

## Electronic Supplementary Information

# Carbene Complexes of Phosphorus(V) Fluorides substituted with Perfluoroalkyl-groups Synthesized by Oxidative Addition. Cleavage of the Complexes by HF reveals a new Synthetic Protocol for Ionic Liquids.

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## 1. Experimental Section

### 1.1. General Methods and Materials

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk line techniques unless mentioned otherwise. Solvents were dried using a Braun MB-SPS 800 system. All other chemicals were purchased from available commercial sources and were used as received.

#### *NMR spectroscopy*

NMR spectra were recorded with a Bruker Model Avance III 300 spectrometer. Operating frequency:  $^{31}\text{P}$  111.92 MHz,  $^{19}\text{F}$  282.40 MHz,  $^{13}\text{C}$  75.47 MHz,  $^1\text{H}$  300.13 MHz with positive shifts being downfield from the external standards (85% orthophosphoric acid ( $^{31}\text{P}$ ),  $\text{CCl}_3\text{F}$  ( $^{19}\text{F}$ ) and TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ )).

#### *MS spectrometry*

ESI mass spectra were recorded using an Bruker Esquire 3000 ion trap mass spectrometer equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as nebulizer gas and dry gas.

#### *IR spectrometry*

IR spectra were recorded on a Bruker ALPHA FT-IR, equipped with a diamond ATR unit.

#### *Computational Details*

All electronic structure calculations were carried out using the Gaussian09 program package using the hybrid B3LYP functional in conjunction with the 6-311G(2d,p) basis set.<sup>1</sup> For all structures a full geometrical optimization and calculation of harmonic vibrational frequencies was performed.

#### *Synthesis of the starting materials*

Compounds **1a**, **1b**, **2a**, and the halo-perfluoroalkylphosphines were prepared according to procedures reported elsewhere.<sup>2-4</sup>

## 1.2. Synthesis of the carbene complexes of phosphorus(V)

### Compound 5a

A solution of  $\text{Br}_2\text{PCF}_3$  (0.56 g, 2.17 mmol) in diethyl ether (10 ml) was placed into a 25 ml Schlenk flask. At -78 °C **1a** (0.88 g, 6.47 mmol) was slowly added using a syringe. During a period of 12 h, the reaction mixture was allowed to reach room temperature. All volatile components were removed under reduced pressure. The solid residue was washed with small amounts of cold water. Drying *in vacuo* gave **5a** (0.40 g). Yield: 0.40 g (67% based on  $\text{Br}_2\text{PCF}_3$ ).  $M_r = 274.12$ . Pale yellow solid.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = 3.2$  (s, 6H,  $-\text{CH}_3$ ), 3.8 (d, 4H,  $^4J_{\text{PH}} = 1$  Hz,  $-\text{CH}_2-$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = 36.0$  (quint,  $-\text{CH}_3$ ,  $^4J_{\text{CF}} = 4$  Hz,  $-\text{CH}_3$ ), 51.4 (d,  $-\text{CH}_2-$ ,  $^3J_{\text{CP}} = 11$  Hz), 173.3 (d, quint, carbene-C,  $^1J_{\text{CP}} = 305$  Hz,  $^2J_{\text{CF}} = 57$  Hz).  $^{13}\text{C}\{^{19}\text{F}\}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = 126.2$  (d,  $-\text{CF}_3$ ,  $^1J_{\text{CP}} = 415$  Hz).  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = -70.5$  (d, quint, 3F,  $-\text{CF}_3$ ,  $^2J_{\text{PF}} = 150$  Hz,  $^3J_{\text{FF}} = 14$  Hz), -62.5 (d, quart, 4F, P-F,  $^1J_{\text{PF}} = 877$  Hz,  $^3J_{\text{FF}} = 14$  Hz).  $^{31}\text{P}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = -152.7$  (quint, quart,  $^1J_{\text{PF}} = 876$  Hz,  $^2J_{\text{PF}} = 149$  Hz). ESI MS positive range  $m/z$  (%): 570 (n.a.), 297 (100) [ $\text{M}+\text{Na}^+$ ].

