

# Tris(pentafluoroethyl)difluorophosphorane and *N*-Heterocyclic Carbenes: Adduct Formation and Frustrated Lewis Pair Reactivity

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The synthesis and characterization of Lewis acid/base adducts between tris(pentafluoroethyl)difluorophosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> and selected *N*-heterocyclic carbenes (NHCs) R<sub>2</sub>Im (1,3-diorganyl-imidazolin-2-ylidene) and phosphines are reported. For NHCs with small alkyl substituents at nitrogen (R=Me, *n*Pr, *i*Pr) the adducts NHC·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (**2a–h**) were isolated. The reaction with the sterically more demanding NHCs Dipp<sub>2</sub>Im (1,3-bis-(2,6-di-*iso*-propylphenyl)-imidazolin-2-ylidene) (**1i**) and *t*Bu<sub>2</sub>Im (1,3-di-*tert*-butyl-imidazolin-2-ylidene) (**1j**) afforded the *a*NHC adducts **3i** and **3j** (*a* denotes “abnormal” NHC coordination via a backbone carbon atom). The use of *t*BuMelm (1-*tert*-butyl-3-methyl-imidazolin-2-ylidene) (**1m**) led to partial decomposition of the NHC and formation of the salt [tBuMelm–H][Melm·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>] (**4m**). The phosphorane

PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> forms adducts with PMe<sub>3</sub> but does not react with PPh<sub>3</sub> or PCy<sub>3</sub>. The *mer-cis* isomer of literature-known Me<sub>3</sub>P·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (**5a**) was structurally characterized. Mixtures of the phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> and the sterically encumbered NHCs *t*Bu<sub>2</sub>Im, Dipp<sub>2</sub>Im, and Dipp<sub>2</sub>Im<sup>H<sub>2</sub></sup> (1,3-bis-(2,6-di-*iso*-propylphenyl)-imidazolidin-2-ylidene) (**1k**) showed properties of FLPs (Frustrated Lewis Pairs) as these mixtures were able to open the ring of THF (tetrahydrofuran) to yield NHC–(CH<sub>2</sub>)<sub>4</sub>O–PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> **6i–k**. Furthermore, the deprotonation of the weak C–H acids CH<sub>3</sub>CN, acetone, and ethyl acetate was achieved, which led to the formation of the corresponding imidazolium salts and the phosphates [PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>2</sub>CN)]<sup>–</sup> (**7**), [PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(OC(=CH<sub>2</sub>)CH<sub>3</sub>)]<sup>–</sup> (**8**) and [PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>2</sub>CO<sub>2</sub>Et)]<sup>–</sup> (**9**).

## Introduction

Although the first Frustrated Lewis Pair (FLP)<sup>[1]</sup> was described in 1942 by Brown *et al.* who observed no adduct formation between 2,6-lutidine and BMe<sub>3</sub>,<sup>[2]</sup> the term “Frustrated Lewis Pair” was introduced more than half a century later by Stephan.<sup>[3]</sup> FLPs consist of a Lewis base and a Lewis acid, which do not form a traditional Lewis acid/base adduct, but the presence of both reactive centers leads to a synergistic effect which enables reactions of molecules which are inert in the absence of one of these components. In their seminal 2006

paper,<sup>[3]</sup> Stephan and co-workers observed the addition of H<sub>2</sub> to the intramolecular FLP (C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sub>2</sub>P(C<sub>6</sub>F<sub>4</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> with heterolytic cleavage of the hydrogen-hydrogen bond. As the product (C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sub>2</sub>PH(C<sub>6</sub>F<sub>4</sub>)BH(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> can be reconverted into the starting material at 80 °C the H<sub>2</sub>-addition is reversible.<sup>[3]</sup> Based on this observation, further FLPs were developed and subsequently employed as catalysts in hydrogenation reactions, which were previously restricted to transition metal catalysts.<sup>[4]</sup> In the following years, many other small molecules like CO,<sup>[5]</sup> CO<sub>2</sub>,<sup>[6]</sup> N<sub>2</sub>O,<sup>[6d,7]</sup> SO<sub>2</sub>,<sup>[8]</sup> azides,<sup>[9]</sup> or molecules with weakly acidic C–H bonds<sup>[10]</sup> were activated using FLPs. As a consequence, FLPs have attracted also attention as catalysts for various organic transformations.<sup>[11]</sup> Mixtures of tris(pentafluorophenyl)borane B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and bulky *N*-heterocyclic carbenes (NHCs) like *t*Bu<sub>2</sub>Im (1,3-di-*tert*-butyl-imidazolin-2-ylidene) and Dipp<sub>2</sub>Im (1,3-bis-(2,6-di-*iso*-propylphenyl)-imidazolin-2-ylidene) are important examples for FLPs that activate H<sub>2</sub>,<sup>[12]</sup> P<sub>4</sub>,<sup>[13]</sup> S<sub>8</sub>, Se,<sup>[14]</sup> or tetrahydrofuran (THF).<sup>[15]</sup>

A limited number of Lewis acid/base adducts of phosphoranes PR<sub>5</sub> and NHCs were reported in the literature, and only very few examples of FLP behavior with PR<sub>5</sub>/NHC systems were given, so far.<sup>[16]</sup> The first synthesized adduct of an electrophilic phosphorane with an NHC (*trans*-Mes<sub>2</sub>Im–PF<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>); Mes<sub>2</sub>Im = 1,3-bis-(2,4,6-trimethylphenyl)-imidazolin-2-ylidene) was reported by Arduengo and co-workers already in 1997.<sup>[17]</sup> A few years later, the same group described adduct formation between Mes<sub>2</sub>Im<sup>Cl</sup> (4,5-dichloro-1,3-bis-(2,4,6-trimethylphenyl)-imidazolin-2-ylidene) and PF<sub>5</sub> (Scheme 1, top).<sup>[18]</sup> Another synthetic route to form NHC·PF<sub>5</sub> adducts is the oxidative

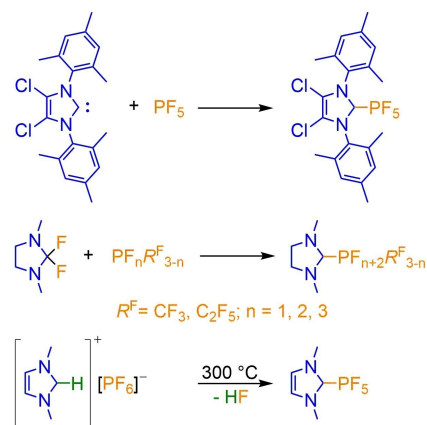
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Scheme 1. Synthetic routes to NHC-phosphorane adducts.<sup>[16a,19a,20a,24]</sup>

addition of a difluoroorganyl to  $\text{PF}_3$  (Scheme 1, middle).<sup>[16a,19]</sup> A further entry towards such adducts is the thermolysis of imidazolium hexafluorophosphate ionic liquids, e.g. 1,3-dimethyl-1*H*-imidazolium hexafluorophosphate (Scheme 1, bottom).<sup>[20]</sup> The adducts  $\text{Me}_2\text{Im} \cdot \text{PF}_5$  ( $\text{Me}_2\text{Im} = 1,3\text{-dimethyl-imidazolin-2-ylidene}$ ) and *trans*- $\text{Me}_2\text{Im} \cdot \text{PF}_4\text{Ph}$  have been recently employed in  $^{18}\text{F}$  PET imaging.<sup>[21]</sup>

The reaction between  $\text{PF}_5$  and tertiary phosphines  $\text{PR}_3$ , to yield the adducts  $\text{R}_3\text{P} \cdot \text{PF}_5$  ( $\text{R} = \text{Me}, \text{Ph}$ ), was reported by Reid and co-workers.<sup>[22]</sup> In contrast, the use of diphosphines  $o\text{-C}_6\text{H}_4(\text{PR}_2)_2$  resulted in the formation of the phosphonium phosphates  $[\text{PF}_4(\text{C}_6\text{H}_4(\text{PR}_2)_2)]^+[\text{PF}_6]^-$  ( $\text{R} = \text{Me}, \text{Ph}$ ).<sup>[22]</sup> Perfluoroalkyl-phosphoranes of the general formula  $\text{PF}_n\text{R}^{\text{F}}_{3-n}$  ( $\text{R}^{\text{F}} = \text{perfluoroalkyl}, n = 1\text{--}3$ ) are stronger *Lewis* acids than  $\text{PF}_5$  and provide an increased steric shielding at the central phosphorus atom.<sup>[23]</sup> A few NHC adducts of the perfluoroalkylphosphoranes  $\text{PF}_4\text{R}^{\text{F}}$  ( $\text{R}^{\text{F}} = \text{CF}_3, \text{C}_2\text{F}_5$ ) and  $\text{PF}_3(\text{C}_2\text{F}_5)_2$  have been obtained from the perfluoroalkylphosphines  $\text{PX}_{3-n}\text{R}^{\text{F}}_n$  ( $\text{X} = \text{halogen}, n = 1, 2$ ) and a difluoroorganyl precursor (Scheme 1, middle).<sup>[24]</sup> In contrast, with tris(perfluoroalkyl)difluorophosphoranes, NHC adducts are unknown, whereas adducts with other neutral *Lewis* bases have been reported, e.g. with  $\text{PMe}_3$ .<sup>[25]</sup> Tris(pentafluoroethyl)difluorophosphorane  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  is a liquid at r.t. (boiling point: 91–92 °C) that is stable under inert conditions.<sup>[26]</sup> Thus, it can be handled much more easily than the gaseous phosphorus pentafluoride.  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  is a strong *Lewis* acid with a fluoride ion affinity (FIA) of 405.4  $\text{kJ mol}^{-1}$ , which is ca. 10  $\text{kJ mol}^{-1}$  higher than that of  $\text{PF}_5$ .<sup>[27]</sup> Tris(perfluoroalkyl)difluorophosphorane  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  is produced on industrial scale *via* electrochemical fluorination (ECF) of triethylphosphine in anhydrous  $\text{HF}$ <sup>[26,28]</sup> according to the Simons process.<sup>[29]</sup> In contact with water or moisture it undergoes slow hydrolysis. It was applied as *Lewis* acidic catalyst in Diels-Alder reactions,<sup>[30]</sup> and Michael additions<sup>[31]</sup> or in transfer hydrogenations.<sup>[32]</sup> As a strong *Lewis* acid,  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  reacts with nucleophiles such as  $\text{H}^-$ ,<sup>[33]</sup>  $\text{HO}^-$ ,  $\text{CH}_3\text{C}(=\text{O})\text{O}^-$ ,<sup>[34]</sup>  $\text{F}^-$ ,<sup>[23,28]</sup> or  $\text{Cl}^-$ .<sup>[35]</sup> The reaction with a fluoride source resulted in the formation of the corresponding fluorophosphate anion  $[\text{PF}_3(\text{C}_2\text{F}_5)_3]^-$  (**FAP** anion), which has been found to be a highly valuable building block for materials applications, e.g. for preparation of the

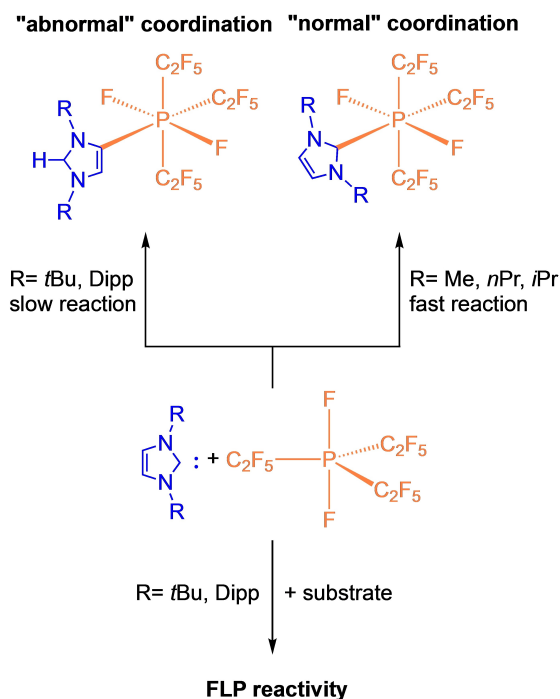
conducting salt  $\text{Li}[\text{PF}_3(\text{C}_2\text{F}_5)_3]$  (**LiFAP**)<sup>[36]</sup> and room temperature ionic liquids (RTILs).<sup>[37]</sup> Ignat'ev, Hoge, and co-workers reported the use of  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  as fluoride acceptor for several main group compounds forming cations with the **FAP** counter-anion. For instance, the fluoride transfer from  $\text{Ph}_3\text{PF}_2$  and  $\text{Ph}_3\text{BiF}_2$  to the phosphorane yielded  $[\text{Ph}_3\text{PF}]\text{FAP}$  and  $[\text{Ph}_3\text{BiF}]\text{FAP}$ ,<sup>[38]</sup> respectively, and the reaction with  $\text{Et}_2\text{N}-\text{CF}_2-\text{CHF}-\text{CF}_3$  (Ishikawa's reagent) led to the isolation of the iminium phosphate  $[\text{Et}_2\text{N}=\text{CF}-\text{CHF}-\text{CF}_3]\text{FAP}$ .<sup>[39]</sup> Neutral  $(\text{C}_2\text{F}_5)_3\text{GeF}$  was synthesized by fluoride transfer from  $[(\text{C}_2\text{F}_5)_3\text{GeF}_2]^-$  salts to  $\text{PF}_2(\text{C}_2\text{F}_5)_3$ .<sup>[40]</sup> Furthermore, Ignat'ev, Hoge, and co-workers observed FLP-like behavior with the sterically demanding phosphorane  $\text{PF}_2(\text{C}_2\text{F}_5)_3$ , that in conjunction with triethylamine activates acetonitrile to give the ammonium salt  $[\text{Et}_3\text{NH}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CN})]$ .<sup>[41]</sup> In the absence of acetonitrile, a complex reaction sequence of  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  with  $\text{Et}_3\text{N}$  to finally yield  $\text{PF}_2(\text{C}_2\text{F}_5)_2(\text{C}_2\text{H}_5\text{NET}_2)$  was observed.<sup>[42]</sup>

In the last years, some of us reported on several occasions on the reactivity of NHCs and related molecules<sup>[16c,43]</sup> with main group element hydrides<sup>[44]</sup> and main group element *Lewis* acids.<sup>[45]</sup> Very recently, we established the *Lewis* acid tris(pentafluoroethyl)difluorophosphorane  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  as fluoride acceptor in transition metal chemistry, which led to the convenient synthesis of cationic transition metal complexes with the **FAP** counterion as a weakly coordinating anion.<sup>[27]</sup> Fluoride abstraction using  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  was achieved for various previously described NHC transition metal complexes such as *trans*- $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{F})(\text{Ar}^{\text{F}})]$  ( $\text{iPr}_2\text{Im} = 1,3\text{-di-iso-propyl-imidazolin-2-ylidene}$ ;  $\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5$ ;  $4\text{-CF}_3\text{-C}_6\text{F}_4$ ;  $4\text{-C}_6\text{F}_5\text{-C}_6\text{F}_4$ )<sup>[46]</sup> and  $[(\text{Dipp}_2\text{Im})\text{CuF}]$ .<sup>[47]</sup> These results have stimulated us to study the reactivity of the NHCs employed for complex stabilization towards the *Lewis*-acidic phosphorane (Scheme 2).

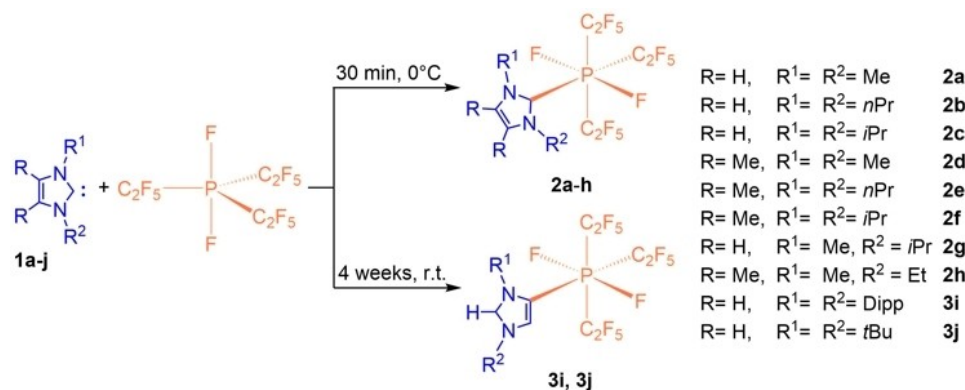
Herein we report on the synthesis, structures and spectroscopic data of a series of *Lewis* acid/base adducts of selected NHCs and the phosphorane  $\text{PF}_2(\text{C}_2\text{F}_5)_3$ . We demonstrate that simple adducts  $\text{NHC} \cdot \text{PF}_2(\text{C}_2\text{F}_5)_3$  are formed for NHCs with small alkyl nitrogen substituents ( $\text{R} = \text{Me}, n\text{Pr}, i\text{Pr}$ , Scheme 2), whereas sterically more demanding NHCs such as  $\text{Dipp}_2\text{Im}$  and  $t\text{Bu}_2\text{Im}$  afford *a*NHC adducts, in which the NHC binds in an "abnormal" coordination mode *via* an NHC backbone carbon atom to phosphorus (Scheme 2). Furthermore, we demonstrate that mixtures of the phosphorane  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  and the sterically encumbered NHCs  $\text{Dipp}_2\text{Im}$ ,  $t\text{Bu}_2\text{Im}$ , and  $\text{Dipp}_2\text{Im}^{\text{H}2}$  (1,3-bis-(2,6-di-*iso*-propylphenyl)-imidazolidin-2-ylidene) reveal FLP reactivity (Scheme 2). In addition, we present selected results on a parallel study on reactions of small ( $\text{PMe}_3$ ) and sterically more demanding phosphines ( $\text{PPh}_3$  and  $\text{PCy}_3$ ) with  $\text{PF}_2(\text{C}_2\text{F}_5)_3$ .

## Results and Discussion

**Adduct formation of  $\text{NHC} \cdot \text{PF}_2(\text{C}_2\text{F}_5)_3$ .** We started our investigations by reacting tris(pentafluoroethyl)difluorophosphorane with selected *N*-heterocyclic carbenes. The corresponding adducts  $\text{NHC} \cdot \text{PF}_2(\text{C}_2\text{F}_5)_3$  **2a-h** were isolated upon reaction of  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  in diethyl ether with  $\text{Me}_2\text{Im}$  (**1a**),  $n\text{Pr}_2\text{Im}$  (1,3-di-*n*-propyl-imidazolin-2-ylidene) (**1b**),  $i\text{Pr}_2\text{Im}$  (**1c**),  $\text{Me}_2\text{Im}^{\text{Me}}$  (1,3,4,5-



Scheme 2. Reactivity of NHCs towards  $\text{PF}_2(\text{C}_2\text{F}_5)_3$ .



Scheme 3. Synthesis of NHC· $\text{PF}_2(\text{C}_2\text{F}_5)_3$  adducts.

Table 1. Chemical shifts [ppm] and P–F coupling constants [Hz] of the adducts **2a–h**,<sup>[a]</sup> the “abnormal” adducts **3i**<sup>[b]</sup> and **3j**,<sup>[b]</sup> and the imidazolium salt **4m**<sup>[a]</sup> at r.t.

	$\delta(^{31}\text{P})$	$\text{CF}_3$	$\delta(^{19}\text{F})$ $\text{PF}_2$	$\text{CF}_2$	$\delta(^{13}\text{C})$ N–C–N	$^1J_{\text{P-F}}$	$^2J_{\text{P-F}}$
<b>2a</b>	–142.5	–78.4/–80.0	–92.5	–114.5/–116.0	155.5	899	103/102
<b>2b</b>	–140.0	–78.4/–79.4	–90.8	–113.8/–114.4	156.0	910	105/103
<b>2c</b>	–138.4	–77.7/–78.0	–88.5	–111.0/–114.2	155.4	926	106/102
<b>2d</b>	–142.3	–78.5/–79.9	–90.7	–114.4/–115.7	154.5	908	105/102
<b>2e</b>	–139.7	–77.8/–78.2	–90.5	–111.0/–114.2	154.4	920	105/103
<b>2f</b>	–137.0	–77.3/–77.9	–85.3	–110.2/–113.6	156.8	942	109/99
<b>2g</b>	–140.2	–78.4/–79.5	–84.7/–98.4	–111.9/–114.5/–116.2	155.5	914/898	108/102
<b>2h</b>	–141.1	–78.6/–79.4	–84.0/–99.0	–110.5/–114.4/–116.3	154.1	915/900	103/101
<b>3i</b>	–146.7	–78.5/–79.7	–91.3/–101.9	–104.7/–114.3/–117.5	131.3	877/844	107/99
<b>3j</b>	–146.0	–78.8/–80.0	–88.1/–90.7	–101.0/–115.3/–118.7	126.3	875/849	110/100
<b>4m</b>	–145.7	–78.1/–78.4	–97.6/–98.8	–113.3/–113.7/–117.0	154.9	857/846	103/98

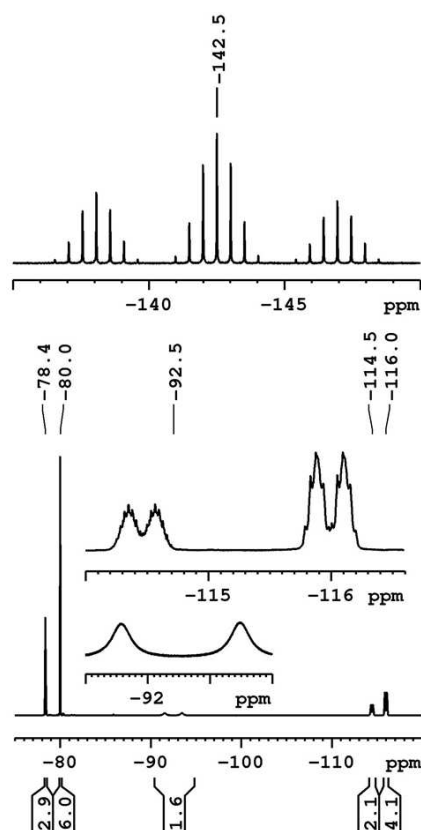
[a] in  $\text{C}_6\text{D}_6$ . [b] in  $\text{CD}_2\text{Cl}_2$ .

tetramethyl-imidazolin-2-ylidene) (**1d**),  $n\text{Pr}_2\text{Im}^{\text{Me}}$  (1,3-di-*n*-propyl-4,5-dimethyl-imidazolin-2-ylidene) (**1e**),  $i\text{Pr}_2\text{Im}^{\text{Me}}$  (1,3-di-*iso*-propyl-4,5-dimethyl-imidazolin-2-ylidene) (**1f**),  $i\text{PrMeIm}$  (1-*iso*-propyl-3-methyl-imidazolin-2-ylidene) (**1g**), and  $\text{EtMeIm}^{\text{Me}}$  (1-ethyl-3,4,5-trimethyl-imidazolin-2-ylidene) (**1h**) in 72–95% yield (Scheme 3). No reaction was observed between the phosphorane and the bulkier carbenes  $\text{Dipp}_2\text{Im}$  (**1i**),  $t\text{Bu}_2\text{Im}$  (**1j**),  $\text{Dipp}_2\text{Im}^{\text{H}^2}$  (**1k**) and  $\text{cAAC}^{\text{Me}}$  (1-(2,6-di-*iso*-propylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene) using the same conditions (30 min at 0°C).

