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C−F Bond Activation by Transient Phosphenium Dications

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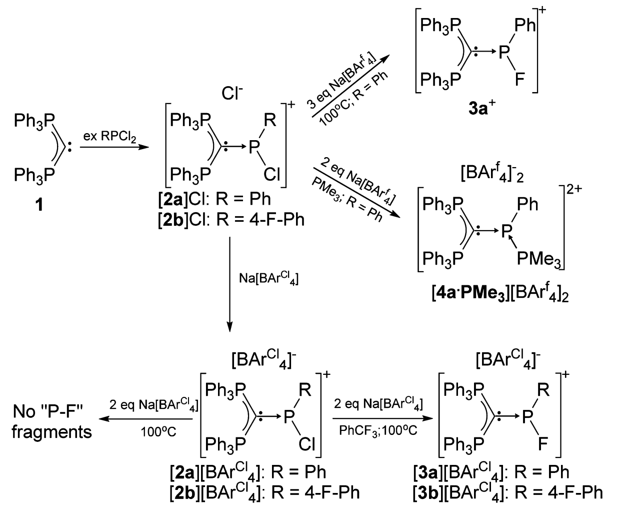
Supporting Information

ABSTRACT: C−F bond cleavage by transient phosphorus(III)-based dications $[RP(C(PPh_3)_2)]^{2+}$ (**4a**$^{2+}$, R = Ph; **4b**$^{2+}$, R = 4-F-Ph) is reported. These dications were generated by reaction of the corresponding monocationic precursors with excess $Na[BAr_4^{Cl}]$. Evidence for the existence of transient dicationic species was obtained by trapping the dication **4a**$^{2+}$ with PMe_3. According to theoretical analysis, the low-lying lowest unoccupied molecular orbitals of these species were responsible for the observed activation of C−F bonds.

Organic compounds containing C−F bonds continue to attract the attention of the scientific community because of their importance in both industrial and academic research. C−F bonds not only are among the strongest single bonds, in general, but also are the strongest single bond that carbon forms with any other element.[1] Considering that these particular bonds show exceptional kinetic inertness, it is not surprising that various organofluorine compounds are extremely useful as durable goods such as poly(tetrafluoroethylene) and high-performance lubricants. However, the inherent thermodynamic and kinetic C−F bond stability renders these perfluorinated compounds environmentally persistent and difficult to degrade and/or recycle.[2] For example, the atmospheric half-life for CF_4 is greater than 5.0×10^4 years so the disposal of organofluorine waste remains a challenge.[3] Significant efforts have been made to develop various methods for C−F bond activation. Metal-mediated C−F bond cleavage reactions[4] are predominant in this field, but more attractive nonmetal systems are also emerging. Silicon-based compounds (e.g., Et_3Si^+) dominate the nonmetal field presumably because of silicon's high affinity for fluorine; the Si−F bond dissociation energy is ~140 kcal/mol.[5] In fact, most systems capable of catalytic C−F activation use silanes as fluorine scavengers.[6] Lewis acidic boron- and aluminum-based compounds were also reported to be effective in C−F bond functionalization.[5,7,8] Recently, Stephan and co-workers have shown that organofluorophosphonium cations [i.e., phosphorus(V)-based cations] could be used in catalytic C−F activation corresponding to the very first examples of this type of activation performed at a phosphorus center.[9] However, there are no examples of phosphorus(III)-based species being involved in a C−F bond activation. Therefore, we report a transient phosphorus(III)-based dication capable of activating C−F bonds of the $[BAr^f_4]^-$ anion $[Ar^f = (CF_3)_2\text{-}C_6H_3]$ and α,α,α-trifluorotoluene ($PhCF_3$).