### Compound 5b

Compound **5b** was synthesized following the procedure for **5a**. Quantities used:  $\text{Br}_2\text{PCF}_3$  (0.54 g, 2.10 mmol), **1b** (0.83 g, 6.00 mmol). Yield: 0.34 g (59% based on  $\text{Br}_2\text{PCF}_3$ ).  $M_r = 276.14$ . Colorless solid.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = 3.2$  (s, 12H,  $-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = 44.6$  (m,  $-\text{CH}_3$ ).  $^{13}\text{C}\{^{19}\text{F}\}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = 126.2$  (d,  $^1J_{\text{CP}} = 416$  Hz).  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = -70.2$  (d, quint, 3F,  $-\text{CF}_3$ ,  $^2J_{\text{FP}} = 148$  Hz,  $^3J_{\text{FF}} = 14$  Hz), -62.1 (d, quart, 4F, P-F,  $^1J_{\text{PF}} = 916$  Hz,  $^3J_{\text{FF}} = 14$  Hz).  $^{31}\text{P}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = -149.7$  (quint, quart,  $^1J_{\text{PF}} = 916$  Hz,  $^2J_{\text{PF}} = 149$  Hz). ESI MS positive range  $m/z$  (%): 437.2 (n.a.), 299 (100) [ $\text{M}+\text{Na}^+$ ], 119.0 (64) [ $\text{FPCF}_3$ ]<sup>+</sup>.

### Compound 6a

Compound **6a** was synthesized following the procedure for **5a**. Quantities used:  $\text{F}_2\text{PC}_2\text{F}_5$  (0.72 g, 3.82 mmol), **1a** (0.52 g, 3.82 mmol). Yield: 1.22 g (99% based on  $\text{F}_2\text{PC}_2\text{F}_5$ ).  $M_r = 324.13$ . Colorless solid.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = 3.2$  (m, 6H,  $-\text{CH}_3$ ), 3.8 (m, 4H,  $-\text{CH}_2-$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = 36.0$  (m,  $-\text{CH}_3$ ), 51.4 (d,  $-\text{CH}_2-$ ,  $^3J_{\text{CP}} = 11$  Hz).  $^{13}\text{C}\{^{19}\text{F}\}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = 120.3$  (d,  $-\text{CF}_3$ ,  $^2J_{\text{CP}} = 30$  Hz).  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = -120.5$  (d, quint, quart, 2F,  $-\text{CF}_2-$ ,  $^2J_{\text{PF}} = 104$  Hz,  $^3J_{\text{FF}} = 9$  Hz,  $^3J_{\text{FF}} = 1$  Hz), -83.6 (quint, m, 3F,  $-\text{CF}_3$ ,  $^4J_{\text{FF}} =$

7 Hz), -60.1 (d, pseudo-sex, 4F, P-F,  $^1J_{PF} = 886$  Hz,  $^{3,4}J_{FF} = 8$  Hz).  $^{31}P$  NMR (CD<sub>3</sub>CN)  $\delta = -151.3$  (quint,t,m,  $^1J_{PF} = 886$  Hz,  $^2J_{PF} = 102$  Hz).

### Compound 6b

Compound **6b** was synthesized following the procedure for **5a**. Quantities used: F<sub>2</sub>PC<sub>2</sub>F<sub>5</sub> (0.15 g, 0.78 mmol), **1b** (0.11 g, 0.78 mmol). Yield: 0.18 g (71% based on F<sub>2</sub>PC<sub>2</sub>F<sub>5</sub>). M<sub>r</sub> = 326.14. Colorless solid.  $^1H$  NMR (CD<sub>3</sub>CN)  $\delta = 3.2$  (m, 12H, -CH<sub>3</sub>).  $^{13}C\{^1H\}$  NMR (CD<sub>3</sub>CN)  $\delta = 44.6$  (pseudo-sex, -CH<sub>3</sub>,  $^4J_{CF}, ^3J_{CP} = 4$  Hz), 182.1 (d,quint, carbene-C,  $^1J_{CP} = 321$  Hz,  $^2J_{CF} = 56$  Hz).  $^{13}C\{^{19}F\}$  NMR (CD<sub>3</sub>CN)  $\delta = 116.4$  (d, -CF<sub>2</sub>-,  $^1J_{CP} = 321$  Hz), 120.3 (d, -CF<sub>3</sub>,  $^2J_{CP} = 30$  Hz).  $^{19}F$  NMR (CD<sub>3</sub>CN)  $\delta = -120.2$  (d,quint, 2F, -CF<sub>2</sub>-,  $^2J_{PF} = 101$  Hz,  $^3J_{FF} = 9$  Hz), -83.5 (quint,m, 3F, -CF<sub>3</sub>,  $^4J_{FF} = 7$  Hz), -59.7 (d,t,quart, 4F, P-F,  $^1J_{FP} = 925$  Hz,  $^3J_{FF} = 9$  Hz,  $^4J_{FF} = 7$  Hz).  $^{31}P$  NMR (CD<sub>3</sub>CN)  $\delta = -148.1$  (quint,t,m,  $^1J_{PF} = 926$  Hz,  $^2J_{PF} = 102$  Hz).