Adduct formation is evident from NMR spectroscopy, most characteristically from  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra of the adducts. Whereas the parent phosphorane gives rise to a triplet of septets at ca. –50 ppm in the  $^{31}\text{P}$  NMR spectrum, the signals of the adducts **2a–h** were detected in the region between –138.4 and –142.5 ppm (Table 1) in  $\text{C}_6\text{D}_6$  solution. Due to the additional substituent at phosphorus and conversion of five to six coordination, the resonances of the adducts in the  $^{31}\text{P}$  NMR spectra are shifted approximately 90 ppm towards higher field in comparison to the starting material  $\text{PF}_2(\text{C}_2\text{F}_5)_3$ . No trend can be observed between the calculated  $\text{pK}_\text{a}$  values<sup>[48]</sup> of the corresponding imidazolium salts, i.e. the conjugate acids of the carbenes **1a**, **1c**, **1d**, and **1f** and the  $^{31}\text{P}$  NMR resonances of the adducts **2a**, **2c**, **2d**, and **2f**. In the  $^{19}\text{F}$  NMR spectrum of trigonal bipyramidal  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  (fluorine substituents in axial positions)

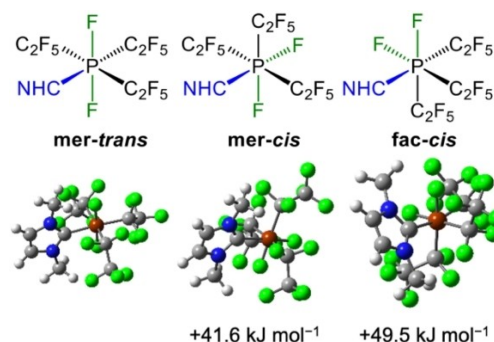
one multiplet is observed for the CF<sub>3</sub> and CF<sub>2</sub> groups, as all pentafluoroethyl substituents are chemically equivalent.<sup>[23]</sup> Equivalency of the C<sub>2</sub>F<sub>5</sub> groups is lost on coordination of an additional substituent at phosphorus in the adducts **2a–f** and thus the CF<sub>3</sub> and CF<sub>2</sub> groups give rise to two sets of resonances in the <sup>19</sup>F NMR spectra of these compounds.

For example, in the <sup>19</sup>F NMR spectrum of Me<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (**2a**) the multiplets of the CF<sub>3</sub> groups were observed at –78.4 and –80.0 ppm with 1:2 integrations of the resonances (Figure 1, bottom). The fluorine atoms attached to phosphorus were detected as doublet of multiplets at –92.5 ppm with a <sup>1</sup>J<sub>P-F</sub> coupling constant of 899 Hz. The doublets of multiplets of the CF<sub>2</sub> groups appeared at –114.5 (<sup>2</sup>J<sub>P-F</sub> = 102 Hz) and –116.0 ppm (<sup>2</sup>J<sub>P-F</sub> = 103 Hz) with intensities of 2 and 4, respectively. The origin of the coupling was confirmed by <sup>19</sup>F{<sup>31</sup>P} NMR spectroscopy. The resonances of the carbenic carbon atoms in the <sup>13</sup>C {<sup>1</sup>H} NMR spectra of **2a–h** were not observed due to coupling with phosphorus and fluorine. However, in the <sup>13</sup>C{<sup>1</sup>H},<sup>1</sup>H HMBC spectra coupling of the carbenic carbon atoms to the backbone protons (**2a–c**) or the protons of the substituents at nitrogen (**2d–h**) was observed which allowed evaluation of the chemical shifts. As a consequence of the bonding to phosphorus, the resonances of the carbenic carbon atoms are shifted towards higher field compared to the free NHCs and were detected in the area between 154.1 and 156.8 ppm (Table 1).

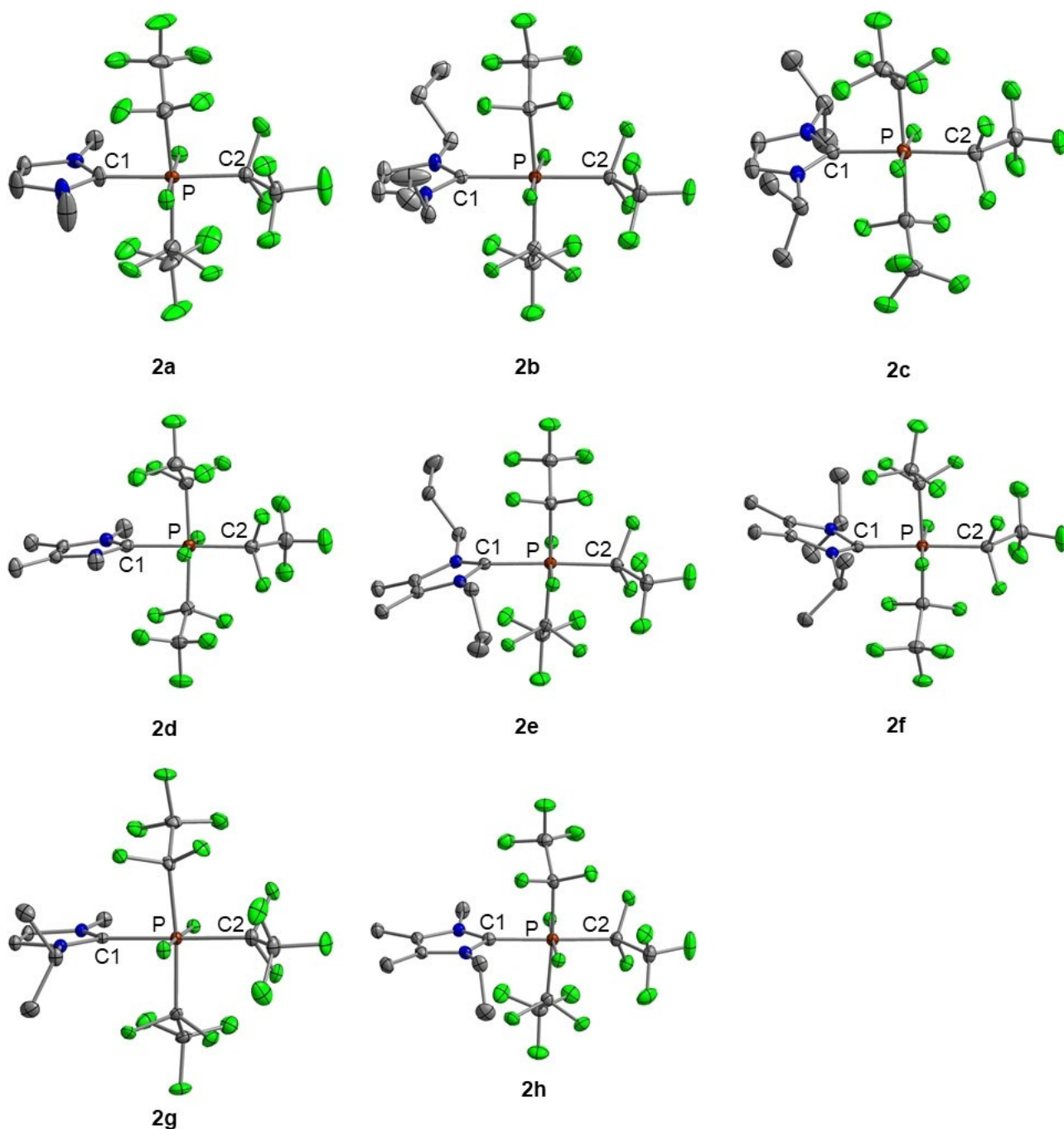


**Figure 1.** <sup>31</sup>P NMR spectrum (top) and <sup>19</sup>F NMR spectrum (bottom) of Me<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (**2a**) in C<sub>6</sub>D<sub>6</sub>.

Three stereoisomers for the NHC·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> adducts are conceivable (Figure 2), as was depicted for the related phosphates [PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>X]<sup>–</sup> (X=OH, OPh, OEt, OAc).<sup>[49]</sup> These isomers differ in the positioning of the three C<sub>2</sub>F<sub>5</sub> substituents (*fac* vs. *mer*) and the fluoride substituents with respect to each other (*cis* vs. *trans*) leading to the three isomers *mer-trans*-NHC·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>, *mer-cis*-NHC·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>, and *fac-cis*-NHC·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>. The *mer-cis* isomer should be easily distinguished by <sup>19</sup>F NMR spectroscopy, because the fluorine substituents of this isomer are chemically inequivalent and aligned *trans* to one of the pentafluoroethyl groups and to the NHC ligand, respectively (Figure 2). As a consequence, two separate resonances are expected for the phosphorus bound fluorine atoms of this isomer. For the *fac-cis* and *mer-trans* isomer only one signal should be observed for these chemically equivalent fluorine atoms, at different frequencies for each isomer. For the adducts **2a–h** the formation of a mixture of different isomers can be excluded according to <sup>31</sup>P NMR spectroscopy, as only one signal was observed. In addition, the <sup>19</sup>F NMR spectra of **2a–f** reveal only one resonance for the fluorine atoms bonded to phosphorus. Thus, the presence of the *mer-cis* isomer can be ruled out, but a differentiation between the *fac-cis* and *mer-trans* isomer is not possible. In the adducts **2g** and **2h** the asymmetry of the NHC is reflected in the <sup>19</sup>F NMR spectra and two separate resonances for the fluorine substituents at phosphorus were detected (*vide infra*). Crystal structure analysis of the compounds **2a–h** clearly demonstrates that these compounds adopt the *mer-trans* configuration in the solid-state (Figure 3). This is also in agreement with quantum chemical calculations performed for the stereoisomers of Me<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (**2a**). The *mer-trans* isomer is the most stable isomer and the *mer-cis* (+41.6 kJ mol<sup>–1</sup>) and *fac-cis* (+49.5 kJ mol<sup>–1</sup>) isomers lie at significantly higher energies (Figure 2). However, the *mer-trans* isomer of the “abnormal” adduct *a*Me<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> was calculated to be 8.2 kJ mol<sup>–1</sup> lower in energy than the *mer-trans* isomer with normal coordination of the carbene. Thus, adduct **2a** should be a kinetically controlled product formed at lower temperatures, whereas the “abnormal” adduct *a*Me<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> is the thermodynamically more stable isomer. However, heating a



**Figure 2.** Possible stereoisomers of the NHC·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> adducts and their relative energies (exemplified at Me<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>) calculated at the DFT/PBE0/def2-TZVP-level of theory.



**Figure 3.** Molecular structures of **2a** (top, left), **2b** (top, middle), **2c** (top, right), **2d** (middle, left), **2e** (middle, middle), **2f** (middle, right), **2g** (bottom, left) and **2h** (bottom, right) in the solid-state (ellipsoids set at the 50% probability level). All hydrogen atoms are omitted for clarity.

solution of **2a** in toluene to 110 °C overnight did not result in isomerization of the adduct.

The same result was obtained on calculation of the energies of the isomers of the adduct **3i**. The “abnormal” *mer-trans* isomer lies at lower energy compared to the *fac-cis* (+4.9 kJ mol<sup>-1</sup>) and the *mer-cis* (+57.9 kJ mol<sup>-1</sup>) isomer of this adduct. In addition, the *mer-trans* isomer with “normal” carbene coordination is 87.5 kJ mol<sup>-1</sup> higher in energy than the “abnormal” coordinated isomer. The results of the quantum chemical calculations are confirmed by the solid-state structure

of compound **3i** which adopts the *mer-trans* geometry with an “abnormal” coordination to phosphorus (*vide infra*).

The adducts crystallize in the monoclinic space groups *P2<sub>1</sub>* (**2b–d**) and *P2<sub>1</sub>/c* (**2e**, **2f**, **2h**) or in the orthorhombic space group *Pnma* (**2a**, **2g**), respectively, with one molecule in the asymmetric unit for all adducts but **2c**, which has two independent molecules in the asymmetric unit. The phosphorus atoms in the adducts are distorted octahedrally surrounded by two fluorine atoms, three C<sub>2</sub>F<sub>5</sub> groups and the corresponding

NHC. All solid-state structures show the *mer-trans* isomer, in which the NHC substituent lies in *trans* position to one of the  $C_2F_5$  groups and the fluorine atoms at phosphorus are mutual *trans*. This is in agreement with the  $^{19}F$  NMR spectroscopic data presented above. The distances between the carbene carbon atoms and the phosphorus atoms range from 1.953(1) to 1.989(1) Å and are in most cases slightly shorter than the corresponding C2–P bond lengths (1.964(1) to 1.995(2) Å) to the pentafluoroethyl substituent in *trans* position to the NHC. The C1–P distances are larger than those observed for  $Me_2Im \cdot PF_5$  (1.874(2) Å)<sup>[20a]</sup> or  $Mes_2Im^Cl \cdot PF_5$  (1.898(3) Å),<sup>[18]</sup> which is most probably a consequence of the higher steric demand of the pentafluoroethyl groups in comparison to the fluorine substituents of the  $PF_5$  adducts. The NHCs and the opposing  $C_2F_5$  groups are nearly linearly aligned with C1–P–C2 angles varying from 173.77(6)° to 178.63(14)°. Table 2 summarizes the most important metric parameters of the adducts. NHC coordination to the phosphorane phosphorus atom in **2a–c** can also be evidenced by  $^1H$  NMR spectroscopy. The resonances of the olefinic protons of the carbene moieties of **2a–c** were observed as doublets with  $^4J_{P-H}$  coupling constants of approximately 2 Hz. The origin of the coupling was confirmed by the corresponding  $^1H\{^{31}P\}$  NMR spectra, in which these signals were detected as singlets. Furthermore, in the  $^1H$  NMR spectrum of **2a** coupling between the protons of the methyl groups and the fluorine atoms at phosphorus was observed (Figure S1 of the SI).

In the case of non-symmetric carbenes with different substituents at the nitrogen atoms the asymmetry of the NHC is reflected in the  $^{19}F$  NMR spectra of the adducts **2g** and **2h**. In the solid-state structures of **2a–h** (Figure 3) the fluorine substituents at phosphorus face in the same direction as the substituents at the nitrogen atoms. Consequently, different alkyl groups at the latter result in diastereotopic fluorine atoms bonded to phosphorus as was evident from the  $^{19}F$  NMR spectra of **2g** and **2h**. For **2g** these fluorine atoms were detected as doublet of doublets of multiplets at –84.7 ( $^1J_{P-F}$  = 898 Hz) and –98.4 ppm ( $^1J_{P-F}$  = 914 Hz), respectively, with a  $^2J_{F-F}$  coupling constant of 119 Hz. The signal of the  $CF_3$  group *trans* to the carbene carbon atom was observed at –78.4 ppm (Figure 4 and Figure S27 of the SI). The two remaining  $CF_3$  groups give rise to a multiplet at –79.5 ppm. The  $CF_2$  groups were detected at –111.9, –114.5 and –116.2 ppm, respectively. From the  $^{19}F\{^{31}P\}$

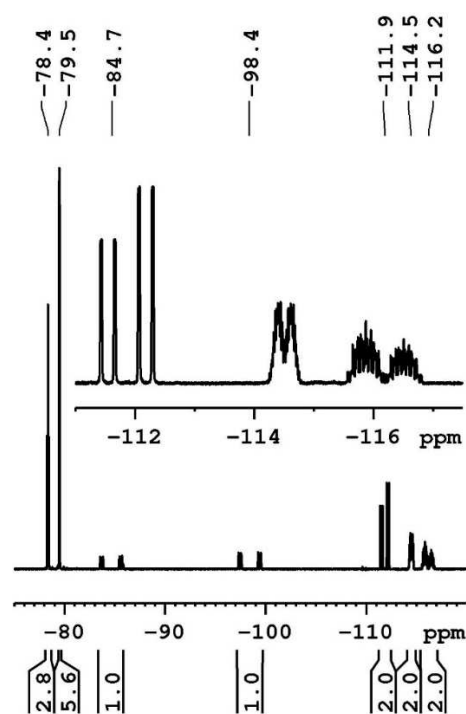


Figure 4.  $^{19}F$  NMR spectrum of  $iPrMelm \cdot PF_2(C_2F_5)_3$  (**2g**) in  $C_6D_6$  at r.t.

NMR spectrum it is evident that the doublet splitting of the multiplets at –116.2 ppm with a coupling constant of 299 Hz does not arise from coupling with phosphorus. However, the same coupling constant was observed for the doublet of doublets of doublets at –111.9 ppm, which implies F–F coupling. In addition, these two resonances show a roof effect towards each other (Figure 4). Judged by the coupling constant of 299 Hz, this is most probably coupling of the geminal diastereotopic fluorine atoms of the  $CF_2$  groups, which belong to the pentafluoroethyl groups in mutual *trans* position. Consequently, the doublet of multiplets ( $^2J_{P-F}$  = 102 Hz) observed at –114.5 ppm is caused by the remaining  $CF_2$  group. The same splitting of signals was also observed in the  $^{19}F$  NMR spectrum of compound **2h** (Figure S31 of the SI). The  $^{19}F$  and  $^{31}P$  NMR spectra of mixtures of the NHCs  $Dipp_2Im$  (**1i**) or  $tBu_2Im$  (**1j**) and the phosphorane  $PF_2(C_2F_5)_3$  provided no evidence for a reaction within 30 min, which was in stark contrast to the formation of the normal adducts **2a–h** that was completed after 30 min according to NMR spectroscopy. The reaction was continued, and the backbone coordinated “abnormal” adducts  $\alpha NHC \cdot PF_2(C_2F_5)_3$  (NHC =  $Dipp_2Im$  **3i**;  $tBu_2Im$  **3j**) precipitated from etheric solutions of these mixtures over a period of several weeks (Scheme 3). In contrast to the adducts **2a–h**, **3i**, and **3j** are sparingly soluble in benzene. Due to the asymmetry of the NHC resulting the “abnormal” coordination in **3i** and **3j** two sets of resonances were observed in the  $^1H$  NMR spectra for the substituents at the nitrogen atoms (Figure S33 and S37 of the SI). The  $^{19}F$  NMR spectra of **3i** and **3j** are similar to those obtained for the adducts **2g** and **2h** showing two separate resonances for the diastereotopic fluorine substituents at

Table 2. Selected bond lengths [Å] and angles [°] of the NHC· $PF_2(C_2F_5)_3$  adducts **2a–h**, and the “abnormal” adducts **3i**, **3j** and **3l**.

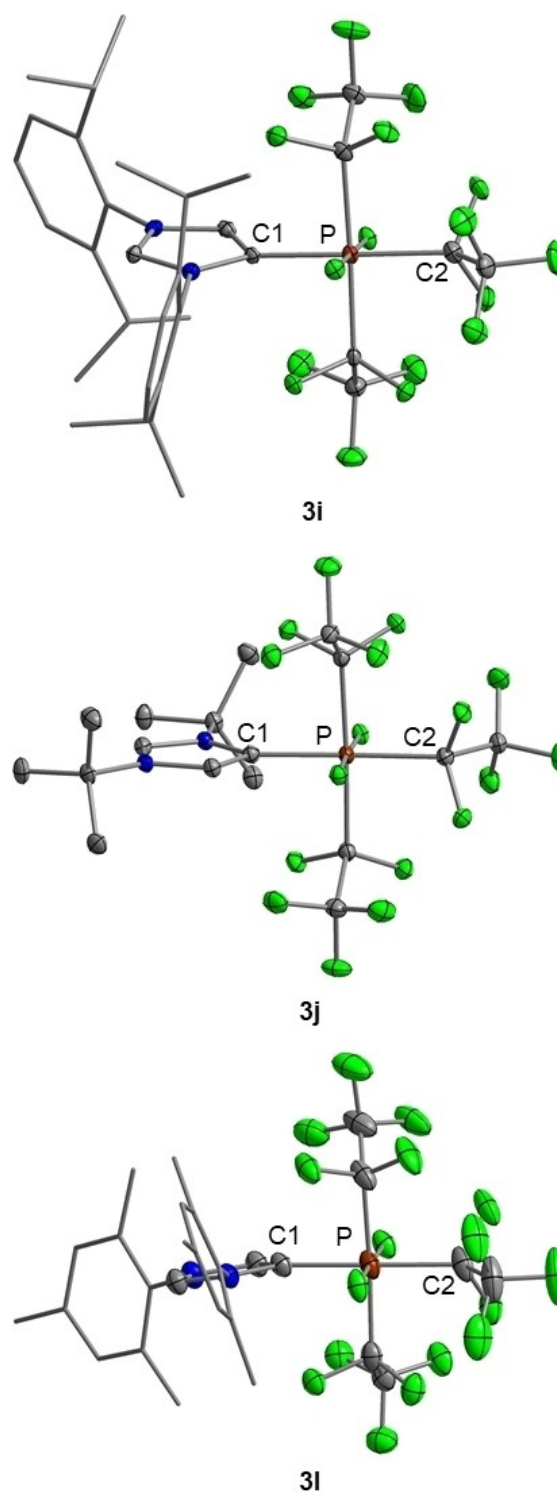
	C1–P	C2–P	C1–P–C2
<b>2a</b>	1.953(1)	1.964(1)	175.10(5)
<b>2b</b>	1.984(2)	1.988(2)	176.40(12)
<b>2c</b>	1.977(2)	1.975(2)	177.91(7)
<b>2d</b>	1.961(3)	1.985(3)	178.63(14)
<b>2e</b>	1.970(1)	1.952(1)	177.97(5)
<b>2f</b>	1.989(1)	1.995(1)	173.77(6)
<b>2g</b>	1.970(2)	1.972(2)	177.91(7)
<b>2h</b>	1.962(1)	1.980(1)	177.52(6)
<b>3i</b>	1.914(2)	1.984(2)	176.87(11)
<b>3j</b>	1.911(1)	1.992(1)	177.03(6)
<b>3l</b>	1.906(2)	1.985(3)	177.40(10)

phosphorus (Figure S35 and S39 of the SI). The  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectroscopic data of **3i** and **3j** are summarized in Table 1. The reaction of  $\text{Mes}_2\text{Im}$  (**1l**) and  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  did not result in a clean adduct formation. Instead, a product mixture was obtained according to  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectroscopy. One of the species detected is the  $[\text{PF}_3(\text{C}_2\text{F}_5)_3]^-$  (**FAP**) anion, as the resonances of this anion were detected in the  $^{19}\text{F}$  NMR spectrum of the crude product. The group of Arduengo also observed formation of the  $[\text{PF}_6]^-$  anion in the course of the investigation of the reaction of  $\text{Mes}_2\text{Im}$  and  $\text{PF}_5$ .<sup>[18]</sup>

Crystals suitable for X-ray diffraction were obtained for **3i**, **3j**, and for  $a\text{Mes}_2\text{Im} \cdot \text{PF}_2(\text{C}_2\text{F}_5)_3$  (**3l**) (Figure 5). The  $a\text{NHC}$  adducts crystallize in the triclinic space group  $P1$  (**3i**) and the orthorhombic space groups  $Pbca$  (**3j**) and  $Pna2_1$  (**3l**), respectively, with one molecule in the asymmetric unit. The fluorine atoms at phosphorus are in mutual *trans* position in analogy to the adducts **2a–h**. In contrast to the NHC substituents in **2a–h**, the bulkier carbenes in **3i**, **3j**, and **3l** are bound to phosphorus *via* the olefinic backbone. This “abnormal” binding mode is a common feature of adducts of these NHCs.<sup>[50]</sup> The C1–P distances (**3i**: 1.914(2) Å; **3j**: 1.911(1) Å; **3l**: 1.906(2) Å) are the same within standard deviation (3  $\sigma$ ) and shorter than the C–P distances from the carbene carbon atoms to phosphorus in **2a–h** (1.953(1) to 1.984(2) Å). The C2–P bond lengths to the *trans*- $\text{C}_2\text{F}_5$  substituent are independent of the NHC coordination mode as these distances (**3i**: 1.984(2) Å; **3j**: 1.992(1) Å; **3l**: 1.985(3) Å) are in the range of those observed in the adducts **2a–h** (1.964(10) to 1.995(2) Å). The C1–P–C2 angles in **3i**, **3j** and **3l** are nearly  $180^\circ$  and thus very similar to the corresponding angles in **2a–h** (Table 2).