Recently, our group has reported the first example of a coordinatively unsaturated phosphorus(III) dication, $[^iPr_2NP(C(PPh_3)_2)]^{2+}$, and its reactivity toward water and methanol.[10] Our next goal was to potentially enhance the Lewis acidic properties of the dication by replacing the amino substituent with phenyl (Ph) and 4-fluorophenyl (4-FPh) groups. Using the procedure described for the synthesis of an amino-substituted dication, the corresponding monocationic precursors $[RPCl(C(PPh_3)_2)]Cl$ ([**2a**]Cl, R = Ph; [**2b**]Cl, R = 4-FPh) were synthesized by the addition of the free carbone[11] $C(PPh_3)_2$ (**1**) to a benzene solution containing excess of $RPCl_2$ (R = Ph, 4-FPh), as described in Scheme 1. The carbone-for-chloride replacement was manifested by the presence of a triplet (~111 ppm) and a doublet (~26 ppm) in the ^{31}P NMR spectra corresponding to the central and carbone's phosphorus atoms, respectively. The structural identity of these two monocationic precursors was elucidated by single-crystal X-ray diffraction when the chloride anion was replaced by SbF_6^-. However, [**2a**][SbF_6] (see the Supporting Information) exhibited a high degree of

Scheme 1. General Synthetic Procedures



$Ar^f = 3,5\text{-}(CF_3)_2\text{-}C_6H_3$; $Ar^{Cl} = 3,5\text{-}Cl_2\text{-}C_6H_3$

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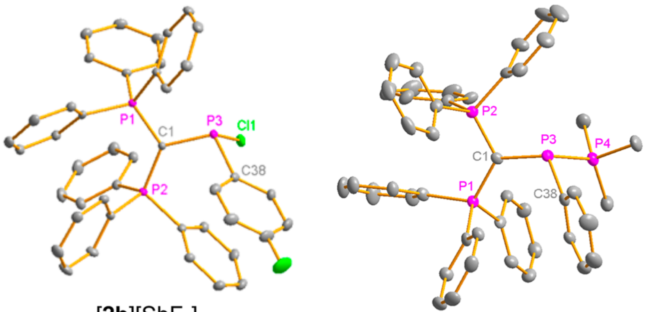
disorder, resulting in ambiguous structural parameters that are excluded from further discussion. The value for the sum of the bond angles of 312.01(7)° around the central phosphorus atom for **2b**$^+$ (Figure 1) confirmed the expected pyramidal geometry for these species. Both the P3−C1 [1.7828(13) Å] and P3−Cl1 [2.1271(5) Å] bond distances for **2b**$^+$ were somewhat shorter than the analogous bond distances for [^{i}Pr$_2$NPCl(C(PPh$_3$)$_2$)]$^+$ [1.812(5) and 2.173(2) Å, respectively].[10a] This was expected considering the greater π-electron donation ability of the amino substituent with respect to 4-FPh and Ph. However, a shorter P−Cl bond for **2b**$^+$ (and presumably for **2a**$^+$) suggested that chloride abstraction from **2a**$^+$/**2b**$^+$ and subsequent formation of the target dications could be more challenging than those in the case of the amino analogue.



[**2b**][SbF$_6$]

[**4a·PMe$_3$**][BAr$^f_4$]$_2$

Figure 1. Single crystal X-ray structures for [**2b**][SbF$_6$] and [**4a·PMe$_3$**][BAr$^f_4$]$_2$ at 50% probability. The counterions and hydrogen atoms were omitted for clarity.

Indeed, the P−Cl bond was not cleaved after the addition of 2 or 3 equiv of Na[BAr$^f_4$] to a solution containing either [**2a**]Cl or [**2b**]Cl at room temperature. However, leaving the reaction mixture of [**2a**]Cl and 3 equiv of Na[BAr$^f_4$] in 1,2-difluorobenzene at 100 °C overnight in an J. Young NMR tube resulted in the disappearance of the triplet signals at δ_P assigned to [**2a**]$^+$ and the appearance of a new doublet of triplets at δ_P 162.2. The signal was assigned to the central phosphorus, with the carbone substituent causing the triplet splitting, while the value for the doublet coupling constant of 976 Hz suggested the formation of a P−F fragment. The presence of this fragment was confirmed by observing an analogous signal in the ^{19}F NMR spectrum at −161.2 ppm having the same value for the coupling constant. The crude product, containing other unidentified products according to ^{31}P and ^{19}F NMR spectroscopy, was also subjected to electrospray mass spectrometry (ES-MS), resulting in the identification of a signal at *m/z* 663.2006 (calcd for $C_{43}H_{35}FP_3$: *m/z* 663.1936) whose isotope pattern was in excellent agreement with that of the fluorinated monocation [PhPF(C(PPh$_3$)$_2$)]$^+$ (**3a**$^+$). Unfortunately, unsuccessful attempts have been made to structurally elucidate this compound. However, additional evidence for the identity of **3a**$^+$ was gained by reacting [**2a**][BAr$^{Cl}_4$] (Ar^{Cl} = 3,5-Cl$_2$C$_6$H$_3$; see below) with excess KF, resulting in identical ^{19}F and ^{31}P NMR spectroscopic data.