### Compound 7a

Compound **7a** was synthesized following the procedure for **5a**. Quantities used: ClP(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub> (0.57 g, 1.88 mmol), **1a** (0.51 g, 3.75 mmol). Yield: 0.76 g (95% based on ClP(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>). M<sub>r</sub> = 424.14. Pale yellow solid.  $^1H$  NMR (CD<sub>3</sub>CN)  $\delta = 3.3$  (t, 6H,  $^5J_{HF} = 3$  Hz), 3.8 (s, 4H, -CH<sub>2</sub>-).  $^{13}C\{^1H\}$  NMR (CD<sub>3</sub>CN)  $\delta = 37.3$  (t, -CH<sub>3</sub>,  $^4J_{CH} = 11$  Hz), 52.5 (d,  $^3J_{CP} = 9$  Hz).  $^{13}C\{^{19}F\}$  NMR (CD<sub>3</sub>CN)  $\delta = 120.0$  (d, -CF<sub>3</sub>,  $^2J_{CP} = 25$  Hz), 120.2 (d, -CF<sub>3</sub>,  $^2J_{CP} = 25$  Hz).  $^{19}F$  NMR (CD<sub>3</sub>CN)  $\delta = -118.2$  (d,m, 2F, -CF<sub>2</sub>-,  $^2J_{PF} = 99$  Hz), -117.5 (d,m, 2F, -CF<sub>2</sub>-,  $^2J_{PF} = 92$  Hz), -83.1 (pseudo-d, 3F, -CF<sub>3</sub>, J = 17 Hz), -81.6 (pseudo-quint, 3F, -CF<sub>3</sub>, J = 10 Hz), -72.2 (d,d,m, 2F, P-F<sup>a</sup>,  $^1J_{FP} = 903$  Hz,  $^2J_{FF} = 35$  Hz), -33.1 (d,m, 1F, P-F<sup>b</sup>,  $^1J_{PF} = 852$  Hz).  $^{31}P$  NMR (CD<sub>3</sub>CN)  $\delta = -151.3$  (t,d,t,t,  $^1J_{PF}^b = 903$  Hz,  $^1J_{PF}^a = 853$  Hz,  $^2J_{PF} = 99$  Hz,  $^2J_{PF} = 92$  Hz).

### Compound 7b

Compound **7b** was synthesized following the procedure for **5a**. Quantities used: BrP(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub> (0.33 g, 0.96 mmol), **1b** (0.27 g, 1.69 mmol). Yield: 0.40 g (98% based on BrP(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>). M<sub>r</sub> = 426.16. Pale yellow solid.  $^1H$  NMR (CD<sub>3</sub>CN)  $\delta = 3.2$  (t, 12H, -CH<sub>3</sub>,  $^5J_{FH} = 3$  Hz).  $^{13}C\{^1H\}$  NMR (CD<sub>3</sub>CN)  $\delta = 45.0$  (t, -CH<sub>3</sub>,  $^4J_{CF} = 5$  Hz), 185.3 (d,m, carbene-C,  $^1J_{CP} = 255$  Hz).  $^{13}C\{^{19}F\}$  NMR (CD<sub>3</sub>CN)  $\delta = 120.0$  (d, -CF<sub>3</sub>,  $^2J_{CP} = 15$  Hz), 120.3 (d, -CF<sub>3</sub>,  $^2J_{CP} = 18$  Hz).  $^{19}F$  NMR (CD<sub>3</sub>CN)  $\delta = -117.9$  (d,m, 2F, -CF<sub>2</sub>-,  $^2J_{PF} = 99$  Hz), -115.8 (d,m, 2F, -CF<sub>2</sub>-,  $^2J_{PF} = 90$  Hz), -82.8 Hz (pseudo-d, 3F, -CF<sub>3</sub>, J = 17 Hz), -81.4 (pseudo-quint, 3F, -CF<sub>3</sub>, J =