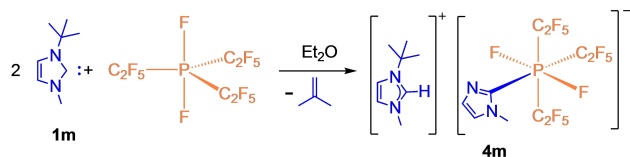
The reaction of *t*BuMelm (1-*tert*-butyl-3-methyl-imidazolin-2-ylidene) (**1m**) with  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  in  $\text{Et}_2\text{O}$  did not result in formation of an adduct like **2a–h** or **3i**, **3j**. Instead, the ionic compound  $[\text{tBuMelm-H}][\text{Melm} \cdot \text{PF}_2(\text{C}_2\text{F}_5)_3]$  (**4m**) (Scheme 4) was isolated after 30 min reaction time at  $0^\circ\text{C}$ . The formation of **4m** can be rationalized by elimination of a *tert*-butyl cation from an initial adduct  $\text{tBuMelm} \cdot \text{PF}_2(\text{C}_2\text{F}_5)_3$  and subsequent deprotonation of the *tert*-butyl cation with *t*BuMelm to give  $[\text{tBuMelm-H}][\text{Melm} \cdot \text{PF}_2(\text{C}_2\text{F}_5)_3]$  (**4m**) with release of isobutene. The degradation of a carbene with dissociation of one of the substituents at nitrogen was also reported earlier for the reaction of NHCs with transition metal complexes.<sup>[51]</sup>

The  $^1\text{H}$  NMR spectrum of **4m** shows two sets of resonances for all protons but the *tert*-butyl group, which confirms the loss of isobutene from one equivalent of the carbene. Additionally, a broad signal for the imidazolium proton was detected at 8.68 ppm (Figure S42 of the SI). Furthermore, an  $^1\text{H}$  NMR experiment proved the formation of isobutene *via* the typical set of resonances, a septet at 4.75 ppm and a triplet at 1.60 ppm (Figure S41 of the SI). The  $^{19}\text{F}$  NMR spectrum of **4m** is similar to those of the adducts **2g** and **2h** that also contain unsymmetrically substituted NHC ligands (Figure S44 of the SI). The  $^{31}\text{P}$  NMR spectrum of **4m** shows a triplet of multiplets at  $-145.7$  ppm, which is at slightly higher field compared to the signals of the adducts **2a–h** (Table 1). In the ESI-(+)MS (electrospray ionization mass spectrometry) spectrum of **4m** the imidazolium cation was observed at  $m/z^+ = 139.12$  and in the



**Figure 5.** Molecular structures of the  $a\text{NHC}$  adducts **3i** (top), **3j** (middle), and **3l** in the solid-state (ellipsoids set at the 50% probability level; Me, *i*Pr and phenyl groups are shown as wire-and-stick-model). All hydrogen atoms and a solvent molecule (**3i**) are omitted for clarity.

negative mode the phosphate anion was detected at  $m/z^- = 506.99$ . Crystals of **4m** suitable for X-ray diffraction were grown by diffusion of hexane into a solution of **4m** in benzene (Figure 6).



Scheme 4. Reactivity of *t*BuMelm (**1m**) towards  $\text{PF}_2(\text{C}_2\text{F}_5)_3$ .

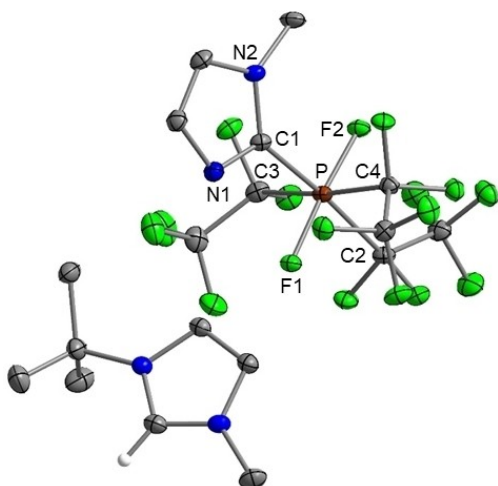


Figure 6. Molecular structure of  $[\text{tBuMelm-H}][\text{Melm-PF}_2(\text{C}_2\text{F}_5)_3]$  (**4m**) in the solid-state (ellipsoids set at the 50% probability level). All hydrogen atoms with the exception of the imidazolium proton are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–P 1.889(1), C2–P 2.000(1), C3–P 1.982(1), C4–P 1.984(1), C1–N1 1.330(2), C1–N2 1.376(2), F1–P 1.6268(7), F2–P 1.6431(7); C1–P–C2 175.62(5), C3–P–C4 173.68(5), F1–P–F2 174.80(4).

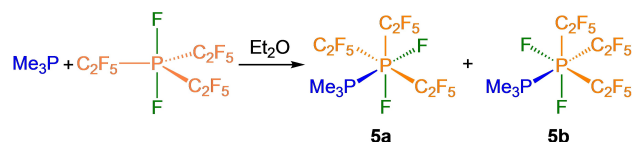
Compound **4m** crystallizes in the orthorhombic space group *Pbca* with one molecule in the asymmetric unit. The solid-state structure shows the  $[\text{tBuMelm-H}]^+$  cation and the NHC-substituted phosphate anion. The absence of the *tert*-butyl group, which was formerly bound to one of the NHC nitrogen atoms of the anion confirms the partial degradation of the carbene observed spectroscopically. The distance between the carbene carbon atom and the phosphorus atom is 1.8892(12) Å and thus significantly shorter than the C1–P bond lengths of the adducts **2a–h** (1.953(1)–1.989(1) Å). This can be rationalized as the imidazolyl ligand formed on degradation of the NHC has a different electronic structure compared to NHCs and the endocyclic and exocyclic bond distances are significantly affected. For the imidazolyl ligand one of the lone pairs is located in an exocyclic nitrogen  $sp^2$  orbital and the six electron  $\pi$  system contains two double bonds and the lone pair of the Me substituted nitrogen atom. This fact is reflected in the X-ray crystal structure of compound **4m** as the distance C1–N1 (1.330(2) Å) is shorter than C1–N2 (1.376(2) Å) and the C1–P bond is significantly smaller compared to the C–P bonds to NHC carbene carbon atoms in the adducts **2a–h**. Thus, the ligand attached to the phosphorane may best be described as an anionic vinyl/aryl ligand and thus a stronger electron donor. Consequently, the distance from phosphorus to the pentafluoroethyl carbon atom in *trans* position to the NHC (2.000(1) Å) in

**4m** is slightly elongated in comparison to the bond lengths in the adducts **2a–h** (1.964(1) to 1.995(2) Å).

Due to their similar donor but different steric properties compared to NHCs,<sup>[52]</sup> we also studied analogous reactions with selected phosphines to elucidate the influence of the steric demand of the phosphine on adduct formation. Thus, the reaction of  $\text{PMe}_3$  with the phosphorane, which was previously reported by one of us,<sup>[25]</sup> was repeated and the formation of a mixture of isomers was confirmed (Scheme 5). However, we were able to isolate crystals of the *mer-cis* isomer **5a** suitable for X-ray diffraction (Figure 7).

**5a** crystallizes in the orthorhombic space group  $P2_12_1$  with one molecule in the asymmetric unit. The phosphorus atom of the  $\text{PMe}_3$  moiety is directly bound to the phosphorus atom of the phosphorane and is located in *trans* position to one of the fluorine substituents. This is in contrast to all other  $\text{NHC}\cdot\text{PF}_2(\text{C}_2\text{F}_5)_3$  adducts reported herein that have the NHC substituent in *trans* position to one of the  $\text{C}_2\text{F}_5$  groups. The F1–P1 distance in **5a** is within 3  $\sigma$  identical with that observed for  $\text{Me}_3\text{P}\cdot\text{PF}_5$ . The P–P distance in **5a** of 2.4184(10) Å is significantly longer compared to that observed in  $\text{Me}_3\text{P}\cdot\text{PF}_5$  (2.246(4) Å),<sup>[22]</sup> which reflects the influence of the sterically much more demanding  $\text{C}_2\text{F}_5$  groups in comparison to simple fluorine substituents in  $\text{Me}_3\text{P}\cdot\text{PF}_5$ . Mixtures of  $\text{PPh}_3$  or  $\text{PCy}_3$  (Cy = cyclohexyl) and the phosphorane in  $\text{Et}_2\text{O}$  did not lead to detection of any new species in the  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra.

**FLP-like reactions of NHCs with  $\text{PF}_2(\text{C}_2\text{F}_5)_3$ .** Since the reaction of the phosphorane with  $\text{Dipp}_2\text{Im}$  (**1i**) and  $\text{tBu}_2\text{Im}$  (**1j**)



Scheme 5. Adduct formation between  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  and  $\text{PMe}_3$ .

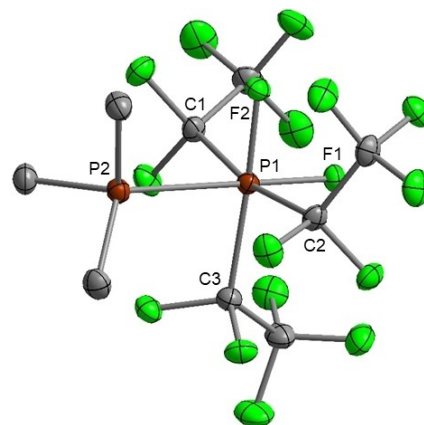


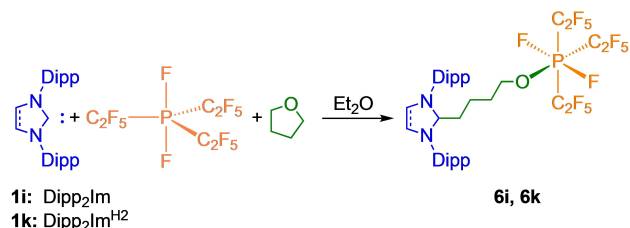
Figure 7. Molecular structure of the *mer-cis* isomer of  $\text{Me}_3\text{P}\cdot\text{PF}_2(\text{C}_2\text{F}_5)_3$  (**5a**) in the solid-state (ellipsoids set at the 50% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–P1 1.962(3), C2–P1 1.973(3), C3–P1 1.977(3), F1–P1 1.617(2), F2–P1 1.629(2), P1–P2 2.418(1); C1–P1–C2 169.04(13), C3–P–F2 175.76(12), F1–P1–P2 179.67(8).



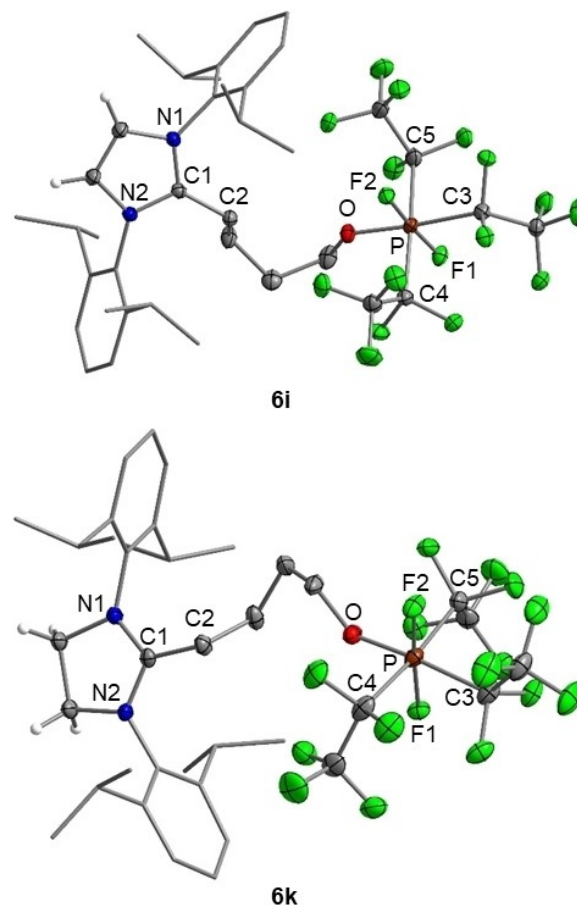
lasts several weeks and no adduct formation was observed with  $\text{Dipp}_2\text{Im}^{\text{H}2}$  (**1k**) at all, we investigated the systems **1i**/ $\text{PF}_2(\text{C}_2\text{F}_5)_3$ , **1j**/ $\text{PF}_2(\text{C}_2\text{F}_5)_3$ , and **1k**/ $\text{PF}_2(\text{C}_2\text{F}_5)_3$  with respect to their FLP reactivity potential in the activation of small molecules. Tamm and co-workers reported previously ring cleavage of THF using FLPs that consist of NHCs and  $\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>[15]</sup> Although a mixture of THF and the phosphorane led to polymerization, etheric solutions of **1i** or **1k**,  $\text{PF}_2(\text{C}_2\text{F}_5)_3$ , and THF did not solidify. Instead, the compounds  $\text{NHC}-(\text{CH}_2)_4\text{O}-\text{PF}_2(\text{C}_2\text{F}_5)_3$  ( $\text{NHC}=\text{Dipp}_2\text{Im}$  **6i**,  $\text{Dipp}_2\text{Im}^{\text{H}2}$  **6k**) with ring-opened THF were isolated (Scheme 6). The reaction between  $t\text{Bu}_2\text{Im}$  (**1j**), the phosphorane, and THF was unselective. Among others the resonances of the  $\alpha\text{NHC}$  adduct **3j** were detected in the  $^{19}\text{F}$  NMR spectrum of the crude product.

Formation of **6i** and **6k** is evident from NMR spectroscopy. In addition to the resonances of the imidazolyl substituent the  $\text{CH}_2$  groups of the incorporated THF unit were observed as multiplets at 3.61, 2.45, 1.25, and 1.14 ppm (**6i**) and at 3.58, 2.04, 1.21, and 1.07 ppm (**6k**) in the  $^1\text{H}$  NMR spectra of **6i** and **6k**, respectively (Figure S46 and S50 of the SI). Compound **6i** gives rise to multiplets at  $-80.4$  and  $-81.5$  ppm for the  $\text{CF}_3$  groups, a doublet of multiplets at  $-94.3$  ppm with a  $^1J_{\text{P-F}}$  coupling constant of 894 Hz for the fluorine atoms at phosphorus and doublets of multiplets at  $-113.3$  and  $-113.9$  ppm ( $^2J_{\text{P-F}}=83, 87$  Hz) for the  $\text{CF}_2$  groups in the  $^{19}\text{F}$  NMR spectrum (Figure S48 of the SI). The  $^{31}\text{P}$  NMR spectrum of **6i** revealed a triplet of quintets of triplets at  $-149.8$  ppm ( $^1J_{\text{P-F}}=894$  Hz,  $^2J_{\text{P-F}}=87$  Hz,  $^2J_{\text{P-F}}=83$  Hz). There is no significant difference in the  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra of **6i** and **6k**. Colorless blocks of **6i** and **6k** suitable for X-ray diffraction were grown by vapor diffusion of pentane into a solution of **6i** in  $\text{CH}_2\text{Cl}_2$  and a solution of **6k** in THF, respectively (Figure 8).

Compound **6i** crystallizes in the orthorhombic space group  $Pbca$  and **6k** in the monoclinic space group  $P2_1/c$ , both with one molecule in the asymmetric unit. The solid-state structures confirm the THF cleavage and carbene addition to the  $\alpha\text{-CH}_2$  moiety of THF. The oxygen atom is bound to phosphorus leading to an inner salt. In *trans* position to the oxygen atom of the phosphate moiety lies one of the pentafluoroethyl groups with angles  $\text{C}3-\text{P}-\text{O}$  of  $172.67(7)^\circ$  (**6i**) and  $173.33(6)^\circ$  (**6k**), respectively. The phosphorus atom of the *mer-trans*-phosphate is octahedrally surrounded by the  $\text{C}_2\text{F}_5$  groups, the oxygen atom of the former THF molecule and the fluorine atoms, which are in *mutual trans* position. The bond lengths  $\text{C}1-\text{C}2$  (**6i**:  $1.495(2)$  Å; **6k**:  $1.489(2)$  Å) are identical with those found in



**Scheme 6.** Ring opening of THF with the FLPs  $\text{Dipp}_2\text{Im}/\text{PF}_2(\text{C}_2\text{F}_5)_3$  and  $\text{Dipp}_2\text{Im}^{\text{H}2}/\text{PF}_2(\text{C}_2\text{F}_5)_3$ .



**Figure 8.** Molecular structures of **6i** (top) and **6k** (bottom) in the solid-state (ellipsoids set at the 50% probability level; *i*Pr and phenyl groups are shown as wire-and-stick-model). All hydrogen atoms with the exception of the protons of the backbone and a solvent molecule (**6i**) are omitted for clarity. Selected bond lengths [Å] and angles [ $^\circ$ ]: **6i**:  $\text{C}1-\text{C}2$   $1.495(2)$ ,  $\text{C}1-\text{N}1$   $1.343(2)$ ,  $\text{C}1-\text{N}2$   $1.345(2)$ ,  $\text{O}-\text{P}$   $1.649(2)$ ,  $\text{C}3-\text{P}$   $1.982(2)$ ,  $\text{C}4-\text{P}$   $1.963(2)$ ,  $\text{C}5-\text{P}$   $1.963(2)$ ,  $\text{F}1-\text{P}$   $1.642(1)$ ,  $\text{F}2-\text{P}$   $1.621(1)$ ;  $\text{C}3-\text{P}-\text{O}$   $172.62(7)$ ,  $\text{C}4-\text{P}-\text{C}5$   $173.63(8)$ ,  $\text{F}1-\text{P}-\text{F}2$   $175.31(6)$ ; **6k**:  $\text{C}1-\text{C}2$   $1.489(2)$ ,  $\text{C}1-\text{N}1$   $1.324(2)$ ,  $\text{C}1-\text{N}2$   $1.323(2)$ ,  $\text{O}-\text{P}$   $1.641(1)$ ,  $\text{C}3-\text{P}$   $1.978(2)$ ,  $\text{C}4-\text{P}$   $1.962(2)$ ,  $\text{C}5-\text{P}$   $1.968(2)$ ,  $\text{F}1-\text{P}$   $1.622(8)$ ,  $\text{F}2-\text{P}$   $1.6451(9)$ ;  $\text{C}3-\text{P}-\text{O}$   $173.33(6)$ ,  $\text{C}4-\text{P}-\text{C}5$   $174.73(7)$ ,  $\text{F}1-\text{P}-\text{F}2$   $175.44(5)$ .

$t\text{Bu}_2\text{Im}-(\text{CH}_2)_4\text{O}-\text{B}(\text{C}_6\text{F}_5)_3$  ( $1.498(2)$  Å)<sup>[15a]</sup> and  $\text{Ad}_2\text{Im}-(\text{CH}_2)_4\text{O}-\text{B}(\text{C}_6\text{F}_5)_3$  ( $1.495(2)$  Å;  $\text{Ad}_2\text{Im}=1,3$ -diadamantyl-imidazolin-2-ylidene) within standard deviation and are slightly longer than  $d(\text{C}1-\text{C}2)$  of  $\text{Dipp}_2\text{Im}-(\text{CH}_2)_4\text{O}-\text{B}(\text{C}_6\text{F}_5)_3$  ( $1.479(3)$  Å).<sup>[15b]</sup> The oxygen phosphorus distances (**6i**:  $1.649(1)$  Å; **6k**:  $1.641(1)$  Å) are close and similar to the one observed for the phosphate anion of  $[\text{PPh}_4][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{OH})]$  ( $1.647(3)$  Å) but slightly shorter than the one reported for  $[\text{DMAP}-\text{H}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{OEt})]$  ( $\text{DMAP}=4$ -dimethylaminopyridine) ( $1.662(2)$  Å).<sup>[49]</sup> The distances between phosphorus and the carbon atom of the  $\text{C}_2\text{F}_5$  group in *trans* position to oxygen amount to  $1.982(2)$  Å and  $1.978(2)$  Å (**6i**) and are in both cases in the range of the C–P distances of the adducts **2a–h** (Table 2).

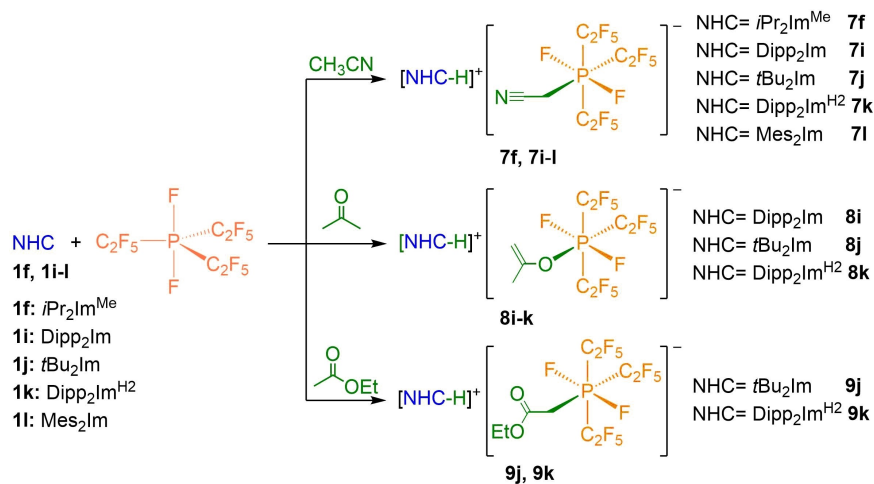
We further examined the possibility of activating weakly acidic C–H bonds with the FLPs composed of an NHC and  $\text{PF}_2(\text{C}_2\text{F}_5)_3$ . Activation of the  $\alpha\text{-C}-\text{H}$  bonds of various (thio)ethers by the FLPs  $[t\text{Bu}_2\text{PH}-(\text{C}_6\text{H}_5)\text{CPh}_2][\text{X}]$  ( $\text{X}=\text{OSO}_2\text{CF}_3$ ,  $\text{B}(\text{C}_6\text{F}_5)_4$ ) was

reported by Weigand, Stephan and co-workers.<sup>[53]</sup> As stated in the introduction, Hoge, Ignat'ev, and co-workers reported the deprotonation of acetonitrile with  $\text{NEt}_3$  in the presence of the phosphorane to give the ammonium salt  $[\text{Et}_3\text{NH}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CN})]$ .<sup>[41]</sup> Exchange of  $\text{NEt}_3$  with the NHCs as bases afforded the corresponding imidazolium salts  $[\text{NHC-H}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CN})]$  (NHC=Dipp<sub>2</sub>Im **7i**; *t*Bu<sub>2</sub>Im **7j**; Dipp<sub>2</sub>Im<sup>H2</sup> **7k**) (Scheme 7, top). Although the carbenes *i*Pr<sub>2</sub>Im<sup>Me</sup> (**1f**) and Mes<sub>2</sub>Im (**1l**) readily react with  $\text{PF}_2(\text{C}_2\text{F}_5)_3$ , the ionic compounds  $[\text{iPr}_2\text{Im}^{\text{Me}}\text{-H}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CN})]$  (**7f**) and  $[\text{Mes}_2\text{Im-H}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CN})]$  (**7l**) were also obtained by addition of the phosphorane to a solution of the corresponding carbene in acetonitrile (Scheme 7, top). The <sup>19</sup>F and <sup>31</sup>P NMR spectra of the compounds **7** are in agreement with the reported values for the ammonium salt  $[\text{Et}_3\text{NH}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CN})]$ , which illustrates the formation of the phosphate anion.<sup>[41]</sup> In addition, the characteristic resonances of the CH<sub>2</sub> groups of the deprotonated acetonitrile were observed as doublet of multiplets at 2.33 ppm with <sup>2</sup>J<sub>P-H</sub> = 15 Hz, which is also in accordance with previous reports.<sup>[41]</sup> Furthermore, in the <sup>1</sup>H NMR spectra the imidazolium protons were detected at 8.33 (**7f**), 8.92 (**7i**), 8.41 (**7j**), 8.30 ppm (**7k**) and 8.69 ppm (**7l**) in CD<sub>3</sub>CN, respectively, which is indicative for imidazolium cation formation. In addition, these cations were detected in the corresponding ESI-(+)MS spectra (see Experimental Details). In the negative mode the  $[\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CN})]^-$  anion was detected at *m/z*<sup>-</sup> = 465.96. Moreover, **7f**, **7j**, **7k**, and **7l** were analyzed by X-ray diffraction (Figure S106–S109 of the SI). The reaction of the NHCs **1a–e**, CH<sub>3</sub>CN, and the phosphorane resulted in product mixtures which could not be purified.

Although the reaction between acetone,  $\text{NEt}_3$ , and  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  was reported to be unselective,<sup>[41]</sup> pure products were obtained upon use of the NHCs **1i**, **1j**, or **1k**, as Lewis base. After workup of the reaction mixtures, the salts  $[\text{NHC-H}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{OC}(=\text{CH}_2)\text{CH}_3)]^-$  (NHC=Dipp<sub>2</sub>Im **8i**; *t*Bu<sub>2</sub>Im **8j**; Dipp<sub>2</sub>Im<sup>H2</sup> **8k**) were isolated (Scheme 7, middle). The characteristic resonances of the imidazolium H atoms in the <sup>1</sup>H NMR spectra of **8i–k** prove imidazolium salt formation (Figure S74, S78 and S82 of the SI).