Even though the source of the fluoride (the anion or solvent) was not immediately evident, it was suspected that the transient and highly reactive nature of the dication [PhP(C(PPh$_3$)$_2$)]$^{2+}$ ([**4a**]$^{2+}$) was responsible for the observed fluoride abstraction. The most appealing evidence for the existence of this dication was gained by a trapping experiment involving the addition of PMe$_3$ in a solution containing [**2a**]Cl and 2 equiv of Na[BAr$^f_4$] (Scheme 1). The ^{31}P NMR spectrum of this reaction mixture contained three second-order signals at δ_P −6.4 (doublet of triplets), 11.4 (doublet of triplets), and 28.7 (doublet), while the ES-MS spectrum revealed the presence of a peak at *m/z* 360.1197 (calcd for [$C_{46}H_{44}P_4$]$^{2+}$: *m/z* 360.1191). These results were consistent with formation of the adduct [PhP(PMe$_3$)(C(PPh$_3$)$_2$)][BAr$^f_4$]$_2$ ([**4a·PMe$_3$**][BAr$^f_4$]$_2$). Indeed, single-crystal X-ray analysis of this product confirmed its identity as the PMe$_3$-trapped adduct of the **4a**$^{2+}$ dication (Figure 1). The P3−C1 [1.792(4) Å] and P3−C38 [1.826(4) Å] bond distances are essentially equivalent with respect to **2b**$^+$, while the P3−P4 [2.217(2) Å] bond distance is quite comparable with the analogous distance observed for [Ph$_2$P-PMe$_3$]$^+$ [2.187(2) Å].[12]

In order to gather more information on the source of the fluoride ion, Na[BAr$^f_4$] was replaced with Na[BAr$^{Cl}_4$]. In fact, the noncoordinating chloride ions of the monocationic precursors [**2a**]Cl and [**2b**]Cl were first replaced by [BAr$^{Cl}_4$]$^-$ to obtain [**2a**][BAr$^{Cl}_4$] and [**2b**][BAr$^{Cl}_4$], respectively (Scheme 1). Then, to a 1,2-difluorobenzene solution containing either of these two monocations was added 2 equiv of Na[BAr$^{Cl}_4$], and the mixture was heated to 100 °C and kept overnight. In both instances, there was no evidence for any "P−F" fragment formation eliminating the solvent as the fluoride source in the original reaction. Then, to the same reaction mixtures was added 1 equiv of PhCF$_3$, and after heating for several hours, the formation of **3a**$^+$ and [4-F-PhPF(C(PPh$_3$)$_2$)]$^+$ (**3b**$^+$) was detected. These observations clearly indicated that the source of the fluoride in the initial experiment(s) was the [BAr$^f_4$]$^-$ anion.[13]

Furthermore, heating a 1:1 molar mixture of Na[BAr$^{Cl}_4$] and PhCF$_3$ showed no reactivity, based on ^{19}F NMR spectroscopy, providing more evidence that the transient dications were responsible for C−F cleavage of the fluorinated compounds (PhCF$_3$ and BAr$^f_4$$^-$). Unfortunately, other fluorinated substrates such as (CF$_3$CH$_2$)$_2$O, C$_6$F$_5$Br, and CF$_3$(CF$_2$)$_6$CHF$_2$ were not activated by the transient dications because there was no evidence for the formation of a P−F fragment after the introduction of these substrates in the reaction mixture containing a monocationic precursor ([**2a**][BAr$^{Cl}_4$] or [**2b**][BAr$^{Cl}_4$]) and 2 equiv of Na[BAr$^{Cl}_4$]. This is presumably due to the absence of a Ph group adjacent to the targeted C−F bond cleavage in these substrates with respect to PhCF$_3$ and BAr$^f_4$$^-$ because the presence of Ph ring(s) was reported to assist in stabilization of the corresponding carbocations.[14] Nevertheless, to the best of our knowledge, the transient dications formed in this work are the first examples of compounds containing a phosphorus(III) center capable of cleaving C−F bonds.