11 Hz), -72.9 (d,d,m, 2F, P-F<sup>a</sup>, <sup>1</sup>J<sub>PF</sub> = 934 Hz, <sup>2</sup>J<sub>FF</sub> = 40 Hz), -34.4 (d,m, 1F, P-F<sup>b</sup>, <sup>1</sup>J<sub>PF</sub> = 890 Hz). <sup>31</sup>P NMR (CD<sub>3</sub>CN) δ = -146.8 (t,d,t,t, <sup>1</sup>J<sub>PF</sub><sup>b</sup> = 934 Hz, <sup>1</sup>J<sub>PF</sub><sup>a</sup> = 890 Hz, <sup>2</sup>J<sub>PF</sub> = 99 Hz, <sup>2</sup>J<sub>PF</sub> = 90 Hz).

### 1.3. Cleavage of the carbene-phosphorus(V) adducts with aHF

#### Synthesis of compound 8a

To a solution of **3a** (0.30 g, 1.34 mmol) in dichloromethane (4 ml) an excess of aHF (0.2 g, 10.00 mmol) was condensed at -196 °C. After stirring for 12 h all volatile components were removed under reduced pressure. 1,3-dimethylimidazolinium hexafluorophosphate (0.32 g) was obtained as an analytically pure colorless solid. Yield: 0.32 g (98% based on **3a**). M<sub>r</sub> = 244.12. <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ = 7.3 (s, 1H, CH), 3.9 (d, 4H, -CH<sub>2</sub>-, <sup>2</sup>J<sub>HH</sub> = 0.7 Hz), 3.1 (s, 6H, -CH<sub>3</sub>, <sup>1</sup>J<sub>CH</sub> = 141 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN) δ = 157.9 (s, CH), 50.5 (s, -CH<sub>2</sub>-), 34.0 (s, -CH<sub>3</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ = -72.9 (d, <sup>1</sup>J<sub>PF</sub> = 707 Hz). <sup>31</sup>P NMR (CD<sub>3</sub>CN) δ = -144.6 (sept, <sup>1</sup>J<sub>PF</sub> = 707 Hz). ESI MS negative range m/z (%): 144.6 (100) [PF<sub>6</sub>]<sup>-</sup>; positive range m/z (%): 343.1 (100) [(C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>)<sub>2</sub>PF<sub>6</sub>]<sup>+</sup>, 99.1 [C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>]<sup>+</sup>. IR (ATR) [cm<sup>-1</sup>]: 2958 w, 1567 m, 1456 w, 1409 w, 1292 m, 1216 w, 1019 w, 944 m, 672 m, 645 w, 549 s, 527 w. Elemental analysis (%) calcd for [C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>][PF<sub>6</sub>] (244.12): C 24.60 H 4.54 N 11.48. Found: C 24.62 H 4.72 N 11.08.

#### Synthesis of compound 8b

Compound **8b** was synthesized following the procedure for **8a**. Quantities used: **3b** (0.41 g, 1.81 mmol), aHF (0.2 g, 10.00 mmol). Yield: 0.41 g (92% based on **3b**). M<sub>r</sub> = 246.13. <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ = 7.4 (s, 1H, CH), 3.3 (s, 6H, -CH<sub>3</sub>), 3.2 (s, 6H, -CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN) δ = 156.3 (s, CH), 45.4 (s, -CH<sub>3</sub>), 38.4 (s, -CH<sub>3</sub>). <sup>19</sup>F NMR (CD<sub>3</sub>CN) δ = -72.9 (d, <sup>1</sup>J<sub>PF</sub> = 707 Hz). <sup>31</sup>P NMR (CD<sub>3</sub>CN) δ = -144.6 (sept, <sup>1</sup>J<sub>PF</sub> = 707 Hz). ESI MS negative range m/z (%): 390.8 (2) [C<sub>5</sub>H<sub>13</sub>N<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>]<sup>-</sup>, 144.6 (100) [PF<sub>6</sub>]<sup>-</sup>; positive range m/z (%): 347.1 (100) [(C<sub>5</sub>H<sub>13</sub>N<sub>2</sub>)<sub>2</sub>PF<sub>6</sub>]<sup>+</sup>, 101.1 [C<sub>5</sub>H<sub>13</sub>N<sub>2</sub>]<sup>+</sup>. IR (ATR) [cm<sup>-1</sup>]: 2958 w, 1703 m, 1567 m, 1497 w, 1423 w, 1404 m, 1289 w, 1171 w, 1063 w, 979 w, 917 w, 875 w, 819 vs, 774 s, 666 w, 555 s, 525 m, 428 m. Elemental analysis (%) calcd for [C<sub>5</sub>H<sub>13</sub>N<sub>2</sub>][PF<sub>6</sub>] (246.13): C 24.40 H 5.32 N 11.38. Found: C 24.48 H 5.46 N 11.02.