In addition, the phosphate anion  $[\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{OC}(=\text{CH}_2)\text{CH}_3)]^-$  gives rise to a singlet at 1.69 ppm for the CH<sub>3</sub> group and two broad singlets at 4.29 and 3.88 ppm for the methylene protons of the olefinic group in the <sup>1</sup>H NMR spectra. In comparison to acetone (2.08 ppm in CD<sub>3</sub>CN),<sup>[54]</sup> the resonance of the methyl group in the phosphate anion is shifted towards higher field. Due to a significant divergence in multiplicity and chemical shift of the signals of the olefinic CH<sub>2</sub> moiety (**8i–k**), compared to the compounds **7**, we conclude that the acetone is bound to phosphorus *via* oxygen. Stephan, Lips, and co-workers used a FLP consisting of a trisila-cyclo-propylidene and B(C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub> to deprotonate acetone and in the resulting salt the acetone moiety is bound to boron *via* oxygen.<sup>[10c]</sup> In the <sup>19</sup>F NMR spectra of **8i–k** the multiplets of the CF<sub>3</sub> groups were observed at –80.5 and –81.5 ppm with intensities of 3 and 6, respectively. The fluorine atoms at phosphorus were detected as doublet of multiplets at –86.6 ppm with <sup>1</sup>J<sub>P-F</sub> = 890 Hz and the CF<sub>2</sub> groups give rise to a doublet of multiplets (<sup>2</sup>J<sub>P-F</sub> = 92 Hz) at –114.0 ppm. In the <sup>31</sup>P NMR spectrum a triplet of multiplets at –148.0 ppm was found.

The reactions of the FLPs NHC/ $\text{PF}_2(\text{C}_2\text{F}_5)_3$  with ethylacetate led to isolation of the imidazolium phosphates  $[\text{NHC-H}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CO}_2\text{Et})]$  (NHC=*t*Bu<sub>2</sub>Im **9j**; Dipp<sub>2</sub>Im<sup>H2</sup> **9k**) (Scheme 7, bottom). The reaction of Dipp<sub>2</sub>Im (**1i**) with  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  and ethyl acetate resulted in a product mixture that could not be purified. Besides the resonances of the corresponding imidazolium salts, compounds **9j** and **9k** give rise to a quartet at 3.99 ppm for the CH<sub>2</sub> group of the phosphate anion, a doublet of multiplets at 2.52 ppm with <sup>2</sup>J<sub>P-H</sub> ≈ 15 Hz for the methylene group at phosphorus, and a triplet at 1.16 ppm for the methyl group of the phosphate anion. The coupling of the methylene protons with phosphorus and the chemical shift which is similar to that of compounds **7** and the ammonium salt  $[\text{Et}_3\text{NH}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CN})]$ <sup>[41]</sup> leads to the conclusion, that the deprotonated ethyl acetate moiety is bound to phosphorus *via* the carbon atom. The resonances in the <sup>19</sup>F NMR spectra of the phosphate anion  $[\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CO}_2\text{Et})]^-$  were very broad at r.t. but at –35 °C well resolved signals were observed (Fig-



Scheme 7. Deprotonation of exemplary weak C–H acidic organic compounds by NHC/ $\text{PF}_2(\text{C}_2\text{F}_5)_3$  FLPs.

ure S92 of the SI). The multiplets of the  $\text{CF}_3$  groups were detected at  $-79.6$  and  $-80.1$  ppm and the fluorine atoms at phosphorus as doublet of doublets at  $-91.5$  and  $-104.5$  ppm with  $^1J_{\text{P-F}}$  coupling constants of 800 and 875 Hz, respectively ( $^2J_{\text{F-F}} = 103$  Hz). The  $\text{CF}_2$  groups give rise to a doublet of doublets of quartets at  $-112.0$  ppm ( $^2J_{\text{F-F}} = 293$  Hz;  $^2J_{\text{P-F}} = 91$  Hz;  $^3J_{\text{F-F}} = 7.9$  Hz), a doublet of multiplets at  $-115.1$  ppm ( $^2J_{\text{P-F}} = 97$  Hz) and a doublet of multiplets at  $-119.5$  ppm ( $^2J_{\text{F-F}} = 293$  Hz). In the  $^{31}\text{P}$  NMR spectra of **9j** and **9k** a triplet of multiplets at  $-143.0$  ppm was observed. In the ESI(-)MS spectra the phosphate anion was detected at  $512.99$  m/z<sup>-</sup>. In addition, crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a solution of **9j** in THF and **9k** in  $\text{CH}_2\text{Cl}_2$ , respectively (Figure 9).

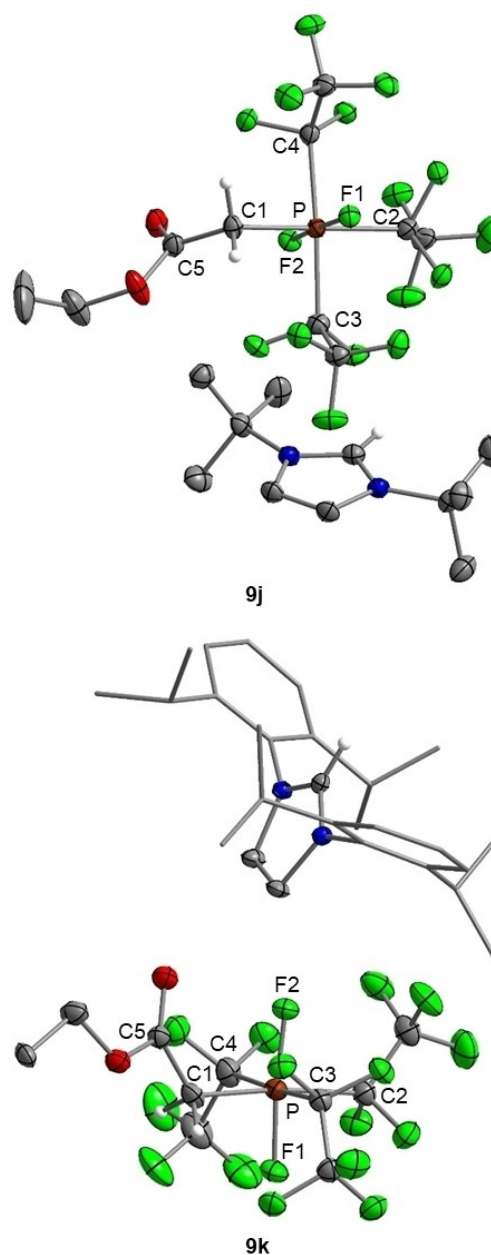
Both **9j** and **9k** crystallize in the orthorhombic space group  $P2_12_1$  with one molecule in the asymmetric unit. The solid-state structures reveal the presence of the corresponding imidazolium salt and the  $[\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CO}_2\text{Et})]^-$  anion. The fluorine atoms at phosphorus are in mutual *trans* position and the  $\text{CH}_2\text{CO}_2\text{Et}$  moiety is bound *via* carbon to phosphorus, which is in agreement with the NMR spectroscopic data obtained in solution. There is no significant difference in the bonding parameters of the phosphate anions of **9j** and **9k**. The distances C1–P (**9j**: 1.905(3) Å; **9k**: 1.886(4) Å) are slightly shorter than  $d(\text{C}_{\text{carbene}}-\text{P})$  in the adducts **2a–h** (Table 2) but similar to  $d(\text{C1}-\text{P})$  of the anion of **4m** (1.8892(12) Å) and the phosphate anion of  $[\text{Et}_3\text{NH}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CN})]$  (1.9206(12) Å).<sup>[41]</sup> The C2–P distance (**9j**: 2.000(3) Å; **9k**: 2.004(4) Å) is by and large unaffected by the substituent in *trans* position (cf. Table 2).

## Conclusion

NHC phosphorane adducts  $\text{NHC}\cdot\text{PF}_2(\text{C}_2\text{F}_5)_3$  (**2a–h**) can be obtained easily from the corresponding NHC and the phosphorane  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  in  $\text{Et}_2\text{O}$ , if the NHC is sterically not too demanding and substituted with small to middle sized alkyl groups such as Me, *n*Pr, or *i*Pr at nitrogen. Bulkier NHCs like Dipp<sub>2</sub>Im (**1i**) and *t*Bu<sub>2</sub>Im (**1j**) show a different reactivity and the corresponding NHC phosphorane adducts  $\text{NHC}\cdot\text{PF}_2(\text{C}_2\text{F}_5)_3$  do not form instantaneously. However, after a period of several weeks adducts were isolated in which the NHC ligand coordinates *via* the NHC backbone in its “abnormal” coordination mode, *i.e.* at a sterically less demanding position. The reaction of *t*BuMelm (**1m**) with  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  led to the ionic compound [*t*BuMelm–H][Melm– $\text{PF}_2(\text{C}_2\text{F}_5)_3$ ] (**4m**) with decomposition of one equivalent *t*BuMelm of the NHC employed.

NHC reactivity contrasts the reactivity of phosphines with the phosphorane, as only the smallest phosphine under consideration,  $\text{PMe}_3$ , gave Lewis acid/base adducts  $\text{Me}_3\text{P}\cdot\text{PF}_2(\text{C}_2\text{F}_5)_3$ . The *mer-cis* isomer **5a** was structurally characterized. Larger cone-shaped phosphines such as  $\text{PPh}_3$  and  $\text{PCy}_3$  do not react with the phosphorane.

$\text{NHC}/\text{PF}_2(\text{C}_2\text{F}_5)_3$  mixtures (NHC = **1i–k**) of the larger “standard” NHCs (*t*Bu<sub>2</sub>Im, Dipp<sub>2</sub>Im, Dipp<sub>2</sub>Im<sup>H2</sup>) and the phosphorane  $\text{PF}_2(\text{C}_2\text{F}_5)_3$  reveal FLP reactivity. These mixtures were used for THF ring cleavage to form  $\text{NHC}-(\text{CH}_2)_4\text{O}-\text{PF}_2(\text{C}_2\text{F}_5)_3$



**Figure 9.** Molecular structures of **9j** (top) and **9k** (bottom) in the solid-state (ellipsoids set at the 50% probability level; *i*Pr and phenyl groups of **9k** are shown as wire-and-stick-model). All hydrogen atoms with the exception of one of the imidazolium H atoms and the  $\text{CH}_2$ -group attached to phosphorus are omitted for clarity. Selected bond lengths [Å] and angles [°]: **9j**: C1–P 1.905(3), C2–P 2.000(3), C3–P 1.998(3), C4–P 1.987(3), C1–C5 1.508(4), F1–P 1.643(2), F2–P 1.635(2); C1–P–C2 174.93(13), C3–P–C4 176.25(12), F1–P–F2 174.90(9); **9k**: C1–P 1.886(4), C2–P 2.004(4), C3–P 1.980(4), C4–P 1.990(3), C1–C5 1.518(5), F1–P 1.651(2), F2–P 1.632(2); C1–P–C2 174.17(16), C3–P–C4 175.58(17), F1–P–F2 174.13(12).

(NHC=Dipp<sub>2</sub>Im **6i**; Dipp<sub>2</sub>Im<sup>H2</sup> **6k**) and for the deprotonation of C–H acidic compounds such as acetonitrile, acetone, and ethyl acetate with formation of the corresponding imidazolium salts and  $[\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CN})]^-$  (**7**),  $[\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{OC}(\text{=CH}_2)\text{CH}_3)]^-$  (**8**) and  $[\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CO}_2\text{Et})]^-$  (**9**) phosphate counterions. This reactivity will be more fully exploited in the near future.

## Experimental Section

**General:** The compounds **1a–c**,<sup>[55]</sup> **1d**,<sup>[56]</sup> **1e**,<sup>[57]</sup> **1f**,<sup>[56]</sup> **1g**,<sup>[55]</sup> **1h**, **1i**,<sup>[58]</sup> **1j**,<sup>[59]</sup> **1k**,<sup>[58]</sup> **1l**,<sup>[58]</sup> and **1m**<sup>[60]</sup> were prepared according to literature procedures. PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> was synthesized via electrochemical fluorination (ECF) starting from triethylphosphine as described in the literature.<sup>[26]</sup> All other starting materials were purchased from commercial sources and used without further purification. All solvents for synthetic reactions were HPLC grade, further treated to remove traces of water using an Innovative Technology Inc. Pure-Solv Solvent Purification System. All reactions and subsequent manipulations were performed under an argon atmosphere in an Innovative Technology Inc. glovebox or using standard Schlenk techniques. NMR spectra were recorded on a Bruker Avance NEO 400, a Bruker Avance Nanobay 400 and a Bruker Avance 500 spectrometer, using C<sub>6</sub>D<sub>6</sub>, CD<sub>2</sub>Cl<sub>2</sub>, or CD<sub>3</sub>CN as solvent. Assignment of the <sup>1</sup>H NMR spectra was supported by <sup>1</sup>H,<sup>1</sup>H and <sup>13</sup>C,<sup>1</sup>H correlation experiments. <sup>13</sup>C NMR spectra were broad-band proton-decoupled (<sup>13</sup>C{<sup>1</sup>H}). Assignment of the <sup>13</sup>C NMR data was supported by <sup>13</sup>C,<sup>1</sup>H correlation experiments. Chemical shifts are listed in parts per million (ppm) and were calibrated against residual solvent signals ( $\delta$ (<sup>1</sup>H): C<sub>6</sub>HD<sub>5</sub> 7.16; CHDCl<sub>2</sub> 5.32; CHD<sub>2</sub>CN 1.94), solvent signals ( $\delta$ (<sup>13</sup>C): C<sub>6</sub>D<sub>6</sub> 128.06; CD<sub>2</sub>Cl<sub>2</sub> 53.84; CD<sub>3</sub>CN 118.26, 1.32),<sup>[54]</sup> or external CFC<sub>3</sub> ( $\delta$ (<sup>19</sup>F): 0) and 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta$ (<sup>31</sup>P): 0). If not otherwise noted <sup>19</sup>F and <sup>31</sup>P NMR spectra were not proton decoupled. Coupling constants are quoted in Hertz. IR spectra were recorded on solid samples on a Bruker Alpha FT-IR spectrometer using an ATR unit at r.t. Values are given in cm<sup>-1</sup>. Elemental analyses were performed in the microanalytical laboratory of the Institute of Inorganic Chemistry of the University of Würzburg with an Elementar vario micro cube. The high-resolution mass analysis was performed on a Thermo Scientific Exactive Plus mass spectrometer, equipped with an Orbitrap Mass Analyzer.

In the <sup>13</sup>C{<sup>1</sup>H} NMR spectra the resonances of the pentafluoroethyl groups were typically not observed under the conditions of the measurement. The signals of the carbene carbon atoms of the adducts **2a–h**, the  $\alpha$ NHC adducts **3i** and **3j**, and the salt **4m** were also not observed. However, the chemical shift of these carbon atoms could be estimated by the <sup>13</sup>C{<sup>1</sup>H}, <sup>1</sup>H HMBC spectra. <sup>15</sup>J denotes coupling through space.

**General Synthesis of adducts 2a–h:** The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> was added at 0 °C to a solution of the NHC in Et<sub>2</sub>O. The resulting solution was stirred at 0 °C for 30 min and all volatiles were removed under reduced pressure. The remaining solid was dried *in vacuo*.

**Me<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2a)**

Reaction between Me<sub>2</sub>Im (**1a**) (220 mg, 2.29 mmol) and PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (540  $\mu$ L, 2.29 mmol) in Et<sub>2</sub>O (8 mL) yielded **2a** (903 mg, 1.73 mmol, 76%) as an orange solid. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 5.30 (d, 2H, <sup>4</sup>J<sub>P-H</sub> = 1.5 Hz, N–CH–CH–N), 3.12 (t, 6H, <sup>15</sup>J<sub>F-H</sub> = 3.5 Hz, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 155.5 (N–C–N), 123.4 (N–CH–CH–N), 40.5 (CH<sub>3</sub>); <sup>19</sup>F NMR (470.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = –78.4 (m, 3F, CF<sub>3</sub>), –80.0 (m, 6F, CF<sub>3</sub>), –92.5 (d<sub>br</sub>, 2F, <sup>1</sup>J<sub>P-F</sub> = 899 Hz, PF<sub>2</sub>), –114.5 (d, m, 2F, <sup>2</sup>J<sub>P-F</sub> = 102 Hz, CF<sub>2</sub>), –116.0 (d, m, 4F, <sup>2</sup>J<sub>P-F</sub> = 103 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = –142.5 (t, quint, t, <sup>1</sup>J<sub>P-F</sub> = 899 Hz, <sup>2</sup>J<sub>P-F</sub> = 103 Hz, <sup>2</sup>J<sub>P-F</sub> = 102 Hz); IR ([cm<sup>-1</sup>): 2950 (vw), 2796 (vw), 1646 (vw), 1608 (vw), 1586 (vw), 1485 (w), 1406 (vw), 1373 (vw), 1300 (m), 1217 (s), 1168 (s), 1132 (s), 1123 (s), 1087 (s), 1072 (m), 1017 (w), 956 (s), 823 (m), 758 (m), 743 (m), 712 (vw), 636 (w), 616 (m), 597 (m), 562 (vs), 533 (vs), 452 (w), 428 (m); elemental analysis calcd (%) for C<sub>11</sub>H<sub>8</sub>F<sub>17</sub>N<sub>2</sub>P: C 25.30, H 1.54, N 5.37; found: C 26.57, H 1.89, N 6.23.

**nPr<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2b)**

Reaction between nPr<sub>2</sub>Im (**1b**) (284 mg, 1.87 mmol) and PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (440  $\mu$ L, 1.87 mmol) in Et<sub>2</sub>O (7 mL) yielded **2b** (1.02 g, 1.76 mmol, 95%) as an orange solid. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 5.88 (d, 2H, <sup>4</sup>J<sub>P-H</sub> = 1.8 Hz, N–CH–CH–N), 3.94 (m, 4H, N–CH<sub>2</sub>), 1.26 (sext, 4H, <sup>3</sup>J<sub>H-H</sub> = 7.4 Hz, CH<sub>3</sub>–CH<sub>2</sub>), 0.50 (t, 6H, <sup>3</sup>J<sub>H-H</sub> = 7.4 Hz, CH<sub>2</sub>–CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 156.0 (N–C–N), 121.5 (N–CH–CH–N), 54.0 (N–CH<sub>2</sub>), 23.3 (CH<sub>3</sub>–CH<sub>2</sub>), 10.8 (CH<sub>3</sub>); <sup>19</sup>F NMR (470.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = –78.4 (m, 3F, CF<sub>3</sub>), –79.4 (m, 6F, CF<sub>3</sub>), –90.8 (d<sub>br</sub>, 2F, <sup>1</sup>J<sub>P-F</sub> = 910 Hz, PF<sub>2</sub>), –113.8 (d, m, 4F, <sup>2</sup>J<sub>P-F</sub> = 105 Hz, CF<sub>2</sub>), –114.4 (d, m, 2F, <sup>2</sup>J<sub>P-F</sub> = 103 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = –140.0 (t, quint, t, <sup>1</sup>J<sub>P-F</sub> = 910 Hz, <sup>2</sup>J<sub>P-F</sub> = 105 Hz, <sup>2</sup>J<sub>P-F</sub> = 103 Hz); IR ([cm<sup>-1</sup>): 2975 (w), 2945 (w), 2886 (w), 1664 (vw), 1610 (vw), 1590 (vw), 1566 (vw), 1480 (w), 1462 (w), 1428 (vw), 1388 (vw), 1368 (vw), 1304 (m), 1293 (m), 1213 (vs), 1184 (vs), 1149 (m), 1121 (vs), 1088 (s), 1066 (m), 1002 (w), 964 (m), 953 (s), 912 (w), 828 (s), 757 (m), 741 (m), 717 (w), 677 (vw), 635 (w), 600 (s), 558 (vs), 530 (vs), 455 (w), 431 (m); elemental analysis calcd (%) for C<sub>15</sub>H<sub>16</sub>F<sub>17</sub>N<sub>2</sub>P: C 31.16, H 2.79, N 4.84; found: C 31.40, H 2.50, N 5.26.

**iPr<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2c)**

Reaction between iPr<sub>2</sub>Im (**1c**) (544 mg, 3.57 mmol) and PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (840  $\mu$ L, 3.57 mmol) in Et<sub>2</sub>O (10 mL) yielded **2c** (1.64 g, 2.84 mmol, 79%) as an orange solid. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 6.14 (d, 2H, <sup>4</sup>J<sub>P-H</sub> = 1.8 Hz, N–CH–CH–N), 5.32 (sept, 2H, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, iPr–CH), 0.84 (d, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, iPr–CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 155.4 (N–C–N), 119.0 (N–CH–CH–N), 53.7 (iPr–CH), 23.5 (iPr–CH<sub>3</sub>); <sup>19</sup>F NMR (470.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = –77.7 (m, 6F, CF<sub>3</sub>), –78.0 (m, 3F, CF<sub>3</sub>), –88.5 (d, m, 2F, <sup>1</sup>J<sub>P-F</sub> = 926 Hz, PF<sub>2</sub>), –111.0 (d, m, 4F, <sup>2</sup>J<sub>P-F</sub> = 106 Hz, CF<sub>2</sub>), –114.2 (d, m, 2F, <sup>2</sup>J<sub>P-F</sub> = 102 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = –138.4 (t, quint, t, <sup>1</sup>J<sub>P-F</sub> = 926 Hz, <sup>2</sup>J<sub>P-F</sub> = 106 Hz, <sup>2</sup>J<sub>P-F</sub> = 102 Hz); IR ([cm<sup>-1</sup>): 3173 (vw), 2982 (vw), 1595 (vw), 1551 (vw), 1467 (w), 1438 (vw), 1400 (w), 1379 (w), 1295 (m), 1263 (w), 1212 (vs), 1181 (vs), 1119 (vs), 1085 (vs), 957 (m), 884 (vw), 830 (m), 789 (w), 756 (m), 742 (m), 677 (vw), 658 (vw), 630 (m), 599 (s), 580 (m), 556 (vs), 532 (vs), 432 (m); elemental analysis calcd (%) for C<sub>15</sub>H<sub>16</sub>F<sub>17</sub>N<sub>2</sub>P: C 31.16, H 2.79, N 4.84; found: C 31.53, H 2.63, N 4.78.

**Me<sub>2</sub>Im<sup>Me</sup>·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2d)**

Reaction between Me<sub>2</sub>Im<sup>Me</sup> (**1d**) (128 mg, 1.03 mmol) and PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (240  $\mu$ L, 1.02 mmol) in Et<sub>2</sub>O (5 mL) yielded **2d** (360 mg, 654  $\mu$ mol, 63%) as a pale yellow solid. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 3.18 (s, 6H, N–CH<sub>3</sub>), 0.94 (s, 6H, C–CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 154.5 (N–C–N), 127.2 (C–CH<sub>3</sub>), 35.9 (N–CH<sub>3</sub>), 8.8 (C–CH<sub>3</sub>); <sup>19</sup>F NMR (470.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = –78.5 (m, 3F, CF<sub>3</sub>), –79.9 (m, 6F, CF<sub>3</sub>), –90.7 (d<sub>br</sub>, 2F, <sup>1</sup>J<sub>P-F</sub> = 908 Hz, PF<sub>2</sub>), –114.4 (d, m, 2F, <sup>2</sup>J<sub>P-F</sub> = 105 Hz, CF<sub>2</sub>), –115.7 (d, m, 4F, <sup>2</sup>J<sub>P-F</sub> = 102 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = –142.3 (t, t, quint, <sup>1</sup>J<sub>P-F</sub> = 908 Hz, <sup>2</sup>J<sub>P-F</sub> = 105 Hz, <sup>2</sup>J<sub>P-F</sub> = 102 Hz); IR ([cm<sup>-1</sup>): 2976 (vw), 1656 (w), 1467 (w), 1446 (w), 1404 (vw), 1384 (w), 1370 (w), 1303 (m), 1211 (vs), 1171 (s), 1119 (s), 1104 (m), 1079 (s), 1061 (s), 951 (s), 854 (m), 829 (s), 739 (m), 705 (w), 635 (w), 599 (s), 558 (vs), 530 (vs), 454 (w), 428 (m); elemental analysis calcd (%) for C<sub>13</sub>H<sub>12</sub>F<sub>17</sub>N<sub>2</sub>P: C 28.38, H 2.20, N 5.09; found: C 28.34, H 2.41, N 5.28.