With the aim of better understanding the difference in the reactivity and stability between **4a**$^{2+}$ and **4b**$^{2+}$ ([4-FPhP(C(PPh$_3$)$_2$)]$^{2+}$) on one side and [^{i}Pr$_2$NP(C(PPh$_3$)$_2$)]$^{2+}$ on the other, these dications were subjected to theoretical investigations using the *Gaussian 09* package. The dicationic structures were fully optimized by the B3PW91 method using the 6-31G(d) basis set. Because the nature of the frontier orbitals for these three dications was virtually identical, only the orbitals for **4a**$^+$ are shown in Figure 2.[8a] The lowest unoccupied molecular orbitals (LUMOs) correspond to the π* for the allene-like CPX fragment (**4a**$^{2+}$/**4b**$^{2+}$, X = C; [^{i}Pr$_2$NP(C(PPh$_3$)$_2$)]$^{2+}$, X = N) while the highest occupied molecular orbitals (HOMOs) seem to be mainly nonbonding for the same fragment, with a possible mixing from the lone-pair orbital on the central phosphorus forming helical-like orbitals.[15] The energy levels of the HOMOs for all three dications were also similar (−0.43791, −0.43854, and

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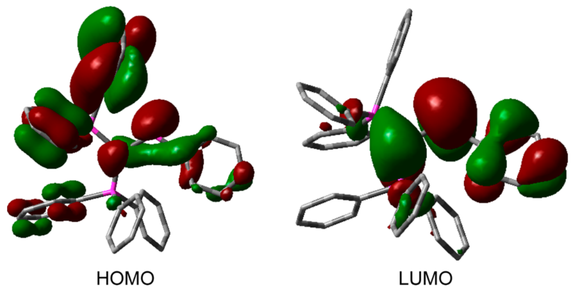

Figure 2. Frontier orbitals for $\mathbf{4a}^{2+}$.

−0.43453 eV for $\mathbf{4a}^{2+}$, $\mathbf{4b}^{2+}$, and $[^{i}Pr_2NP(C(PPh_3)_2)]^{2+}$, respectively). However, the LUMOs for $\mathbf{4a}^{2+}$ (−0.31248 eV) and $\mathbf{4b}^{2+}$ (−0.31315 eV) were found to be much more accessible with respect to $[^{i}Pr_2NP(C(PPh_3)_2)]^{2+}$ (−0.28129 eV). Similar observations were reported when the amino substituents for bis(amino)phosphenium cations were replaced with Ph groups.[16] Thus, the reactivity (C−F activation) and the transient nature of these Ph-substituted phosphenium dications could be attributed to the low-lying LUMOs. Interestingly, according to natural bond order analysis, the partial charges of the central phosphorus for $\mathbf{4a}^{2+}$ (+1.02e) and $\mathbf{4b}^{2+}$ (+1.02e) were found to be less positive in comparison to $[^{i}Pr_2NP(C(PPh_3)_2)]^{2+}$ (+1.22e). This might be due to electron density overcompensation from the carbone substituent to the central phosphorus in $\mathbf{4a}^{2+}/\mathbf{4b}^{2+}$ in comparison to $[^{i}Pr_2NP(C(PPh_3)_2)]^{2+}$. Nevertheless, this suggested that Lewis acid type behavior of a compound might not necessarily be governed by its electron depletion at the central element as much as by the availability of its LUMO.

In summary, we have demonstrated that a couple of transient phosphenium dications, $[RP(C(PPh_3)_2]^{2+}$ (R = Ph, 4-FPh), were capable of activating α-phenyl C−F bonds. According to theoretical analysis, the greater accessibility of the LUMOs for these transient species in comparison to $[^{i}Pr_2NP(C(PPh_3)_2]^{2+}$ was the main reason for the observed reactivity. We are currently exploring the possibility of designing a catalytic cycle for C−F bond activation, and all results will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, details for the general experimental procedures, crystallographic techniques, and theoretical analysis. 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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