growth of the resonance attributable to Et_3SiF was evidenced by the ^{19}F NMR spectra of the reaction mixtures. Trifluorotoluene is almost consumed within 24 h while higher catalyst loadings are required (10 mol %) to achieve significant conversion of 1,4-$C_6H_4(CHF_2)_2$. In the case of perfluorotoluene, incomplete reaction of the aliphatic C–F bonds is achieved after 24 h. The aryl C–F bonds remain untouched. Mechanistically, these hydrodefluorinations are thought to proceed via a mechanism analogous to those described for other strong, main-group based Lewis acids, including $B(C_6F_5)_3$,[19] **2**,[9b] silylium[20] and carbenium ions[21] and aluminium species.[22] This would involve an abstraction of fluoride by **5** from the fluoroalkane to give **4** and a carbocation. The latter intermediate reacts with silane to give alkane and generates silylium cation which abstracts F from **4** to regenerate **5**. This mechanism is supported by the observation that **5** does not react with Et_3SiH even after several days reaction time. In addition, a further competition experiment confirmed the reaction of fluoroalkane with **5** in the presence of silylium cation precluding the involvement of a silylium ion as a hydrodefluorination catalyst[9b] (see Supporting Information).

The utility of **5** in catalytic hydrosilylation of alkenes and alkynes was also investigated. Within 14 to 24 h at 45 °C complete hydrosilylation of 1-hexene (**8a**), *cis*-2-hexene (**8b**), cyclohexene (**8c**) and 1-methylcyclohexene (**8d**) was observed in the presence of Et_3SiH and 2 mol % of **5** (Table 2) affording the corresponding hydrosilylation products **9a–d** in high isolated yields (80–90 %). In the case of **8d**, exclusively *anti* 1,2-addition of the Si–H bond to the olefin gives *rac*-**9d** whereas norbornene is selectively transformed to the *exo*-**9e** in a fashion similar to other Lewis acid catalysts $B(C_6F_5)_3$[23] or **2**.[9a] Styrene substrates are also hydrosilylated to the respective products **9g–k**. It is noteworthy, that silylether (**9f**) and chloro functional groups (**9j**) are tolerated by this catalyst. In the case of *p*-methoxy-α-methylstyrene also conversion of the methoxy group to silylether functionalized product **9k** was observed. Finally, alkyne **8l** was selectively converted to the *cis*-substituted alkene **9l**.

Table 2: Catalytic hydrosilylation of alkenes and alkynes.



8a-k **8l** **9a-k** **9l**

9a, 19 h
>99 (89)%[a]

9b, 22 h
98 (90)%[a]

9c, 22 h
>99 (89)%[a]

9d, 22 h
>99 (80)%[a]

9e, 22 h
96 (88)%[a]

9f, 24 h
98 (94)%[a]

9g, 19 h
>99 (91)%[a]

9h, 4 h
>99 (91)%[a]

9i, 4 h
>99 (96)%[a]

9j, 24 h
99 (91)%[a]

9k, 5 h
99 (77)%[a,b]

9l, 24 h
96 (93)%[a]

[a] Conversions were determined by means of ^{1}H NMR spectroscopy using, when necessary, a toluene standard, isolated yields are given in parenthesis. [b] Two equivalents Et_3SiH were utilized.

In summary, we have described the conversion of a cationic phosphine salt to a cationic difluorophosphorane and on to a dicationic fluorophosphonium derivative. The species **5** is shown to be highly Lewis acidic in stoichiometric reactions and to act as a Lewis acid catalyst in hydrodefluorination and hydrosilylation reactions. It is noteworthy that the previously reported electrophilic boranes or fluorophosphonium monocations exploit highly fluorinated, strongly electron-withdrawing substituents. In contrast, the phosphonium dication **5** achieves similar levels of Lewis acidity and reactivity without highly electron withdrawing substituents. Moreover, the synthetic route to **5** is facile, high yielding and amenable to structural modifications, offering the potential of a large family of highly Lewis acidic compounds and catalysts. The impact of structural variations on the reactivity and Lewis acidity of such dicationic phosphonium species is expected to provide new avenues to both Lewis acid catalysis and FLP chemistry. These aspects are the subjects of on-going studies.

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