**nPr<sub>2</sub>Im<sup>Me</sup>·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2e)**

Reaction between nPr<sub>2</sub>Im<sup>Me</sup> (**1e**) (231 mg, 1.28 mmol) and PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (300  $\mu$ L, 1.27 mmol) in Et<sub>2</sub>O (10 mL) yielded **2e** (586 mg, 967  $\mu$ mol, 75%) as a colorless solid. <sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 3.90 (m, 4H, N–CH<sub>2</sub>), 1.45 (m, 4H, CH<sub>3</sub>–CH<sub>2</sub>), 1.21 (s, 6H, N–C–CH<sub>3</sub>), 0.58

(t, 6H,  $^3J_{\text{H-H}}=7.5$  Hz,  $\text{CH}_2\text{-CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=154.4$  (N-C-N), 127.7 (N-C-CH<sub>3</sub>), 51.2 (N-CH<sub>2</sub>), 22.9 (CH<sub>3</sub>-CH<sub>2</sub>), 11.0 (CH<sub>2</sub>-CH<sub>3</sub>), 8.9 (N-C-CH<sub>3</sub>);  $^{19}\text{F}$  NMR (470.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=-77.8$  (m, 6F, CF<sub>3</sub>), -78.2 (m, 3F, CF<sub>3</sub>), -90.5 (d, m, 2F,  $^1J_{\text{P-F}}=920$  Hz, PF<sub>2</sub>), -111.0 (d, m, 4F,  $^2J_{\text{P-F}}=105$  Hz, CF<sub>2</sub>), -114.2 (d, m, 2F,  $^2J_{\text{P-F}}=103$  Hz, CF<sub>2</sub>);  $^{31}\text{P}$  NMR (202.4 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=-139.7$  (t, quint, t,  $^1J_{\text{P-F}}=920$  Hz,  $^2J_{\text{P-F}}=105$  Hz,  $^2J_{\text{P-F}}=103$  Hz); IR ([cm<sup>-1</sup>]): 2985 (w), 2944 (w), 2885 (w), 1654 (w), 1569 (vw), 1488 (w), 1460 (w), 1399 (w), 1358 (m), 1294 (m), 1213 (vs), 1185 (vs), 1121 (vs), 1086 (vs), 1065 (m), 957 (m), 947 (m), 914 (w), 891 (vs), 844 (w), 825 (m), 741 (m), 721 (w), 685 (vw), 643 (w), 599 (vs), 556 (vs), 531 (vs), 430 (m), 407 (vw); elemental analysis calcd (%) for C<sub>17</sub>H<sub>20</sub>F<sub>17</sub>N<sub>2</sub>P: C 33.68, H 3.33, N 4.62; found: C 33.88, H 3.30, N 4.65.

### *iPr*<sub>2</sub>Im<sup>Me</sup>·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2f)

Reaction between *iPr*<sub>2</sub>Im<sup>Me</sup> (1f) (100 mg, 555 μmol) and PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (130 μL, 552 μmol) in Et<sub>2</sub>O (2 mL) yielded 2f (267 mg, 440 μmol, 79%) as a colorless solid.  $^1\text{H}$  NMR (500.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=5.64$  (sept, 2H,  $^3J_{\text{H-H}}=7.0$  Hz, *iPr-CH*), 1.42 (s, 6H, C-CH<sub>3</sub>), 0.98 (d,  $^3J_{\text{H-H}}=7.0$  Hz, *iPr-CH*);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=156.8$  (N-C-N), 128.5 (C-CH<sub>3</sub>), 52.3 (*iPr-CH*), 21.3 (*iPr-CH*), 11.2 (C-CH<sub>3</sub>);  $^{19}\text{F}$  NMR (470.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=-77.3$  (m, 6F, CF<sub>3</sub>), -77.9 (m, 3F, CF<sub>3</sub>), -85.3 (d, m, 2F,  $^1J_{\text{P-F}}=942$  Hz, PF<sub>2</sub>), -110.2 (d, m, 4F,  $^2J_{\text{P-F}}=109$  Hz, CF<sub>2</sub>), -113.6 (d, m, 2F,  $^2J_{\text{P-F}}=99$  Hz, CF<sub>2</sub>);  $^{31}\text{P}$  NMR (202.4 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=-137.0$  (t, quint, t,  $^1J_{\text{P-F}}=942$  Hz,  $^2J_{\text{P-F}}=109$  Hz,  $^2J_{\text{P-F}}=99$  Hz); IR ([cm<sup>-1</sup>]): 2994 (vw), 2954 (vw), 1634 (vw), 1552 (vw), 1468 (w), 1398 (vw), 1378 (w), 1349 (w), 1304 (m), 1287 (m), 1211 (s), 1180 (vs), 1115 (s), 1079 (s), 1059 (m), 961 (m), 948 (m), 897 (w), 834 (s), 763 (w), 741 (w), 722 (w), 685 (w), 637 (w), 599 (s), 568 (m), 551 (s), 531 (vs), 429 (m); elemental analysis calcd (%) for C<sub>17</sub>H<sub>20</sub>F<sub>17</sub>N<sub>2</sub>P: C 33.68, H 3.33, N 4.62; found: C 33.96, H 3.64, N 4.88.

### *iPr*Melm·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2g)

Reaction between *iPr*Melm (1g) (200 mg, 1.61 mmol) and PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (380 μL, 1.61 mmol) in Et<sub>2</sub>O (10 mL) yielded 2g (809 mg, 1.47 mmol, 91%) as an orange solid.  $^1\text{H}$  NMR (500.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=5.80$  (br, 1H, CH-N-CH), 5.42 (br, 1H, CH<sub>3</sub>-N-CH), 5.35 (sept, 1H,  $^3J_{\text{H-H}}=6.4$  Hz, *iPr-CH*), 3.16 (d, 3H,  $^{\text{T}}J_{\text{F-H}}=6.6$  Hz, N-CH<sub>3</sub>), 0.74 (d<sub>br</sub>, 6H,  $^3J_{\text{H-H}}=6.4$  Hz, *iPr-CH*);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=155.5$  (N-C-N), 124.6 (CH<sub>3</sub>-N-CH), 118.2 (CH-N-CH), 53.2 (*iPr-CH*), 41.1 (N-CH<sub>3</sub>), 23.2 (*iPr-CH*);  $^{19}\text{F}$  NMR (470.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=-78.4$  (m, 3F, CF<sub>3</sub>), -79.5 (m, 6F, CF<sub>3</sub>), -84.7 (d, d, m, 1F,  $^1J_{\text{P-F}}=898$  Hz,  $^2J_{\text{P-F}}=119$  Hz, PF), -98.4 (d, d, m, 1F,  $^1J_{\text{P-F}}=914$  Hz,  $^2J_{\text{P-F}}=119$  Hz, PF), -111.9 (d, d, m, 2F,  $^2J_{\text{P-F}}=299$  Hz,  $^2J_{\text{P-F}}=108$  Hz, CF<sub>2</sub>), -114.5 (d, m, 2F,  $^2J_{\text{P-F}}=102$  Hz, CF<sub>2</sub>), -116.2 (d, m, 4F,  $^2J_{\text{P-F}}=299$  Hz, CF<sub>2</sub>);  $^{31}\text{P}$  NMR (202.4 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=-140.2$  (d, d, t, t,  $^1J_{\text{P-F}}=914$  Hz,  $^1J_{\text{P-F}}=898$  Hz,  $^2J_{\text{P-F}}=108$  Hz,  $^2J_{\text{P-F}}=102$  Hz); IR ([cm<sup>-1</sup>]): 2990 (vw), 1621 (vw), 1595 (vw), 1463 (w), 1396 (w), 1373 (vw), 1346 (vw), 1304 (m), 1215 (s), 1200 (m), 1179 (vs), 1152 (m), 1133 (m), 1120 (s), 1102 (s), 1082 (m), 1067 (m), 956 (s), 886 (vw), 862 (vw), 822 (s), 762 (m), 743 (m), 720 (w), 643 (w), 630 (m), 598 (s), 561 (vs), 532 (vs), 464 (vw), 450 (w), 430 (m); elemental analysis calcd (%) for C<sub>13</sub>H<sub>12</sub>F<sub>17</sub>N<sub>2</sub>P: C 28.38, H 2.20, N 5.09; found: C 28.75, H 2.32, N 5.47.

### EtMelm<sup>Me</sup>·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2h)

Reaction between EtMelm<sup>Me</sup> (1h) (154 mg, 1.11 mmol) and PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (260 μL, 1.10 mmol) in Et<sub>2</sub>O (10 mL) yielded 2h (586 mg, 1.04 mmol, 93%) as a brown solid.  $^1\text{H}$  NMR (500.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=3.80$  (q, m, 2H,  $^3J_{\text{H-H}}=7.2$  Hz, CH<sub>2</sub>), 3.19 (s, 3H, N-CH<sub>3</sub>), 1.04 (s, 3H, CH<sub>2</sub>-N-CH<sub>3</sub>), 1.00 (s, 3H, CH<sub>3</sub>-N-CH<sub>3</sub>), 0.92 (t, 3H,  $^3J_{\text{H-H}}=7.2$  Hz, CH<sub>2</sub>-CH<sub>3</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=154.1$  (N-C-N), 127.6 (CH<sub>3</sub>-N-C), 127.1 (CH<sub>2</sub>-N-C), 44.7 (CH<sub>2</sub>), 36.3

(N-CH<sub>3</sub>), 14.5 (CH<sub>2</sub>-CH<sub>3</sub>), 8.8 (CH<sub>3</sub>-N-C-CH<sub>3</sub>), 8.5 (CH<sub>2</sub>-N-C-CH<sub>3</sub>);  $^{19}\text{F}$  NMR (470.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=-78.6$  (3F, CF<sub>3</sub>), -79.4 (m, 6F, CF<sub>3</sub>), -84.0 (d, d, m, 1F,  $^1J_{\text{P-F}}=900$  Hz,  $^2J_{\text{P-F}}=121$  Hz, PF), -99.0 (d, d, m, 1F,  $^1J_{\text{P-F}}=915$  Hz,  $^2J_{\text{P-F}}=121$  Hz, PF), -110.5 (d, d, br, 2F,  $^2J_{\text{P-F}}=298$  Hz,  $^2J_{\text{P-F}}=103$  Hz, CF<sub>2</sub>), -114.4 (d, m, 2F,  $^2J_{\text{P-F}}=101$  Hz, CF<sub>2</sub>), -116.3 (d, m, 2F,  $^2J_{\text{P-F}}=298$  Hz, CF<sub>2</sub>);  $^{31}\text{P}$  NMR (202.4 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta=-141.1$  (d, d, t, t,  $^1J_{\text{P-F}}=915$  Hz,  $^1J_{\text{P-F}}=900$  Hz,  $^2J_{\text{P-F}}=103$  Hz,  $^2J_{\text{P-F}}=101$  Hz); IR ([cm<sup>-1</sup>]): 2985 (vw), 2949 (vw), 1659 (w), 1494 (w), 1444 (w), 1403 (vw), 1385 (w), 1371 (vw), 1353 (w), 1336 (vw), 1296 (m), 1211 (s), 1182 (vs), 1121 (vs), 1086 (s), 1066 (m), 955 (s), 839 (s), 808 (w), 739 (m), 715 (w), 666 (vw), 642 (w), 635 (w), 601 (s), 588 (vs), 531 (vs), 430 (m); elemental analysis calcd (%) for C<sub>14</sub>H<sub>14</sub>F<sub>17</sub>N<sub>2</sub>P: C 29.80, H 2.50, N 4.97; found: C 30.17, H 2.66, N 5.43.

### *aDipp*<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (3i)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (550 μL, 2.34 mmol) was added at room temperature to a solution of *aDipp*<sub>2</sub>Im (1i) (910 mg, 2.34 mmol) in Et<sub>2</sub>O (20 mL). The mixture was stirred for 30 min at room temperature and left standing. Over a period of 4 weeks, crystals were formed in the glass vessel. The crystals were collected by filtration, washed with hexane (2×5 mL) and dried *in vacuo* to give 3i (807 mg, 991 μmol, 42%) as an off-white solid.  $^1\text{H}$  NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta=7.96$  (m, 1H, P-C-CH), 7.60 (t,  $^3J_{\text{H-H}}=7.8$  Hz, aryl-C<sub>para</sub>H), 7.57 (br, 1H, N-CH-N), 7.56 (t, 1H,  $^3J_{\text{H-H}}=7.8$  Hz, aryl-C<sub>meta</sub>H), 7.38 (d, 2H,  $^3J_{\text{H-H}}=7.8$  Hz, aryl-C<sub>meta</sub>H), 7.35 (d, 2H,  $^3J_{\text{H-H}}=7.8$  Hz, aryl-C<sub>meta</sub>H), 2.64 (sept, 2H,  $^3J_{\text{H-H}}=6.8$  Hz, *iPr-CH*), 2.40 (sept, 2H,  $^3J_{\text{H-H}}=6.8$  Hz, *iPr-CH*), 1.36 (d, 6H,  $^3J_{\text{H-H}}=6.8$  Hz, *iPr-CH*), 1.25 (d, 6H,  $^3J_{\text{H-H}}=6.8$  Hz, *iPr-CH*), 1.21 (d, 6H,  $^3J_{\text{H-H}}=6.8$  Hz, *iPr-CH*), 1.04 (d, 6H,  $^3J_{\text{H-H}}=6.8$  Hz, *iPr-CH*);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta=147.6$  (aryl-C<sub>ortho</sub>), 145.9 (aryl-C<sub>ortho</sub>), 138.0 (P-C-CH), 133.5 (aryl-C<sub>ipso</sub>), 132.6 (aryl-C<sub>para</sub>), 131.7 (aryl-C<sub>para</sub>), 131.3 (N-CH-N), 129.8 (aryl-C<sub>ipso</sub>), 125.2 (aryl-C<sub>meta</sub>), 124.8 (aryl-C<sub>meta</sub>), 29.0 (*iPr-CH*), 27.2 (*iPr-CH*), 24.5 (*iPr-CH*), 24.1 (*iPr-CH*), 22.1 (*iPr-CH*);  $^{19}\text{F}$  NMR (470.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta=-78.5$  (m, 6F, CF<sub>3</sub>), -79.7 (m, CF<sub>3</sub>), -91.3 (d, d, m, 1F,  $^1J_{\text{P-F}}=844$  Hz,  $^2J_{\text{P-F}}=103$  Hz, PF), -101.9 (d, d, m, 1F,  $^1J_{\text{P-F}}=877$  Hz,  $^2J_{\text{P-F}}=103$  Hz, PF), -104.7 (d, d, 2F,  $^2J_{\text{P-F}}=296$  Hz,  $^2J_{\text{P-F}}=107$  Hz, CF<sub>2</sub>), -114.3 (d, m, 2F,  $^2J_{\text{P-F}}=99$  Hz, CF<sub>2</sub>), -117.5 (d, m, 2F,  $^2J_{\text{P-F}}=296$  Hz, CF<sub>2</sub>);  $^{31}\text{P}$  NMR (202.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta=-146.7$  (d, d, t, t,  $^1J_{\text{P-F}}=877$  Hz,  $^1J_{\text{P-F}}=844$  Hz,  $^2J_{\text{P-F}}=107$  Hz,  $^2J_{\text{P-F}}=99$  Hz); IR ([cm<sup>-1</sup>]): 3166 (w), 2968 (w), 2938 (w), 2876 (w), 1593 (vw), 1557 (w), 1506 (vw), 1469 (w), 1390 (w), 1370 (w), 1353 (vw), 1293 (m), 1235 (m), 1209 (vs), 1189 (s), 1178 (vs), 1163 (vs), 1125 (s), 1115 (m), 1098 (m), 1086 (m), 1063 (m), 958 (m), 940 (m), 858 (w), 820 (m), 802 (m), 767 (w), 756 (w), 740 (m), 704 (w), 675 (w), 641 (w), 604 (vs), 566 (vs), 539 (m), 528 (s), 459 (w), 434 (m); elemental analysis calcd (%) for C<sub>33</sub>H<sub>37</sub>F<sub>17</sub>N<sub>2</sub>P: C 48.60, H 4.57, N 3.43; found: C 48.64, H 4.83, N 3.43.

### *a*tBu<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (3j)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (700 μL, 2.97 mmol) was added at room temperature to a solution of *a*tBu<sub>2</sub>Im (1j) (534 mg, 2.96 mmol) in Et<sub>2</sub>O (5 mL). The mixture was stirred for 30 min at room temperature and left standing. Over a period of 4 weeks, crystals were formed in the glass vessel. The crystals were collected by filtration, washed with hexane (2×5 mL) and dried *in vacuo* to give 3j (1.03 g, 1.70 mmol, 57%) as a colorless solid.  $^1\text{H}$  NMR (400.5 MHz, CD<sub>3</sub>CN, 298 K):  $\delta=8.20$  (m, 1H, P-C-CH), 7.63 (br, 1H, N-CH-N), 1.73 (t, 9H,  $^{\text{T}}J_{\text{F-H}}=2.4$  Hz, P-C-N-C(CH<sub>3</sub>)<sub>3</sub>), 1.56 (s, 9H, CH-N-C(CH<sub>3</sub>)<sub>3</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.7 MHz, CD<sub>3</sub>CN, 298 K):  $\delta=147.4$  (P-C-N), 134.9 (P-C-CH), 127.0 (N-CH-N), 67.6 (P-C-N-C(CH<sub>3</sub>)<sub>3</sub>), 60.3 (CH-N-C(CH<sub>3</sub>)<sub>3</sub>), 31.6 (P-C-N-C(CH<sub>3</sub>)<sub>3</sub>), 29.1 (CH-N-C(CH<sub>3</sub>)<sub>3</sub>);  $^{19}\text{F}$  NMR (376.8 MHz, CD<sub>3</sub>CN, 298 K):  $\delta=-79.0$  (m, 6F, CF<sub>3</sub>), -80.3 (m, 3F, CF<sub>3</sub>), -88.1 (d, d, m, 1F,  $^1J_{\text{P-F}}\approx 860$  Hz,  $^2J_{\text{P-F}}=104$  Hz, PF) overlap

with  $-90.3$  (d, d, m, 1F,  $^1J_{P-F} \approx 880$  Hz,  $^2J_{F-F} = 104$  Hz, PF),  $-101.0$  (d, d, m, 2F,  $^2J_{P-F} = 292$  Hz,  $^2J_{P-F} = 113$  Hz, CF<sub>2</sub>),  $-115.3$  (d, m, 2F,  $^2J_{P-F} = 100$  Hz, CF<sub>2</sub>),  $-119.0$  (d, m, 2F,  $^2J_{F-F} = 292$  Hz, CF<sub>2</sub>);  $^{31}\text{P}$  NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = -146.3$  (d, d, t, t,  $^1J_{P-F} \approx 880$  Hz,  $^1J_{P-F} \approx 860$  Hz,  $^2J_{P-F} = 113$  Hz,  $^2J_{P-F} = 100$  Hz); IR ([cm<sup>-1</sup>]): 3208 (w), 3196 (w), 2995 (w), 2946 (vw), 1674 (vw), 1564 (w), 1507 (vw), 1470 (vw), 1411 (vw), 1396 (vw), 1381 (w), 1295 (m), 1266 (w), 1227 (s), 1208 (s), 1177 (vs), 1139 (s), 1124 (s), 1114 (s), 1089 (s), 1063 (m), 1004 (w), 950 (m), 857 (w), 819 (m), 811 (m), 739 (m), 700 (w), 654 (w), 642 (w), 621 (m), 598 (m), 566 (vs), 535 (m), 495 (w), 453 (w), 432 (w); elemental analysis calcd (%) for C<sub>17</sub>H<sub>20</sub>F<sub>17</sub>N<sub>2</sub>P: C 33.68, H 3.33, N 4.62; found: C 33.85, H 3.11, N 4.92.

#### [tBuMelm-H][Melm-PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>] (4 m)

A solution of tBuMelm (1 m) (681 mg, 4.93 mmol) in Et<sub>2</sub>O (15 mL) was cooled to 0 °C and added to a solution of PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (1.05 g, 2.46 mmol) in Et<sub>2</sub>O (5 mL) at 0 °C *via* cannula. The resulting solution was stirred for 30 min at room temperature. All volatiles were removed under reduced pressure and the remaining solid was dried *in vacuo* to give 4 m (1.32 g, 2.04 mmol, 83%) as a brown solid.  $^1\text{H}$  NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 8.68$  (br, 1H, N-CH-N), 6.84 (br, 1H, N-CH), 6.48 (br, 1H, CH<sub>3</sub>-N-CH<sub>anion</sub>), 6.16 (br, 1H, (CH<sub>3</sub>)<sub>3</sub>-C-N-CH), 6.04 (br, 1H, CH<sub>3</sub>-N-CH<sub>cation</sub>), 3.71 (d, 3H,  $^1J_{F-H} = 6.6$  Hz, N-CH<sub>3anion</sub>), 3.26 (s, 3H, N-CH<sub>3cation</sub>), 0.98 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 154.9$  (N-C-N), 134.5 (N-CH-N), 125.0 (P-N-CH), 123.7 (CH<sub>3</sub>-N-CH<sub>anion</sub>), 123.1 (CH<sub>3</sub>-N-CH<sub>cation</sub>), 118.8 ((CH<sub>3</sub>)<sub>3</sub>C-N-CH) 59.8 ((CH<sub>3</sub>)<sub>3</sub>C), 36.2 (N-CH<sub>3anion</sub>), 35.9 (N-CH<sub>3cation</sub>), 28.9 (C(CH<sub>3</sub>)<sub>3</sub>);  $^{19}\text{F}$  NMR (470.6 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = -78.1$  (m, 3F, CF<sub>3</sub>),  $-78.4$  (m, 6F, CF<sub>3</sub>),  $-97.6$  (d, d, m, 1F,  $^1J_{P-F} = 846$  Hz,  $^2J_{F-F} = 106$  Hz, PF),  $-98.8$  (d, d, m, 1F,  $^1J_{P-F} = 857$  Hz,  $^2J_{F-F} = 106$  Hz, PF),  $-113.3$  (d, m, 2F,  $^2J_{F-F} = 293$  Hz,  $^2J_{P-F} = 98$  Hz, CF<sub>2</sub>),  $-113.7$  (d, d, 2F,  $^2J_{F-F} = 293$  Hz,  $^2J_{P-F} = 103$  Hz, PF),  $-117.0$  (d, m, 2F,  $^2J_{F-F} = 293$  Hz, CF<sub>2</sub>);  $^{31}\text{P}$  NMR (202.4 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = -145.7$  (d, d, t, t,  $^1J_{P-F} = 857$  Hz,  $^1J_{P-F} = 846$  Hz,  $^2J_{P-F} = 103$  Hz,  $^2J_{P-F} = 98$  Hz); IR ([cm<sup>-1</sup>]): 3122 (vw), 2990 (vw), 1594 (w), 1571 (w), 1548 (w), 1518 (vw), 1473 (vw), 1448 (w), 1433 (vw), 1410 (w), 1382 (w), 1293 (m), 1282 (m), 1211 (vs), 1178 (vs), 1157 (s), 1137 (m), 1112 (vs), 1098 (s), 1068 (s), 1049 (m), 945 (s), 914 (vw), 863 (vw), 795 (s), 753 (m), 738 (m), 687 (m), 661 (m), 640 (w), 632 (w), 614 (vs), 600 (s), 571 (s), 560 (vs), 531 (vs), 453 (w), 432 (m); ESI-MS (Orbitrap)  $m/z$  [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>15</sub>N<sub>2</sub>: 139.1235, found: 139.1228.  $m/z$  [A]<sup>-</sup> calcd for C<sub>10</sub>F<sub>5</sub>N<sub>2</sub>P: 506.9919, found: 506.9915; elemental analysis calcd (%) for C<sub>18</sub>H<sub>20</sub>F<sub>17</sub>N<sub>4</sub>P: C 33.45, H 3.12, N 8.67; found: C 33.38, H 3.26, N 8.11.