## 2. Crystallographic Section

### X-ray measurements

Data collection for X-ray structure determination of **1a**, **1b**, **5a**, and **6b** were performed on a Bruker Nonius KappaCCD diffractometer, **6b** on an Agilent Supernova, **2a** on a Siemens P4 diffractometer using Mo<sub>Kα</sub> radiation ( $\lambda = 71.073$  pm). For structure solution and refinement, SHELX-97 was used.<sup>5</sup> Crystal and refinement details, as well as CCDC numbers are provided in Table S1.

Table S1

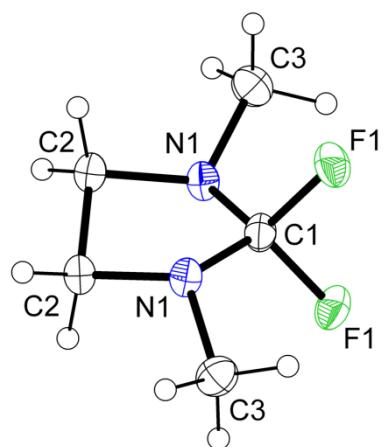
Parameter	<b>1a</b>	<b>1b</b>
empirical formula	C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> F <sub>2</sub>	C <sub>5</sub> H <sub>12</sub> N <sub>2</sub> F <sub>2</sub>
formula weight	136.15	138.17
crystal system	monoclinic	orthorhombic
space group	C2/c	<i>Fdd2</i>
<i>a</i> (Å)	10.2799(8)	15.251(4)
<i>b</i> (Å)	6.1220(5)	15.894(4)
<i>c</i> (Å)	10.4446(5)	5.825(2)
$\alpha$ (°)	90.00	90.00
$\beta$ (°)	96.922(5)	90.00
$\gamma$ (°)	90.00	90.00
volume (Å <sup>3</sup> )	652.52(8)	1411.9(7)
<i>Z</i>	4	8
<i>D</i> <sub>calcd</sub> (g/cm <sup>3</sup> )	1.386	1.300
Abs coeff (mm <sup>-1</sup> )	0.126	0.117
<i>F</i> (000)	288	592
crystal size (mm <sup>3</sup> )	0.25 x 0.24 x 0.24	0.35 x 0.20 x 0.20
θ range for data coll. (°)	4.0 – 30.0	3.7 – 25.0
reflections collected	3850	3718
Independent reflections	946	541
<i>R</i> (int)	0.029	0.0458
observed ( <i>I</i> > 2σ( <i>I</i> ))	828	473
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.072	1.165
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 σ( <i>I</i> )] <sup>a</sup>	0.0336	0.0289
<i>R</i> <sub>w</sub> (all data) <sup>b</sup>	0.0943	0.0572
CCDC	967585	967586

<sup>a</sup>*R*<sub>1</sub> = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|. <sup>b</sup>*R*<sub>w</sub> = {Σ[w(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[w(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]}<sup>1/2</sup>.