#### Dipp<sub>2</sub>Im-(CH<sub>2</sub>)<sub>4</sub>O-PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (6 i)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (105  $\mu\text{L}$ , 0.45 mmol) was added at room temperature to a solution of Dipp<sub>2</sub>Im (1 i) (171 mg, 0.44 mmol) and THF (35.7  $\mu\text{L}$ , 0.44 mmol) in Et<sub>2</sub>O (5 mL). The resulting solution was stirred overnight at room temperature. The precipitate formed was collected by filtration, washed with hexane (2  $\times$  5 mL) and dried *in vacuo* to give 6 i (151 mg, 0.17 mmol, 39%) as a colorless solid.  $^1\text{H}$  NMR (500.1 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = 7.73$  (s, 2H, N-CH-CH-N), 7.69 (t, 2H,  $^3J_{H-H} = 7.8$  Hz, aryl-C<sub>para</sub>H), 7.51 (d, 4H,  $^3J_{H-H} = 7.8$  Hz, aryl-C<sub>meta</sub>H), 3.61 (m, 2H, O-CH<sub>2</sub>), 2.45 (m, 2H, (N-C-N)-CH<sub>2</sub>), 2.30 (sept, 4H,  $^3J_{H-H} = 6.8$  Hz, *iPr*-CH), 1.30 (d, 12H,  $^3J_{H-H} = 6.8$  Hz, *iPr*-CH<sub>3</sub>), 1.25 (m, 2H, (N-C-N)-CH<sub>2</sub>-CH<sub>2</sub>), 1.20 (d, 12H,  $^3J_{H-H} = 6.8$  Hz, *iPr*-CH<sub>3</sub>), 1.14 (m, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (125.8 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = 150.5$  (N-C-N), 146.2 (aryl-C<sub>ortho</sub>), 133.3 (aryl-C<sub>para</sub>), 130.2 (aryl-C<sub>ipso</sub>), 126.2 (aryl-C<sub>meta</sub>), 125.9 (N-CH-CH-N), 66.2 (O-CH<sub>2</sub>), 31.8 (O-CH<sub>2</sub>-CH<sub>2</sub>), 30.1 (*iPr*-CH), 25.6 (*iPr*-CH<sub>3</sub>), 25.2 ((N-C-N)-CH<sub>2</sub>), 24.0 ((N-C-N)-CH<sub>2</sub>-CH<sub>2</sub>), 22.6 (*iPr*-CH<sub>3</sub>);  $^{19}\text{F}$  NMR (470.6 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = -80.4$  (m, 3F, CF<sub>3</sub>),  $-81.5$  (m, 6F, CF<sub>3</sub>),  $-94.3$  (d, m, 2F,

$^1J_{P-F} = 894$  Hz, PF<sub>2</sub>),  $-113.3$  (d, m, 2F,  $^2J_{P-F} = 83$  Hz, CF<sub>2</sub>),  $-113.9$  (d, m, 4F,  $^2J_{P-F} = 87$  Hz, CF<sub>2</sub>);  $^{31}\text{P}$  NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = -149.8$  (t, quint, t,  $^1J_{P-F} = 894$  Hz,  $^2J_{P-F} = 87$  Hz,  $^2J_{P-F} = 83$  Hz); IR ([cm<sup>-1</sup>]): 3188 (vw), 2969 (w), 1591 (vw), 1561 (vw), 1498 (w), 1478 (vw), 1463 (vw), 1392 (w), 1371 (w), 1350 (vw), 1302 (m), 1276 (vw), 1212 (vs), 1173 (vs), 1117 (s), 1098 (s), 1077 (s), 1046 (m), 982 (w), 965 (m), 953 (m), 935 (w), 841 (vw), 798 (s), 759 (m), 741 (m), 731 (w), 700 (w), 675 (s), 640 (w), 605 (vs), 575 (m), 536 (m), 454 (w), 426 (m); elemental analysis calcd (%) for C<sub>37</sub>H<sub>44</sub>F<sub>17</sub>N<sub>2</sub>OP: C 50.12, H 5.00, N 3.16; found: C 49.90, H 5.37, N 3.44.

#### Dipp<sub>2</sub>Im<sup>H<sup>2</sup></sup>-(CH<sub>2</sub>)<sub>4</sub>O-PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (6 k)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (94.6  $\mu\text{L}$ , 402  $\mu\text{mol}$ ) was added at room temperature to a solution of Dipp<sub>2</sub>Im<sup>H<sup>2</sup></sup> (1 k) (157 mg, 402  $\mu\text{mol}$ ) and THF (32.8  $\mu\text{L}$ , 405  $\mu\text{mol}$ ) in Et<sub>2</sub>O (5 mL). The resulting solution was stirred overnight at room temperature. The precipitate formed was collected by filtration, washed with hexane (2  $\times$  5 mL) and dried *in vacuo* to give 6 k (233 mg, 262  $\mu\text{mol}$ , 65%) as a colorless solid.  $^1\text{H}$  NMR (500.1 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = 7.57$  (t, 2H,  $^3J_{H-H} = 7.8$  Hz, aryl-C<sub>para</sub>H), 7.43 (d, 4H,  $^3J_{H-H} = 7.8$  Hz, aryl-C<sub>meta</sub>H), 4.31 (s, 4H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 3.58 (m, 2H, O-CH<sub>2</sub>), 2.98 (sept, 4H,  $^3J_{H-H} = 6.8$  Hz, *iPr*-CH), 2.04 (m, (N-C-N)-CH<sub>2</sub>), 1.33 (d, 12H,  $^3J_{H-H} = 6.8$  Hz, *iPr*-CH<sub>3</sub>), 1.32 (d, 12H,  $^3J_{H-H} = 6.8$  Hz, *iPr*-CH<sub>3</sub>), 1.21 (m, 2H, (N-C-N)-CH<sub>2</sub>-CH<sub>2</sub>), 1.07 (m, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (125.8 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = 171.7$  (N-C-N), 147.3 (aryl-C<sub>ortho</sub>), 132.5 (aryl-C<sub>para</sub>), 130.5 (aryl-C<sub>ipso</sub>), 126.6 (aryl-C<sub>meta</sub>), 66.1 (O-CH<sub>2</sub>), 53.4 (N-CH<sub>2</sub>-CH<sub>2</sub>-N), 32.0 (O-CH<sub>2</sub>-CH<sub>2</sub>), 29.8 (*iPr*-CH<sub>3</sub>), 26.4 ((N-C-N)-CH<sub>2</sub>), 26.3 (*iPr*-CH<sub>3</sub>), 23.5 (*iPr*-CH<sub>3</sub>), 22.4 ((N-C-N)-CH<sub>2</sub>-CH<sub>2</sub>);  $^{19}\text{F}$  NMR (470.6 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = -80.3$  (m, 3F, CF<sub>3</sub>),  $-81.4$  (m, 6F, CF<sub>3</sub>),  $-94.2$  (d, m, 2F,  $^1J_{P-F} = 890$  Hz, PF<sub>2</sub>),  $-113.2$  (d, m, 2F,  $^2J_{P-F} = 85$  Hz, CF<sub>2</sub>),  $-113.9$  (d, m, 4F,  $^2J_{P-F} = 90$  Hz, CF<sub>2</sub>);  $^{31}\text{P}$  NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = -149.8$  (t, quint, t,  $^1J_{P-F} = 890$  Hz,  $^2J_{P-F} = 90$  Hz,  $^2J_{P-F} = 85$  Hz); IR ([cm<sup>-1</sup>]): 2966 (m), 2933 (w), 2911 (w), 2876 (w), 1633 (vw), 1598 (w), 1571 (m), 1536 (w), 1467 (w), 1457 (w), 1392 (w), 1369 (w), 1344 (vw), 1321 (w), 1305 (m), 1294 (m), 1280 (w), 1211 (vs), 1176 (vs), 1115 (s), 1098 (vs), 1067 (m), 1056 (m), 984 (w), 957 (m), 936 (w), 893 (vw), 803 (s), 794 (m), 761 (m), 741 (w), 689 (m), 637 (w), 603 (vs), 575 (s), 554 (m), 537 (s), 453 (w), 430 (m); elemental analysis calcd (%) for C<sub>37</sub>H<sub>46</sub>F<sub>17</sub>N<sub>2</sub>OP: C 50.00, H 5.22, N 3.15; found: C 50.18, H 5.35, N 3.22.

#### [iPr<sub>2</sub>Im<sup>Me</sup>-H][PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>2</sub>CN)] (7 f)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (0.45 mL, 1.91 mmol) was added at room temperature to a solution of *iPr*<sub>2</sub>Im<sup>Me</sup> (1 f) (340 mg, 1.89 mmol) in CH<sub>3</sub>CN (10 mL). The resulting solution was stirred for 3 h at room temperature. All volatiles were removed under reduced pressure and the residue dried *in vacuo* to give 7 f (1.09 g, 1.68 mmol, 89%) as a pale yellow solid.  $^1\text{H}$  NMR (500.1 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = 8.33$  (br, 1H, N-CH-N), 4.48 (sept, 2H,  $^3J_{H-H} = 6.7$  Hz, *iPr*-CH), 2.33 (d, d, m, 2H,  $^2J_{P-H} = 15$  Hz, CH<sub>2</sub>), 2.23 (s, 6H, N-C-CH<sub>3</sub>), 1.48 (d, 12H,  $^3J_{H-H} = 6.7$  Hz, *iPr*-CH<sub>3</sub>);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (125.8 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = 130.2$  (N-CH-N), 127.7 (N-C-CH<sub>3</sub>), 120.2 (N=C), 51.2 (*iPr*-CH), 28.8 (CH<sub>2</sub>), 22.7 (*iPr*-CH<sub>3</sub>), 8.6 (N-C-CH<sub>3</sub>);  $^{19}\text{F}$  NMR (470.5 MHz, CD<sub>3</sub>CN, 238 K):  $\delta = -79.8$  (m, 3F, CF<sub>3</sub>),  $-80.2$  (m, 6F, CF<sub>3</sub>),  $-90.9$  (d, d, m, 1F,  $^1J_{P-F} = 815$  Hz,  $^2J_{F-F} = 97$  Hz, PF),  $-105.0$  (d, d, 1F,  $^1J_{P-F} = 858$  Hz,  $^2J_{F-F} = 97$  Hz, PF),  $-111.9$  (d, d, q, 2F,  $^2J_{F-F} = 295$  Hz,  $^2J_{P-F} = 85$  Hz,  $^3J_{F-F} = 8.3$  Hz, PF),  $-115.6$  (d, m, 2F,  $^2J_{P-F} = 99$  Hz, PF),  $-118.6$  (d, m, 2F,  $^2J_{F-F} = 295$  Hz, CF<sub>2</sub>);  $^{31}\text{P}$  NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = -149.1$  (m); IR ([cm<sup>-1</sup>]): 3141 (w), 3066 (w), 2993 (w), 2946 (w), 2248 (w), 1630 (w), 1557 (w), 1505 (vw), 1467 (w), 1446 (w), 1428 (w), 1399 (w), 1382 (w), 1342 (w), 1293 (m), 1209 (vs), 1168 (vs), 1127 (vs), 1118 (vs), 1099 (m), 1071 (s), 1053 (m), 951 (m), 895 (vs), 843 (m), 800 (s), 763 (w), 738 (m), 726 (w), 682 (m), 657 (w),

639 (m), 620 (m), 593 (m), 562 (m), 552 (m), 522 (s), 431 (m); ESI-MS (Orbitrap)  $m/z$   $[M]^+$  calcd for  $C_{11}H_{21}N_2$ : 181.1705, found: 181.1693.  $m/z$   $[A]^-$  calcd for  $C_8H_2F_{17}NP$ : 465.9653, found: 465.9638; elemental analysis calcd (%) for  $C_{19}H_{23}F_{17}N_3P$ : C 35.25, H 3.58, N 6.49; found: C 35.19, H 3.48, N 6.56.

### [Dipp<sub>2</sub>Im-H][PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>2</sub>CN)] (7i)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (103  $\mu$ L, 438  $\mu$ mol) was added at room temperature to a solution of Dipp<sub>2</sub>Im (1i) (170 mg, 437  $\mu$ mol) and CH<sub>3</sub>CN (60.0  $\mu$ L, 1.15 mmol) in Et<sub>2</sub>O (5 mL). The resulting solution was stirred for 3 h at room temperature. All volatiles were removed under reduced pressure and the residue was suspended in hexane (5 mL), collected by filtration, washed with hexane (5 mL) and dried *in vacuo* to give 7i (314 mg, 367  $\mu$ mol, 84%) as a colorless solid. <sup>1</sup>H NMR (500.1 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 8.92 (t, 1H, <sup>4</sup>J<sub>H-H</sub> = 1.6 Hz, N-CH-N), 7.86 (d, 2H, <sup>4</sup>J<sub>H-H</sub> = 1.6 Hz, N-CH-CH-N), 7.66 (t, 2H, <sup>3</sup>J<sub>H-H</sub> = 7.9 Hz, aryl-C<sub>para</sub>H), 7.48 (d, 4H, <sup>3</sup>J<sub>H-H</sub> = 7.9 Hz, aryl-C<sub>meta</sub>H), 2.42 (sept, 4H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, *i*Pr-CH), 2.33 (d<sub>br</sub>, 2H, <sup>2</sup>J<sub>P-H</sub> = 15 Hz, CH<sub>2</sub>), 1.27 (d, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>), 1.20 (d, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (125.8 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 146.3 (aryl-C<sub>ortho</sub>), 138.7 (N-CH-N), 133.2 (aryl-C<sub>para</sub>), 130.8 (aryl-C<sub>ipso</sub>), 127.1 (N-CH-CH-N), 125.7 (aryl-C<sub>meta</sub>), 120.2 (N≡C), 29.9 (*i*Pr-CH), 28.8 (CH<sub>2</sub>), 24.5 (*i*Pr-CH<sub>3</sub>), 23.8 (*i*Pr-CH<sub>3</sub>); <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN, 238 K):  $\delta$  = -79.8 (m, 3F, CF<sub>3</sub>), -80.2 (m, 6F, CF<sub>3</sub>), -90.9 (d, d, 1F, <sup>1</sup>J<sub>P-F</sub> = 814 Hz, <sup>2</sup>J<sub>F-F</sub> = 95 Hz, PF), -105.0 (d, d, 1F, <sup>1</sup>J<sub>P-F</sub> = 855 Hz, <sup>2</sup>J<sub>F-F</sub> = 95 Hz, PF), -111.9 (d, d, q, 2F, <sup>2</sup>J<sub>F-F</sub> = 295 Hz, <sup>2</sup>J<sub>P-F</sub> = 85 Hz, <sup>3</sup>J<sub>F-F</sub> = 8.3 Hz, CF<sub>2</sub>), -115.6 (d, m, 2F, <sup>2</sup>J<sub>P-F</sub> = 100 Hz, CF<sub>2</sub>), -118.6 (d, m, 2F, <sup>2</sup>J<sub>F-F</sub> = 295 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = -149.1 (m); IR ([cm<sup>-1</sup>]): 3157 (vw), 3097 (vw), 3032 (vw), 2967 (w), 2933 (vw), 2876 (vw), 2250 (w), 1607 (vw), 1538 (w), 1465 (w), 1427 (vw), 1391 (vw), 1370 (w), 1353 (vw), 1330 (w), 1296 (m), 1258 (w), 1214 (vs), 1179 (vs), 1171 (vs), 1134 (m), 1117 (s), 1102 (m), 1094 (m), 1077(s), 1066 (s), 947 (m), 894 (w), 847 (m), 803 (s), 755 (m), 740 (m), 727 (w), 681 (s), 639 (w), 620 (m), 600 (m), 555 (s), 524 (s), 431 (m); ESI-MS (Orbitrap)  $m/z$   $[M]^+$  calcd for C<sub>27</sub>H<sub>37</sub>N<sub>2</sub>: 389.2957, found: 389.2938.  $m/z$   $[A]^-$  calcd for C<sub>8</sub>H<sub>2</sub>F<sub>17</sub>NP: 465.9653, found: 465.9645; elemental analysis calcd (%) for C<sub>35</sub>H<sub>41</sub>F<sub>17</sub>N<sub>3</sub>P: C 49.13, H 4.59, N 4.91; found: C 48.89, H 4.86, N 4.89.

### [tBu<sub>2</sub>Im-H][PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>2</sub>CN)] (7j)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (600  $\mu$ L, 2.55 mmol) was added at room temperature to a solution of tBu<sub>2</sub>Im (1j) (460 mg, 2.55 mmol) and CH<sub>3</sub>CN (140  $\mu$ L, 2.68 mmol) in Et<sub>2</sub>O (8 mL). The resulting solution was stirred for 3 h at room temperature. The precipitate formed was collected by filtration, washed with hexane (5 mL) and dried *in vacuo* to give 7j (921 mg, 1.42 mmol, 56%) as a colorless solid. <sup>1</sup>H NMR (500.1 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 8.41 (t, 1H, <sup>4</sup>J<sub>H-H</sub> = 1.8 Hz, N-CH-N), 7.56 (d, 2H, <sup>4</sup>J<sub>H-H</sub> = 1.8 Hz, N-CH-CH-N), 2.33 (d<sub>br</sub>, 2H, <sup>2</sup>J<sub>P-H</sub> = 15 Hz, CH<sub>2</sub>), 1.62 (s, 18H, CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (125.8 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 132.6 (N-CH-N), 121.2 (N-CH-CH-N), 120.2 (N≡C), 61.2 (C(CH<sub>3</sub>)<sub>3</sub>), 29.7 (CH<sub>3</sub>), 28.8 (CH<sub>2</sub>); <sup>19</sup>F NMR (470.5 MHz, CD<sub>3</sub>CN, 238 K):  $\delta$  = -79.8 (m, 3F, CF<sub>3</sub>), -80.2 (m, 6F, CF<sub>3</sub>), -90.9 (d, d, 1F, <sup>1</sup>J<sub>P-F</sub> = 814 Hz, <sup>2</sup>J<sub>F-F</sub> = 96 Hz, PF), -105.0 (d, d, 1F, <sup>1</sup>J<sub>P-F</sub> = 856 Hz, <sup>2</sup>J<sub>F-F</sub> = 96 Hz, PF), -111.9 (d, d, q, 2F, <sup>2</sup>J<sub>F-F</sub> = 295 Hz, <sup>2</sup>J<sub>P-F</sub> = 86 Hz, <sup>3</sup>J<sub>F-F</sub> = 8.3 Hz, CF<sub>2</sub>), -115.7 (d, m, 2F, <sup>2</sup>J<sub>P-F</sub> = 100 Hz, CF<sub>2</sub>), -118.6 (d, m, 2F, <sup>2</sup>J<sub>F-F</sub> = 295 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = -149.1 (m); IR ([cm<sup>-1</sup>]): 3178 (w), 3159 (w), 2999 (w), 2239 (w), 1593 (w), 1562 (w), 1540 (m), 1469 (w), 1430 (w), 1409 (w), 1380 (m), 1295 (m), 1202 (vs), 1189 (vs), 1167 (vs), 1129 (vs), 1118 (vs), 1073 (s), 1056 (m), 946 (s), 844 (m), 831 (m), 797 (vs), 737 (m), 680 (s), 653 (m), 639 (w), 597 (m), 555 (vs), 522 (vs), 431 (m); ESI-MS (Orbitrap)  $m/z$   $[M]^+$  calcd for C<sub>11</sub>H<sub>21</sub>N<sub>2</sub>: 181.1705, found: 181.1696.  $m/z$   $[A]^-$  calcd for C<sub>8</sub>H<sub>2</sub>F<sub>17</sub>NP: 465.9653, found: 465.9646; elemental analysis

calcd (%) for C<sub>19</sub>H<sub>23</sub>F<sub>17</sub>N<sub>3</sub>P: C 35.25, H 3.58, N 6.49; found: C 35.36, H 3.80, N 6.48.

### [Dipp<sub>2</sub>Im<sup>H2</sup>-H][PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>2</sub>CN)] (7k)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (85.0  $\mu$ L, 361  $\mu$ mol) was added at room temperature to a solution of Dipp<sub>2</sub>Im<sup>H2</sup> (1k) (141 mg, 361  $\mu$ mol) in CH<sub>3</sub>CN (5 mL). The resulting solution was stirred for 2 h at room temperature. All volatiles were removed under reduced pressure and the residue was suspended in hexane (5 mL), collected by filtration, washed with hexane (2  $\times$  5 mL) and dried *in vacuo* to give 7k (243 mg, 283  $\mu$ mol, 78%) as an off-white solid. <sup>1</sup>H NMR (500.1 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 8.30 (br, 1H, N-CH-N), 7.54 (t, 2H, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, aryl-C<sub>para</sub>H), 7.40 (d, 4H, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, aryl-C<sub>meta</sub>H), 4.45 (br, 4H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 3.09 (sept, 4H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, *i*Pr-CH), 2.33 (d, m, 2H, <sup>2</sup>J<sub>P-H</sub> = 15 Hz, P-CH<sub>2</sub>), 1.37 (d, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>), 1.23 (d, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, *i*Pr-CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (125.8 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 159.8 (N-CH-N), 147.6 (aryl-C<sub>ortho</sub>), 132.5 (aryl-C<sub>para</sub>), 130.4 (aryl-C<sub>ipso</sub>), 126.0 (aryl-C<sub>meta</sub>), 120.1 (N≡C), 54.9 (N-CH<sub>2</sub>-CH<sub>2</sub>-N), 29.7 (*i*Pr-CH), 28.8 (P-CH<sub>2</sub>), 25.2 (*i*Pr-CH<sub>3</sub>), 24.0 (*i*Pr-CH<sub>3</sub>); <sup>19</sup>F NMR (470.5 MHz, CD<sub>3</sub>CN, 238 K):  $\delta$  = -79.8 (m, 3F, CF<sub>3</sub>), -80.2 (m, 6F, CF<sub>3</sub>), -90.9 (d, d, m, 1F, <sup>1</sup>J<sub>P-F</sub> = 814 Hz, <sup>2</sup>J<sub>F-F</sub> = 96 Hz, PF), -105.0 (d, d, 1F, <sup>1</sup>J<sub>P-F</sub> = 855 Hz, <sup>2</sup>J<sub>F-F</sub> = 96 Hz, PF), -111.9 (d, d, q, 2F, <sup>2</sup>J<sub>F-F</sub> = 295 Hz, <sup>2</sup>J<sub>P-F</sub> = 85 Hz, <sup>3</sup>J<sub>F-F</sub> = 8.3 Hz, CF<sub>2</sub>), -115.6 (d, m, 2F, <sup>2</sup>J<sub>P-F</sub> = 100 Hz, CF<sub>2</sub>), -118.6 (d, m, 2F, <sup>2</sup>J<sub>F-F</sub> = 295 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = -149.1 (m); IR ([cm<sup>-1</sup>]): 3024 (w), 2970 (w), 2934 (w), 2877 (w), 2249 (w), 1633 (s), 1587 (w), 1503 (vw), 1464 (w), 1447 (w), 1392 (w), 1370 (w), 1325 (w), 1297 (m), 1272 (m), 1214 (vs), 1178 (vs), 1132 (m), 1117 (s), 1099 (s), 1078 (s), 1057 (m), 1015 (w), 952 (m), 880 (vw), 847 (w), 800 (s), 760 (w), 740 (w), 729 (w), 691 (m), 680 (m), 639 (w), 620 (w), 600 (m), 555 (s), 524 (s), 483 (w), 431 (m); ESI-MS (Orbitrap)  $m/z$   $[M]^+$  calcd for C<sub>27</sub>H<sub>39</sub>N<sub>2</sub>: 391.3113, found: 391.3089.  $m/z$   $[A]^-$  calcd for C<sub>8</sub>H<sub>2</sub>F<sub>17</sub>NP: 465.9653, found: 465.9636; elemental analysis calcd (%) for C<sub>35</sub>H<sub>41</sub>F<sub>17</sub>N<sub>3</sub>P: C 49.01, H 4.82, N 4.90; found: C 49.08, H 4.80, N 5.08.

### [Mes<sub>2</sub>Im-H][PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>2</sub>CN)] (7l)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (160  $\mu$ L, 680  $\mu$ mol) was added at room temperature to a solution of Mes<sub>2</sub>Im (1l) (200 mg, 657  $\mu$ mol) in CH<sub>3</sub>CN (3 mL). The resulting solution was stirred for 3 h at room temperature. All volatiles were removed under reduced pressure and the residue was redissolved in Et<sub>2</sub>O (2 mL). Hexane (10 mL) was added, and the resulting solution was stored at -30 °C. Overnight, crystals were formed in the glass vessel. The crystals were collected by filtration, washed with hexane (5 mL) and dried *in vacuo* to give 7l (317 mg, 411  $\mu$ mol, 63%) as a pale yellow solid. <sup>1</sup>H NMR (500.1 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 8.69 (t, 1H, <sup>4</sup>J<sub>H-H</sub> = 1.5 Hz, N-CH-N), 7.71 (d, 2H, <sup>4</sup>J<sub>H-H</sub> = 1.5 Hz, N-CH-CH-N), 7.17 (s, 4H, aryl-C<sub>meta</sub>H), 2.37 (s, 6H, aryl-C<sub>para</sub>-CH<sub>3</sub>), 2.33 (d<sub>br</sub>, 2H, <sup>2</sup>J<sub>P-H</sub> = 15 Hz, CH<sub>2</sub>), 2.12 (s, 12H, aryl-C<sub>ortho</sub>-CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (125.8 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 142.7 (aryl-C<sub>para</sub>), 138.4 (N-CH-N), 135.6 (aryl-C<sub>ipso</sub>), 131.7 (aryl-C<sub>ortho</sub>), 130.6 (aryl-C<sub>meta</sub>), 125.9 (N-CH-CH-N), 120.2 (N≡C), 28.8 (CH<sub>2</sub>), 21.2 (aryl-C<sub>para</sub>-CH<sub>3</sub>), 17.5 (aryl-C<sub>ortho</sub>-CH<sub>3</sub>); <sup>19</sup>F NMR (470.5 MHz, CD<sub>3</sub>CN, 238 K):  $\delta$  = -79.8 (m, 3F, CF<sub>3</sub>), -80.2 (m, 6F, CF<sub>3</sub>), -91.0 (d, d, m, 1F, <sup>1</sup>J<sub>P-F</sub> = 816 Hz, <sup>2</sup>J<sub>F-F</sub> = 94 Hz, PF), -105.0 (d, d, 1F, <sup>1</sup>J<sub>P-F</sub> = 852 Hz, <sup>2</sup>J<sub>F-F</sub> = 94 Hz, PF), -111.9 (d, d, q, 2F, <sup>2</sup>J<sub>F-F</sub> = 295 Hz, <sup>2</sup>J<sub>P-F</sub> = 84 Hz, <sup>3</sup>J<sub>F-F</sub> = 8.3 Hz, CF<sub>2</sub>), -115.6 (d, m, 2F, <sup>2</sup>J<sub>P-F</sub> = 100 Hz, CF<sub>2</sub>), -118.6 (d, m, 2F, <sup>2</sup>J<sub>F-F</sub> = 295 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = -149.1 (m); IR ([cm<sup>-1</sup>]): 3150 (w), 2927 (vw), 2244 (w), 1607 (w), 1546 (m), 1481 (w), 1455 (w), 1429 (w), 1386 (vw), 1295 (m), 1221 (vs), 1208 (vs), 1189 (vs), 1175 (vs), 1131 (s), 1116 (s), 1102 (m), 1092 (m), 1073 (s), 1052 (m), 949 (m), 855 (m), 847 (m), 812 (w), 786 (s), 750 (m), 739 (m), 726 (w), 712 (w), 678 (s), 639 (w), 618 (m), 598 (m), 557 (s), 539 (m), 524 (s), 455 (vw), 439 (w), 429 (m); ESI-MS (Orbitrap)  $m/z$   $[M]^+$  calcd for

$C_{21}H_{25}N_2$ : 305.2018, found: 305.1999.  $m/z$   $[A]^-$  calcd for  $C_8H_5F_{17}NP$ : 465.9653, found: 465.9647; elemental analysis calcd (%) for  $C_{29}H_{27}F_{17}N_3P$ : C 45.15, H 3.53, N 5.45; found: C 45.41, H 3.59, N 5.56.

### [Dipp<sub>2</sub>Im–H][PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(OC(=CH<sub>2</sub>)CH<sub>3</sub>)] (8i)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (92.8 μL, 394 μmol) was added at room temperature to a solution of Dipp<sub>2</sub>Im (1i) (153 mg, 394 μmol) and acetone (29.0 μL, 394 μmol) in Et<sub>2</sub>O (5 mL). The resulting solution was stirred for 4 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in hexane (5 mL), collected by filtration, washed with hexane (2 × 5 mL) and dried *in vacuo* to give **8i** (230 mg, 264 μmol, 67%) as an off-white solid. <sup>1</sup>H NMR (500.1 MHz, CD<sub>3</sub>CN, 298 K): δ = 8.33 (br, 1H, N–CH–N), 7.86 (s, 2H, N–CH–CH–N), 7.65 (t, 2H, <sup>3</sup>J<sub>H–H</sub> = 7.8 Hz, aryl-C<sub>para</sub>H), 7.48 (d, 4H, <sup>3</sup>J<sub>H–H</sub> = 7.8 Hz, aryl-C<sub>meta</sub>H), 4.29 (br, 1H, CH<sub>2</sub>), 3.88 (br, 1H, CH<sub>2</sub>), 2.42 (sept, 4H, <sup>3</sup>J<sub>H–H</sub> = 6.8 Hz, *i*Pr–CH), 1.69 (s, 3H, O–C–CH<sub>3</sub>), 1.27 (d, 12H, <sup>3</sup>J<sub>H–H</sub> = 6.8 Hz, *i*Pr–CH<sub>3</sub>), 1.19 (d, 12H, <sup>3</sup>J<sub>H–H</sub> = 6.8 Hz, *i*Pr–CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>3</sub>CN, 298 K): δ = 156.8 (O–C), 146.3 (aryl-C<sub>ortho</sub>), 138.7 (N–CH–N), 133.2 (aryl-C<sub>para</sub>), 130.8 (aryl-C<sub>ipso</sub>), 127.1 (N–CH–CH–N), 125.7 (aryl-C<sub>meta</sub>), 90.5 (CH<sub>2</sub>), 29.9 (*i*Pr–CH), 24.5 (*i*Pr–CH<sub>3</sub>), 23.8 (*i*Pr–CH<sub>3</sub>), 23.3 (O–C–CH<sub>3</sub>); <sup>19</sup>F NMR (470.5 MHz, CD<sub>3</sub>CN, 298 K): δ = –80.5 (m, 3F, CF<sub>3</sub>), –81.5 (m, 6F, CF<sub>3</sub>), –86.6 (d, m, 2F, <sup>1</sup>J<sub>P–F</sub> = 890 Hz, PF<sub>2</sub>), –114.0 (d, m, 6F, <sup>2</sup>J<sub>P–F</sub> = 94 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K): δ = –148.0 (t, sept, <sup>1</sup>J<sub>P–F</sub> = 892 Hz, <sup>2</sup>J<sub>P–F</sub> = 94 Hz); IR ([cm<sup>–1</sup>]): 3152 (vw), 2969 (w), 2934 (w), 2876 (vw), 1663 (w), 1540 (w), 1465 (w), 1391 (w), 1370 (w), 1353 (vw), 1330 (w), 1304 (m), 1258 (m), 1210 (vs), 1180 (vs), 1120 (s), 1097 (s), 1060 (m), 1036 (m), 956 (m), 891 (w), 859 (vw), 804 (m), 794 (m), 756 (m), 741 (w), 729 (w), 681 (w), 641 (m), 607 (vs), 577 (m), 536 (m), 490 (w), 434 (m); ESI-MS (Orbitrap)  $m/z$   $[M]^+$  calcd for C<sub>27</sub>H<sub>39</sub>N<sub>2</sub>: 389.2957, found: 389.2943.  $m/z$   $[A]^-$  calcd for C<sub>9</sub>H<sub>5</sub>F<sub>17</sub>OP: 482.9806, found: 482.9809; elemental analysis calcd (%) for C<sub>36</sub>H<sub>42</sub>F<sub>17</sub>N<sub>2</sub>OP: C 49.55, H 4.85, N 3.21; found: C 49.18, H 4.68, N 3.31.

### [tBu<sub>2</sub>Im–H][PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(OC(=CH<sub>2</sub>)CH<sub>3</sub>)] (8j)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (158 μL, 671 μmol) was added at room temperature to a solution of tBu<sub>2</sub>Im (1j) (121 mg, 671 μmol) and acetone (49.5 μL, 673 μmol) in Et<sub>2</sub>O (5 mL). The resulting solution was stirred for 3 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in hexane (5 mL), collected by filtration, washed with hexane (2 × 5 mL) and dried *in vacuo* to give **8j** (227 mg, 342 μmol, 51%) as a colorless solid. <sup>1</sup>H NMR (500.1 MHz, CD<sub>3</sub>CN, 298 K): δ = 8.42 (t, 1H, <sup>4</sup>J<sub>H–H</sub> = 1.7 Hz, N–CH–N), 7.56 (d, 2H, <sup>4</sup>J<sub>H–H</sub> = 1.7 Hz, N–CH–CH–N), 4.29 (br, 1H, CH<sub>2</sub>), 3.88 (br, 1H, CH<sub>2</sub>), 1.69 (s, 3H, O–C–CH<sub>3</sub>), 1.62 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>3</sub>CN, 298 K): δ = 156.8 (O–C), 132.6 (N–CH–N), 121.2 (N–CH–CH–N), 90.5 (CH<sub>2</sub>), 61.2 (C(CH<sub>3</sub>)<sub>3</sub>), 29.7 (CH<sub>3</sub>)<sub>3</sub>, 23.3 (O–C–CH<sub>3</sub>); <sup>19</sup>F NMR (470.5 MHz, CD<sub>3</sub>CN, 298 K): δ = –80.5 (m, 3F, CF<sub>3</sub>), –81.5 (m, 6F, CF<sub>3</sub>), –86.6 (d, m, 2F, <sup>1</sup>J<sub>P–F</sub> = 890 Hz, PF<sub>2</sub>), –114.0 (d, m, 6F, <sup>2</sup>J<sub>P–F</sub> = 92 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K): δ = –148.0 (t, sept, <sup>1</sup>J<sub>P–F</sub> = 885 Hz, <sup>2</sup>J<sub>P–F</sub> = 92 Hz); IR ([cm<sup>–1</sup>]): 3188 (w), 2990 (w), 2952 (w), 1634 (w), 1591 (vw), 1560 (vw), 1539 (w), 1470 (w), 1449 (vw), 1433 (vw), 1409 (vw), 1382 (m), 1301 (m), 1260 (m), 1206 (vs), 1168 (vs), 1116 (vs), 1089 (vs), 1055 (m), 1035 (m), 986 (w), 966 (m), 952 (s), 894 (w), 823 (m), 802 (s), 738 (m), 644 (s), 606 (vs), 575 (s), 535 (s), 491 (m), 456 (vw), 431 (m); ESI-MS (Orbitrap)  $m/z$   $[M]^+$  calcd for C<sub>11</sub>H<sub>21</sub>N<sub>2</sub>: 181.1705, found: 181.1695;  $m/z$   $[A-C_3H_4]^-$  calcd for C<sub>6</sub>H<sub>5</sub>F<sub>17</sub>OP: 442.9493, found: 444.9483; elemental analysis calcd (%) for C<sub>20</sub>H<sub>26</sub>F<sub>17</sub>N<sub>2</sub>OP: C 36.16, H 3.94, N 4.22; found: C 36.01, H 3.63, N 4.38.

### [Dipp<sub>2</sub>Im<sup>H2</sup>–H][PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(OC(=CH<sub>2</sub>)CH<sub>3</sub>)] (8k)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (91.0 μL, 387 μmol) was added at room temperature to a solution of Dipp<sub>2</sub>Im<sup>H2</sup> (1k) (151 mg, 387 μmol) and acetone (28.6 μL, 389 μmol) in Et<sub>2</sub>O (5 mL). The resulting solution was stirred for 3 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in hexane (5 mL), collected by filtration, washed with hexane (2 × 5 mL) and dried *in vacuo* to give **8m** (267 mg, 305 μmol, 79%) as a colorless solid. <sup>1</sup>H NMR (500.1 MHz, CD<sub>3</sub>CN, 298 K): δ = 8.30 (br, 1H, N–CH–N), 7.54 (t, 2H, <sup>3</sup>J<sub>H–H</sub> = 7.8 Hz, aryl-C<sub>para</sub>H), 7.40 (d, 4H, <sup>3</sup>J<sub>H–H</sub> = 7.8 Hz, aryl-C<sub>meta</sub>H), 4.45 (s, 4H, N–CH<sub>2</sub>–CH<sub>2</sub>–N), 4.29 (br, 1H, CH<sub>2</sub>), 3.88 (br, 1H, CH<sub>2</sub>), 3.09 (sept, 4H, <sup>3</sup>J<sub>H–H</sub> = 6.8 Hz, *i*Pr–CH), 1.69 (s, 3H, O–C–CH<sub>3</sub>), 1.37 (d, 12H, <sup>3</sup>J<sub>H–H</sub> = 6.8 Hz, *i*Pr–CH<sub>3</sub>), 1.23 (d, 12H, <sup>3</sup>J<sub>H–H</sub> = 6.8 Hz, *i*Pr–CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>3</sub>CN, 298 K): δ = 159.8 (N–CH–N), 156.8 (O–C), 147.6 (aryl-C<sub>ortho</sub>), 132.5 (aryl-C<sub>para</sub>), 130.4 (aryl-C<sub>ipso</sub>), 126.0 (aryl-C<sub>meta</sub>), 90.5 (O–C–CH<sub>2</sub>), 54.9 (N–CH<sub>2</sub>–CH<sub>2</sub>–N), 29.7 (*i*Pr–CH), 25.2 (*i*Pr–CH<sub>3</sub>), 24.0 (*i*Pr–CH<sub>3</sub>), 23.3 (O–C–CH<sub>3</sub>); <sup>19</sup>F NMR (470.5 MHz, CD<sub>3</sub>CN, 298 K): δ = –80.5 (m, 3F, CF<sub>3</sub>), –81.5 (m, 6F, CF<sub>3</sub>), –86.6 (d, m, 2F, <sup>1</sup>J<sub>P–F</sub> = 890 Hz, PF<sub>2</sub>), –114.0 (d, m, 6F, <sup>2</sup>J<sub>P–F</sub> = 92 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K): δ = –148.0 (t, sept, <sup>1</sup>J<sub>P–F</sub> = 885 Hz, <sup>2</sup>J<sub>P–F</sub> = 92 Hz); IR ([cm<sup>–1</sup>]): 3090 (vw), 2970 (w), 2933 (w), 2877 (w), 1632 (s), 1587 (w), 1500 (vw), 1464 (w), 1446 (w), 1392 (vw), 1371 (w), 1346 (vw), 1323 (w), 1305 (m), 1259 (m), 1217 (vs), 1178 (vs), 1121 (s), 1105 (m), 1086 (s), 1058 (m), 1046 (m), 1015 (w), 984 (w), 954 (m), 936 (w), 895 (vw), 882 (vw), 806 (vs), 759 (m), 741 (w), 646 (s), 607 (vs), 577 (m), 537 (m), 485 (w), 435 (m); ESI-MS (Orbitrap)  $m/z$   $[M]^+$  calcd for C<sub>27</sub>H<sub>39</sub>N<sub>2</sub>: 391.3113, found: 391.3096;  $m/z$   $[A]^-$  calcd for C<sub>9</sub>H<sub>5</sub>F<sub>17</sub>OP: 482.9806, found: 482.9794; elemental analysis calcd (%) for C<sub>36</sub>H<sub>44</sub>F<sub>17</sub>N<sub>2</sub>OP: C 49.43, H 5.07, N 3.20; found: C 49.27, H 5.37, N 3.44.

### [tBu<sub>2</sub>Im–H][PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>2</sub>CO<sub>2</sub>Et)] (9j)

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (200 μL, 850 μmol) was added at room temperature to a solution of tBu<sub>2</sub>Im (1j) (150 mg, 832 μmol) and ethyl acetate (83.0 μL, 838 μmol) in Et<sub>2</sub>O (5 mL). The resulting solution was stirred for 3 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in hexane (5 mL), collected by filtration, washed with hexane (2 × 5 mL) and dried *in vacuo* to give **9j** (451 mg, 649 μmol, 78%) as a colorless solid. <sup>1</sup>H NMR (500.1 MHz, CD<sub>3</sub>CN, 298 K): δ = 8.42 (t, 1H, <sup>4</sup>J<sub>H–H</sub> = 1.8 Hz, N–CH–N), 7.56 (d, 2H, <sup>4</sup>J<sub>H–H</sub> = 1.8 Hz, N–CH–CH–N), 3.99 (q, 2H, <sup>3</sup>J<sub>H–H</sub> = 7.1 Hz, CH<sub>3</sub>–CH<sub>2</sub>), 2.52 (d, m, 2H, <sup>2</sup>J<sub>P–H</sub> = 15 Hz, P–CH<sub>2</sub>), 1.62 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.16 (t, 3H, <sup>3</sup>J<sub>H–H</sub> = 7.1 Hz, CH<sub>2</sub>–CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>3</sub>CN, 298 K): δ = 170.5 (O=C), 132.6 (N–CH–N), 121.2 (N–CH–CH–N), 61.1 (C(CH<sub>3</sub>)<sub>3</sub>), 60.0 (CH<sub>3</sub>–CH<sub>2</sub>), 47.4 (P–CH<sub>2</sub>), 29.7 (C(CH<sub>3</sub>)<sub>3</sub>), 14.7 (CH<sub>2</sub>–CH<sub>3</sub>); <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN, 238 K): δ = –79.6 (m, 3F, CF<sub>3</sub>), –80.1 (m, 6F, CF<sub>3</sub>), –91.5 (d, d, m, 1F, <sup>1</sup>J<sub>P–F</sub> = 800 Hz, <sup>2</sup>J<sub>P–F</sub> = 103 Hz, PF), –104.5 (d, d, m, 1F, <sup>1</sup>J<sub>P–F</sub> = 875 Hz, <sup>2</sup>J<sub>P–F</sub> = 103 Hz, PF), –112.0 (d, d, q, 2F, <sup>2</sup>J<sub>P–F</sub> = 293 Hz, <sup>2</sup>J<sub>P–F</sub> = 91 Hz, <sup>3</sup>J<sub>P–F</sub> = 7.9 Hz, CF<sub>2</sub>), –115.1 (d, m, 2F, <sup>2</sup>J<sub>P–F</sub> = 97 Hz, CF<sub>2</sub>), –119.5 (d, m, <sup>2</sup>J<sub>P–F</sub> = 293 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K): δ = –143.0 (m); IR ([cm<sup>–1</sup>]): 3144 (w), 2991 (w), 1732 (m), 1582 (vw), 1563 (vw), 1540 (vw), 1470 (w), 1411 (vw), 1382 (w), 1366 (vw), 1294 (m), 1210 (s), 1179 (s), 1164 (s), 1116 (vs), 1073 (m), 1053 (w), 1036 (w), 942 (m), 886 (w), 864 (w), 853 (w), 807 (w), 792 (m), 740 (m), 705 (m), 659 (w), 634 (w), 606 (m), 553 (m), 532 (m), 517 (m), 427 (w), 407 (vw); ESI-MS (Orbitrap)  $m/z$   $[M]^+$  calcd for C<sub>11</sub>H<sub>21</sub>N<sub>2</sub>: 181.1704, found: 181.1697;  $m/z$   $[A]^-$  calcd for C<sub>10</sub>H<sub>7</sub>F<sub>17</sub>O<sub>2</sub>P: 512.9912, found: 512.9912; elemental analysis calcd (%) for C<sub>21</sub>H<sub>28</sub>F<sub>17</sub>N<sub>2</sub>O<sub>2</sub>P: C 36.32, H 4.06, N 4.03; found: C 36.20, H 3.91, N 4.17.



**[Dipp<sub>2</sub>Im<sup>H2</sup>-H][PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>2</sub>CO<sub>2</sub>Et)] (9k)**

The phosphorane PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (90.4 μL, 384 μmol) was added at room temperature to a solution of Dipp<sub>2</sub>Im<sup>H2</sup> (150 mg, 384 mmol) and ethyl acetate (38.0 μL, 386 μmol) in Et<sub>2</sub>O (5 mL). The resulting solution was stirred for 2 h at room temperature. The precipitate formed was collected by filtration, washed with hexane (5 mL), and dried *in vacuo* to give **9k** (134 mg, 148 μmol, 39%) as a colorless solid. <sup>1</sup>H NMR (500.1 MHz, CD<sub>3</sub>CN, 298 K): δ = 8.31 (br, 1H, N-CH-N), 7.54 (t, 2H, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, aryl-C<sub>para</sub>H), 7.40 (d, 4H, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, aryl-C<sub>meta</sub>H), 4.45 (br, 4H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 3.98 (q, 2H, <sup>3</sup>J<sub>H-H</sub> = 7.1 Hz, CH<sub>3</sub>-CH<sub>2</sub>), 3.08 (sept, 4H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, *i*Pr-CH), 2.51 (d, m, <sup>2</sup>J<sub>P-H</sub> = 15.3 Hz, P-CH<sub>2</sub>), 1.37 (d, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, *i*Pr-CH<sub>3</sub>), 1.23 (d, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, *i*Pr-CH<sub>3</sub>), 1.15 (t, 3H, <sup>3</sup>J<sub>H-H</sub> = 7.1 Hz, CH<sub>2</sub>-CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>3</sub>CN, 298 K): δ = 170.4 (O=C), 159.8 (N-CH-N), 147.6 (aryl-C<sub>ortho</sub>), 132.5 (aryl-C<sub>para</sub>), 130.4 (aryl-C<sub>ipso</sub>), 126.0 (aryl-C<sub>meta</sub>), 60.0 (CH<sub>3</sub>-CH<sub>2</sub>), 54.9 (N-CH<sub>2</sub>-CH<sub>2</sub>-N), 47.4 (P-CH<sub>2</sub>), 29.7 (*i*Pr-CH), 25.2 (*i*Pr-CH<sub>3</sub>), 24.0 (*i*Pr-CH<sub>3</sub>), 14.7 (CH<sub>2</sub>-CH<sub>3</sub>); <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN, 238 K): δ = -79.6 (m, 3F, CF<sub>3</sub>), -80.1 (m, 6F, CF<sub>3</sub>), -91.5 (d, d, m, 1F, <sup>1</sup>J<sub>P-F</sub> = 800 Hz, <sup>2</sup>J<sub>P-F</sub> = 103 Hz, PF), -104.5 (d, d, m, 1F, <sup>1</sup>J<sub>P-F</sub> = 875 Hz, <sup>2</sup>J<sub>P-F</sub> = 103 Hz, PF), -112.0 (d, d, q, 2F, <sup>2</sup>J<sub>P-F</sub> = 293 Hz, <sup>2</sup>J<sub>P-F</sub> = 91 Hz, <sup>3</sup>J<sub>F-F</sub> = 7.9 Hz, CF<sub>2</sub>), -115.1 (d, m, 2F, <sup>2</sup>J<sub>P-F</sub> = 97 Hz, CF<sub>2</sub>), -119.5 (d, m, <sup>2</sup>J<sub>F-F</sub> = 293 Hz, CF<sub>2</sub>); <sup>31</sup>P NMR (202.4 MHz, CD<sub>3</sub>CN, 298 K): δ = -143.0 (m); IR ([cm<sup>-1</sup>]): 3077 (vw), 2964 (w), 2910 (w), 1739 (m), 1633 (s), 1587 (w), 1500 (vw), 1477 (w), 1461 (w), 1447 (w), 1426 (vw), 1390 (vw), 1369 (w), 1345 (vw), 1325 (w), 1294 (m), 1256 (w), 1204 (vs), 1185 (s), 1172 (vs), 1142 (m), 1125 (vs), 1116 (vs), 1098 (m), 1072 (s), 1056 (m), 1049 (m), 1034 (m), 982 (w), 943 (m), 887 (w), 866 (w), 807 (w), 784 (s), 758 (w), 749 (w), 740 (m), 719 (m), 638 (w), 602 (m), 553 (m), 537 (s), 519 (s), 483 (w), 465 (vw), 430 (w); ESI-MS (Orbitrap) *m/z* [M]<sup>+</sup> calcd for C<sub>27</sub>H<sub>39</sub>N<sub>2</sub>: 391.3113, found: 391.3094; *m/z* [A]<sup>-</sup> calcd for C<sub>10</sub>H<sub>7</sub>F<sub>17</sub>O<sub>2</sub>P: 512.9912, found: 512.9896; elemental analysis calcd (%) for C<sub>27</sub>H<sub>39</sub>F<sub>17</sub>N<sub>2</sub>O<sub>2</sub>P: C 49.12, H 5.13, N 3.10; found: C 49.01, H 5.06, N 3.25.

**Crystallographic Details:** Crystal data were collected on a Bruker X8 Apex-2 diffractometer with a CCD area detector and graphite monochromated Mo-Kα radiation or a Rigaku XtaLAB Synergy-DW diffractometer with an Hy-Pix-6000HE detector and monochromated Cu-Kα radiation equipped with an Oxford Cryo 800 cooling unit. Crystals were immersed in a film of perfluoropolyether oil on a MicroMountTM and data were collected at 100 K. Images were processed with Bruker or CrySalis software packages and the structures were solved using the ShelXTL software package.<sup>[61]</sup> All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were assigned to idealized geometric positions.

**Crystal Data for Me<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2a):** C<sub>11</sub>H<sub>8</sub>F<sub>17</sub>N<sub>2</sub>P, M<sub>r</sub> = 522.16, T = 100(2) K, λ = 1.54184 Å, yellow block, 0.183 × 0.230 × 0.272 mm<sup>3</sup>, orthorhombic space group *Pnma*, a = 13.6765(2) Å, b = 11.0137(2) Å, c = 11.32270(10) Å, V = 1705.53(4) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 2.034 Mg/m<sup>3</sup>, μ = 3.210 mm<sup>-1</sup>, F(000) = 1024, 9732 reflections, -17 ≤ h ≤ 16, -13 ≤ k ≤ 13, -8 ≤ l ≤ 14, 5.071° < θ < 74.499°, completeness 99.6%, 1830 independent reflections, 1770 reflections observed with [I > 2σ(I)], 162 parameters, 0 restraints, R indices (all data) R<sub>1</sub> = 0.1025, wR<sub>2</sub> = 0.2361, final R indices [I > 2σ(I)] R<sub>1</sub> = 0.1013, wR<sub>2</sub> = 0.2358, largest difference peak and hole 1.088 and -0.804 e Å<sup>-3</sup>, Goof = 1.271.

**Crystal Data for nPr<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2b):** C<sub>15</sub>H<sub>16</sub>F<sub>17</sub>N<sub>2</sub>P, M<sub>r</sub> = 578.27, T = 100(2) K, λ = 1.54184 Å, colorless block, 0.193 × 0.237 × 0.332 mm<sup>3</sup>, monoclinic space group *P2<sub>1</sub>*, a = 8.45290(10) Å, b = 15.5319(2) Å, c = 8.72920(10) Å, β = 113.0470(10)°, V = 1054.58(2) Å<sup>3</sup>, Z = 2, ρ<sub>calcd</sub> = 1.821 Mg/m<sup>3</sup>, μ = 2.665 mm<sup>-1</sup>, F(000) = 576, 11650 reflections, -7 ≤ h ≤ 10, -19 ≤ k ≤ 19, -10 ≤ l ≤ 10, 5.507° < θ < 74.444°, completeness 1.075/0.91, 3926 independent reflections, 3870 reflections observed with [I > 2σ(I)], 316 parameters, 1 restraints, R indices (all data) R<sub>1</sub> = 0.0258, wR<sub>2</sub> = 0.0659, final R

indices [I > 2σ(I)] R<sub>1</sub> = 0.0255, wR<sub>2</sub> = 0.0657, largest difference peak and hole 0.182 and -0.292 e Å<sup>-3</sup>, Goof = 1.077.

**Crystal Data for *i*Pr<sub>2</sub>Im·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2c):** C<sub>15</sub>H<sub>16</sub>F<sub>17</sub>N<sub>2</sub>P, M<sub>r</sub> = 578.27, T = 100(2) K, λ = 1.54184 Å, colorless block, 0.164 × 0.242 × 0.270 mm<sup>3</sup>, monoclinic space group *P2<sub>1</sub>/c*, a = 9.05740(10) Å, b = 29.9860(3) Å, c = 15.33000(10) Å, β = 90.5910(10)°, V = 4163.33(7) Å<sup>3</sup>, Z = 8, ρ<sub>calcd</sub> = 1.845 Mg/m<sup>3</sup>, μ = 2.700 mm<sup>-1</sup>, F(000) = 2304, 43988 reflections, -8 ≤ h ≤ 11, -37 ≤ k ≤ 36, -19 ≤ l ≤ 18, 2.947° < θ < 74.490°, completeness 99.4%, 8466 independent reflections, 7749 reflections observed with [I > 2σ(I)], 763 parameters, 0 restraints, R indices (all data) R<sub>1</sub> = 0.0389, wR<sub>2</sub> = 0.0927, final R indices [I > 2σ(I)] R<sub>1</sub> = 0.0658, wR<sub>2</sub> = 0.0908, largest difference peak and hole 0.434 and -0.379 e Å<sup>-3</sup>, Goof = 1.051.

**Crystal Data for Me<sub>2</sub>Im<sup>Me</sup>·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2d):** C<sub>13</sub>H<sub>12</sub>F<sub>17</sub>N<sub>2</sub>P, M<sub>r</sub> = 550.22, T = 100(2) K, λ = 1.54184 Å, colorless block, 0.109 × 0.132 × 0.263 mm<sup>3</sup>, monoclinic space group *P2<sub>1</sub>*, a = 8.4653(2) Å, b = 14.9648(3) Å, c = 8.5900(2) Å, β = 118.159(3)°, V = 959.40(4) Å<sup>3</sup>, Z = 2, ρ<sub>calcd</sub> = 1.905 Mg/m<sup>3</sup>, μ = 2.891 mm<sup>-1</sup>, F(000) = 544, 10417 reflections, -8 ≤ h ≤ 10, -18 ≤ k ≤ 18, -10 ≤ l ≤ 10, 5.843° < θ < 74.415°, completeness 1.71/0.89, 3483 independent reflections, 3384 reflections observed with [I > 2σ(I)], 302 parameters, 1 restraints, R indices (all data) R<sub>1</sub> = 0.0330, wR<sub>2</sub> = 0.0849, final R indices [I > 2σ(I)] R<sub>1</sub> = 0.0321, wR<sub>2</sub> = 0.0841, largest difference peak and hole 0.250 and -0.496 e Å<sup>-3</sup>, Goof = 1.056.

**Crystal Data for nPr<sub>2</sub>Im<sup>Me</sup>·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2e):** C<sub>17</sub>H<sub>20</sub>F<sub>17</sub>N<sub>2</sub>P, M<sub>r</sub> = 606.32, T = 100(2) K, λ = 1.54184 Å, colorless block, 0.227 × 0.300 × 0.479 mm<sup>3</sup>, monoclinic space group *P2<sub>1</sub>/c*, a = 9.28150(10) Å, b = 15.14040(10) Å, c = 16.42820(10) Å, β = 93.4550(10)°, V = 2304.39(3) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.748 Mg/m<sup>3</sup>, μ = 2.471 mm<sup>-1</sup>, F(000) = 1216, 47410 reflections, -11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20, 3.974° < θ < 74.503°, completeness 100%, 4717 independent reflections, 4532 reflections observed with [I > 2σ(I)], 338 parameters, 0 restraints, R indices (all data) R<sub>1</sub> = 0.0285, wR<sub>2</sub> = 0.0688, final R indices [I > 2σ(I)] R<sub>1</sub> = 0.0274, wR<sub>2</sub> = 0.0681, largest difference peak and hole 0.295 and -0.314 e Å<sup>-3</sup>, Goof = 1.053.

**Crystal Data for *i*Pr<sub>2</sub>Im<sup>Me</sup>·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2f):** C<sub>17</sub>H<sub>20</sub>F<sub>17</sub>N<sub>2</sub>P, M<sub>r</sub> = 606.32, T = 100(2) K, λ = 1.54184 Å, colorless block, 0.118 × 0.191 × 0.347 mm<sup>3</sup>, monoclinic space group *P2<sub>1</sub>/c*, a = 15.2521(2) Å, b = 9.32460(10) Å, c = 17.5426(2) Å, β = 114.467(2)°, V = 2270.86(6) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.773 Mg/m<sup>3</sup>, μ = 2.507 mm<sup>-1</sup>, F(000) = 1216, 24527 reflections, -19 ≤ h ≤ 15, -11 ≤ k ≤ 11, -17 ≤ l ≤ 21, 3.183° < θ < 74.494°, completeness 99.8%, 4633 independent reflections, 4272 reflections observed with [I > 2σ(I)], 340 parameters, 0 restraints, R indices (all data) R<sub>1</sub> = 0.0357, wR<sub>2</sub> = 0.0901, final R indices [I > 2σ(I)] R<sub>1</sub> = 0.0332, wR<sub>2</sub> = 0.0881, largest difference peak and hole 0.386 and -0.362 e Å<sup>-3</sup>, Goof = 1.046.

**Crystal Data for *i*PrMelm·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2g):** C<sub>13</sub>H<sub>12</sub>F<sub>17</sub>N<sub>2</sub>P, M<sub>r</sub> = 550.22, T = 100(2) K, λ = 0.71073 Å, colorless block, 0.190 × 0.231 × 0.555 mm<sup>3</sup>, orthorhombic space group *Pnma*, a = 16.1976(19) Å, b = 11.0954(12) Å, c = 10.2493(3) Å, V = 1842.0(3) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.984 Mg/m<sup>3</sup>, μ = 0.322 mm<sup>-1</sup>, F(000) = 1088, 13144 reflections, -20 ≤ h ≤ 20, -14 ≤ k ≤ 13, -12 ≤ l ≤ 12, 2.352° < θ < 26.851°, completeness 99.3%, 2069 independent reflections, 1841 reflections observed with [I > 2σ(I)], 171 parameters, 0 restraints, R indices (all data) R<sub>1</sub> = 0.0318, wR<sub>2</sub> = 0.0633, final R indices [I > 2σ(I)] R<sub>1</sub> = 0.0269, wR<sub>2</sub> = 0.0609, largest difference peak and hole 0.468 and -0.286 e Å<sup>-3</sup>, Goof = 1.048.

**Crystal Data for EtMelm<sup>Me</sup>·PF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (2h):** C<sub>14</sub>H<sub>14</sub>F<sub>17</sub>N<sub>2</sub>P, M<sub>r</sub> = 564.24, T = 100(2) K, λ = 1.54184 Å, colorless block, 0.200 × 0.261 × 0.387 mm<sup>3</sup>, monoclinic space group *P2<sub>1</sub>/c*, a = 8.10700(10) Å, b = 14.99700(10) Å, c = 16.45270(10) Å, β = 90.4530(10)°, V = 2000.27(3) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.874 Mg/m<sup>3</sup>, μ = 2.792 mm<sup>-1</sup>, F(000) = 1120, 21240 reflections, -10 ≤ h ≤ 9, -18 ≤ k ≤ 17, -20 ≤ l ≤ 20, 3.989° < θ

<74.483°, completeness 100%, 4096 independent reflections, 3855 reflections observed with  $[I > 2\sigma(I)]$ , 311 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0299$ ,  $wR_2 = 0.0748$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0285$ ,  $wR_2 = 0.0738$ , largest difference peak and hole 0.425 and  $-0.317 \text{ e} \text{ \AA}^{-3}$ , Goof = 1.049.

**Crystal Data for  $\alpha\text{Dipp}_2\text{Im} \cdot \text{PF}_2(\text{C}_2\text{F}_5)_3$  (3i):**  $\text{C}_{37}\text{H}_{46}\text{F}_{17}\text{N}_2\text{OP}$ ,  $M_r = 888.73$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 0.7173 \text{ \AA}$ , colorless block,  $0.166 \times 0.439 \times 0.502 \text{ mm}^3$ , triclinic space group  $P1$ ,  $a = 10.3270(8) \text{ \AA}$ ,  $b = 10.8760(9) \text{ \AA}$ ,  $c = 11.1032(9) \text{ \AA}$ ,  $\alpha = 103.015(3)^\circ$ ,  $\beta = 106.141(3)^\circ$ ,  $\gamma = 112.343(3)^\circ$ ,  $V = 1028.27(15) \text{ \AA}^3$ ,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.435 \text{ Mg/m}^3$ ,  $\mu = 0.176 \text{ mm}^{-1}$ ,  $F(000) = 458$ , 19239 reflections,  $-13 \leq h \leq 13$ ,  $-14 \leq k \leq 14$ ,  $-14 \leq l \leq 14$ ,  $2.057^\circ < \theta < 28.407^\circ$ , completeness 1.91/0.96, 9881 independent reflections, 9203 reflections observed with  $[I > 2\sigma(I)]$ , 533 parameters, 3 restraints, R indices (all data)  $R_1 = 0.0368$ ,  $wR_2 = 0.0700$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0325$ ,  $wR_2 = 0.0678$ , largest difference peak and hole  $0.318$  and  $-0.264 \text{ e} \text{ \AA}^{-3}$ , Goof = 1.022.

**Crystal Data for  $\alpha\text{tBu}_2\text{Im} \cdot \text{PF}_2(\text{C}_2\text{F}_5)_3$  (3j):**  $\text{C}_{17}\text{H}_{20}\text{F}_{17}\text{N}_2\text{P}$ ,  $M_r = 606.32$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless plate,  $0.072 \times 0.138 \times 0.193 \text{ mm}^3$ , orthorhombic space group  $Pbca$ ,  $a = 13.5132(2) \text{ \AA}$ ,  $b = 16.9278(2) \text{ \AA}$ ,  $c = 19.5982(3) \text{ \AA}$ ,  $V = 4483.06(11) \text{ \AA}^3$ ,  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.797 \text{ Mg/m}^3$ ,  $\mu = 2.540 \text{ mm}^{-1}$ ,  $F(000) = 2432$ , 24601 reflections,  $-16 \leq h \leq 16$ ,  $-16 \leq k \leq 21$ ,  $-24 \leq l \leq 24$ ,  $4.512^\circ < \theta < 74.483^\circ$ , completeness 99.8%, 4570 independent reflections, 4208 reflections observed with  $[I > 2\sigma(I)]$ , 340 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0340$ ,  $wR_2 = 0.0841$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0314$ ,  $wR_2 = 0.0821$ , largest difference peak and hole  $0.434$  and  $-0.339 \text{ e} \text{ \AA}^{-3}$ , Goof = 1.016.

**Crystal Data for  $\alpha\text{Mes}_2\text{Im} \cdot \text{PF}_2(\text{C}_2\text{F}_5)_3$  (3l):**  $\text{C}_{27}\text{H}_{24}\text{F}_{17}\text{N}_2\text{P}$ ,  $M_r = 730.45$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.158 \times 0.193 \times 0.310 \text{ mm}^3$ , orthorhombic space group  $Pna2_1$ ,  $a = 15.55960(10) \text{ \AA}$ ,  $b = 13.31460(10) \text{ \AA}$ ,  $c = 14.46400(10) \text{ \AA}$ ,  $V = 2996.50(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.619 \text{ Mg/m}^3$ ,  $\mu = 2.020 \text{ mm}^{-1}$ ,  $F(000) = 1472$ , 31703 reflections,  $-16 \leq h \leq 19$ ,  $-16 \leq k \leq 16$ ,  $-18 \leq l \leq 17$ ,  $4.370^\circ < \theta < 74.487^\circ$ , completeness 1.78/0.93, 5705 independent reflections, 5542 reflections observed with  $[I > 2\sigma(I)]$ , 515 parameters, 391 restraints, R indices (all data)  $R_1 = 0.0295$ ,  $wR_2 = 0.0743$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0286$ ,  $wR_2 = 0.0736$ , largest difference peak and hole  $0.207$  and  $-0.263 \text{ e} \text{ \AA}^{-3}$ , Goof = 1.054.

**Crystal Data for  $[\text{tBuMelm} - \text{H}][\text{Melm} \cdot \text{PF}_2(\text{C}_2\text{F}_5)_3]$  (4m):**  $\text{C}_{18}\text{H}_{20}\text{F}_{17}\text{N}_4\text{P}$ ,  $M_r = 646.35$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.126 \times 0.208 \times 0.264 \text{ mm}^3$ , orthorhombic space group  $Pbca$ ,  $a = 17.28250(10) \text{ \AA}$ ,  $b = 15.68300(10) \text{ \AA}$ ,  $c = 17.88140(10) \text{ \AA}$ ,  $V = 4846.60(5) \text{ \AA}^3$ ,  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.772 \text{ Mg/m}^3$ ,  $\mu = 2.421 \text{ mm}^{-1}$ ,  $F(000) = 2592$ , 50380 reflections,  $-21 \leq h \leq 17$ ,  $-19 \leq k \leq 19$ ,  $-18 \leq l \leq 22$ ,  $4.540^\circ < \theta < 74.494^\circ$ , completeness 100%, 4951 independent reflections, 4746 reflections observed with  $[I > 2\sigma(I)]$ , 366 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0285$ ,  $wR_2 = 0.0708$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0275$ ,  $wR_2 = 0.0700$ , largest difference peak and hole  $0.350$  and  $-0.339 \text{ e} \text{ \AA}^{-3}$ , Goof = 1.025.

**Crystal Data for  $\text{Me}_3\text{P} \cdot \text{PF}_2(\text{C}_2\text{F}_5)_3$  (5a):**  $\text{C}_9\text{H}_9\text{F}_{17}\text{P}_2$ ,  $M_r = 502.10$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.103 \times 0.116 \times 0.159 \text{ mm}^3$ , orthorhombic space group  $P2_12_12_1$ ,  $a = 7.81680(10) \text{ \AA}$ ,  $b = 13.1534(2) \text{ \AA}$ ,  $c = 15.8230(2) \text{ \AA}$ ,  $V = 1626.88(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 2.050 \text{ Mg/m}^3$ ,  $\mu = 4.190 \text{ mm}^{-1}$ ,  $F(000) = 984$ , 9946 reflections,  $-9 \leq h \leq 9$ ,  $-16 \leq k \leq 15$ ,  $-17 \leq l \leq 19$ ,  $4.371^\circ < \theta < 74.491^\circ$ , completeness 1.64/0.95, 3146 independent reflections, 3044 reflections observed with  $[I > 2\sigma(I)]$ , 256 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0297$ ,  $wR_2 = 0.0711$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0286$ ,  $wR_2 = 0.0705$ , largest difference peak and hole  $0.279$  and  $-0.302 \text{ e} \text{ \AA}^{-3}$ , Goof = 1.075.

**Crystal Data for  $\text{Dipp}_2\text{Im} - (\text{CH}_2)_4\text{O} - \text{PF}_2(\text{C}_2\text{F}_5)_3$  (6i):**  $\text{C}_{38}\text{H}_{46}\text{Cl}_2\text{F}_{17}\text{N}_2\text{OP}$ ,  $M_r = 971.64$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.143 \times 0.184 \times 0.267 \text{ mm}^3$ , orthorhombic space group  $Pbca$ ,  $a =$

$18.42170(10) \text{ \AA}$ ,  $b = 19.25760(10) \text{ \AA}$ ,  $c = 24.6498(2) \text{ \AA}$ ,  $V = 8744.71(10) \text{ \AA}^3$ ,  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.476 \text{ Mg/m}^3$ ,  $\mu = 2.646 \text{ mm}^{-1}$ ,  $F(000) = 3984$ , 48954 reflections,  $-21 \leq h \leq 23$ ,  $-23 \leq k \leq 16$ ,  $-30 \leq l \leq 30$ ,  $3.586^\circ < \theta < 74.502^\circ$ , completeness 99.6%, 8914 independent reflections, 8438 reflections observed with  $[I > 2\sigma(I)]$ , 558 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0434$ ,  $wR_2 = 0.1020$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0413$ ,  $wR_2 = 0.1007$ , largest difference peak and hole  $0.802$  and  $-0.416 \text{ e} \text{ \AA}^{-3}$ , Goof = 1.084.

**Crystal Data for  $\text{Dipp}_2\text{Im}^{\text{H}2} - (\text{CH}_2)_4\text{O} - \text{PF}_2(\text{C}_2\text{F}_5)_3$  (6k):**  $\text{C}_{37}\text{H}_{46}\text{F}_{17}\text{N}_2\text{OP}$ ,  $M_r = 888.73$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.360 \times 0.444 \times 0.655 \text{ mm}^3$ , monoclinic space group  $P2_1/c$ ,  $a = 16.29210(10) \text{ \AA}$ ,  $b = 12.58600(10) \text{ \AA}$ ,  $c = 20.02470(10) \text{ \AA}$ ,  $\beta = 99.8720(10)^\circ$ ,  $V = 4045.31(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.459 \text{ Mg/m}^3$ ,  $\mu = 1.617 \text{ mm}^{-1}$ ,  $F(000) = 1832$ , 56455 reflections,  $-18 \leq h \leq 20$ ,  $-15 \leq k \leq 15$ ,  $-25 \leq l \leq 24$ ,  $2.753^\circ < \theta < 74.492^\circ$ , completeness 99.6%, 8243 independent reflections, 7782 reflections observed with  $[I > 2\sigma(I)]$ , 531 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0398$ ,  $wR_2 = 0.0980$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0379$ ,  $wR_2 = 0.0966$ , largest difference peak and hole  $0.379$  and  $-0.312 \text{ e} \text{ \AA}^{-3}$ , Goof = 1.053.

**Crystal Data for  $[\text{tBu}_2\text{Im} - \text{H}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CO}_2\text{Et})]$  (9j):**  $\text{C}_{21}\text{H}_{28}\text{F}_{17}\text{N}_2\text{O}_2\text{P}$ ,  $M_r = 694.42$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.093 \times 0.187 \times 0.299 \text{ mm}^3$ , orthorhombic space group  $P2_12_12_1$ ,  $a = 10.8415(2) \text{ \AA}$ ,  $b = 14.4101(2) \text{ \AA}$ ,  $c = 18.0850(2) \text{ \AA}$ ,  $V = 2825.37(7) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.633 \text{ Mg/m}^3$ ,  $\mu = 2.153 \text{ mm}^{-1}$ ,  $F(000) = 1408$ , 17012 reflections,  $-13 \leq h \leq 12$ ,  $-17 \leq k \leq 17$ ,  $-22 \leq l \leq 14$ ,  $3.922^\circ < \theta < 74.440^\circ$ , completeness 1.69/0.95, 5520 independent reflections, 5311 reflections observed with  $[I > 2\sigma(I)]$ , 395 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0321$ ,  $wR_2 = 0.0787$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0309$ ,  $wR_2 = 0.0778$ , largest difference peak and hole  $0.235$  and  $-0.264 \text{ e} \text{ \AA}^{-3}$ , Goof = 1.053.

**Crystal Data for  $[\text{Dipp}_2\text{Im}^{\text{H}2} - \text{H}][\text{PF}_2(\text{C}_2\text{F}_5)_3(\text{CH}_2\text{CO}_2\text{Et})]$  (9k):**  $\text{C}_{37}\text{H}_{46}\text{F}_{17}\text{N}_2\text{O}_2\text{P}$ ,  $M_r = 904.73$ ,  $T = 100(2) \text{ K}$ ,  $\lambda = 1.54184 \text{ \AA}$ , colorless block,  $0.120 \times 0.148 \times 0.230 \text{ mm}^3$ , orthorhombic space group  $P2_12_12_1$ ,  $a = 10.83810(10) \text{ \AA}$ ,  $b = 17.04570(10) \text{ \AA}$ ,  $c = 22.0709(2) \text{ \AA}$ ,  $V = 4077.44(6) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.474 \text{ Mg/m}^3$ ,  $\mu = 1.634 \text{ mm}^{-1}$ ,  $F(000) = 1864$ , 42934 reflections,  $-13 \leq h \leq 13$ ,  $-21 \leq k \leq 20$ ,  $-27 \leq l \leq 27$ ,  $3.276^\circ < \theta < 74.446^\circ$ , completeness 1.79/1.00, 8335 independent reflections, 8189 reflections observed with  $[I > 2\sigma(I)]$ , 542 parameters, 0 restraints, R indices (all data)  $R_1 = 0.0425$ ,  $wR_2 = 0.1161$ , final R indices  $[I > 2\sigma(I)]$   $R_1 = 0.0419$ ,  $wR_2 = 0.1157$ , largest difference peak and hole  $0.638$  and  $-0.246 \text{ e} \text{ \AA}^{-3}$ , Goof = 1.085.

**Computational Details:** Quantum chemical calculations were performed using the TURBOMOLE V7.3 program suite, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.<sup>[62]</sup> Geometries were optimized using (RI)-DFT calculations<sup>[63]</sup> on an m4 grid employing the PBE0<sup>[64]</sup> functional and def2-TZVP basis sets for all atoms.<sup>[65]</sup> Frequency calculations with the AOFORCE<sup>[66]</sup> module were performed at the same level to ensure that all structures represent true minima by the absence of imaginary frequencies.

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## Conflict of Interest

The authors declare no conflict of interest.

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