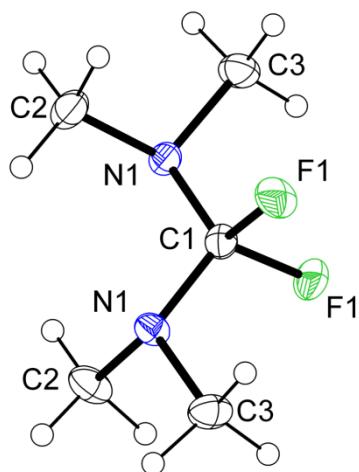
Table S2

Parameter	<b>2a</b>	<b>5a</b>	<b>6a</b>	<b>6b</b>
empirical formula	C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> Cl <sub>2</sub>	C <sub>6</sub> H <sub>10</sub> F <sub>7</sub> N <sub>2</sub> P	C <sub>7</sub> H <sub>10</sub> F <sub>9</sub> N <sub>2</sub> P	C <sub>7</sub> H <sub>12</sub> F <sub>9</sub> N <sub>2</sub> P
formula weight	169.05	274.13	324.14	326.16
temp (K)	173(2)	240(2)	100(2)	100(2)
crystal system	orthorhombic	orthorhombic	triclinic	monoclinic
space group	<i>Pnma</i>	<i>Pnma</i>	<i>P</i> <i>ī</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> (Å)	12.203(3)	8.5939(6)	8.6479(2)	9.3594(2)
<i>b</i> (Å)	8.517(2)	12.2830(8)	10.9687(2)	21.9735(5)
<i>c</i> (Å)	7.388(3)	9.7430(5)	12.7240(3)	12.1644(3)
$\alpha$ (°)	90.00	90.00	87.6528(16)	90.00
$\beta$ (°)	90.00	90.00	70.535(2)	99.7832(13)
$\gamma$ (°)	90.00	90.00	87.9102(17)	90.00
volume (Å <sup>3</sup> )	767.8(4)	1028.46(11)	1136.68(4)	2465.33(10)
<i>Z</i>	4	4	4	8
<i>D</i> <sub>calcd</sub> (g/cm <sup>3</sup> )	1.462	1.770	1.894	1.757
Abs coeff (mm <sup>-1</sup> )	0.760	0.344	0.352	0.325
<i>F</i> (000)	352	552	648.0	1312
crystal size (mm <sup>3</sup> )	0.70 x 0.50 x 0.10	0.30 x 0.10 x 0.06	0.40 x 0.13 x 0.11	0.30 x 0.30 x 0.20
θ range for data coll. (°)	3.2 – 27.5	3.6 – 27.5	3 – 30.0	3.0 – 27.5
reflections collected	4033	9353	53254	39261
Independent reflections	942	1210	6614	5610
<i>R</i> (int)	0.0956	0.045	0.030	0.055
observed ( <i>I</i> > 2σ( <i>I</i> ))	772	918	6011	4044
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.006	1.059	1.065	1.039
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 σ( <i>I</i> )] <sup>a</sup>	0.0760	0.0476	0.0276	0.0419
<i>R</i> <sub>w</sub> (all data) <sup>b</sup>	0.2072	0.1414	0.0773	0.1150
CCDC	967587	967588	967589	967590

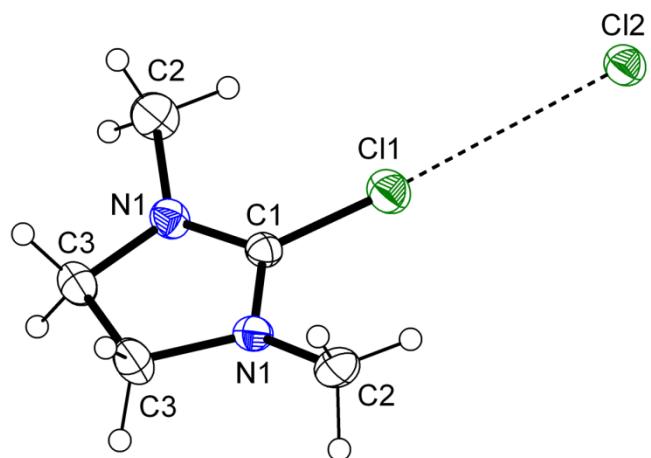
<sup>a</sup>*R*<sub>1</sub> = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|. <sup>b</sup>*R*<sub>w</sub> = {Σ[w(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[w(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]}<sup>1/2</sup>



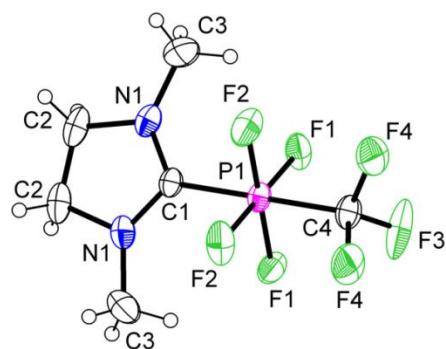
**Figure S1.** Atom labeling for the crystal structure of **1a**.



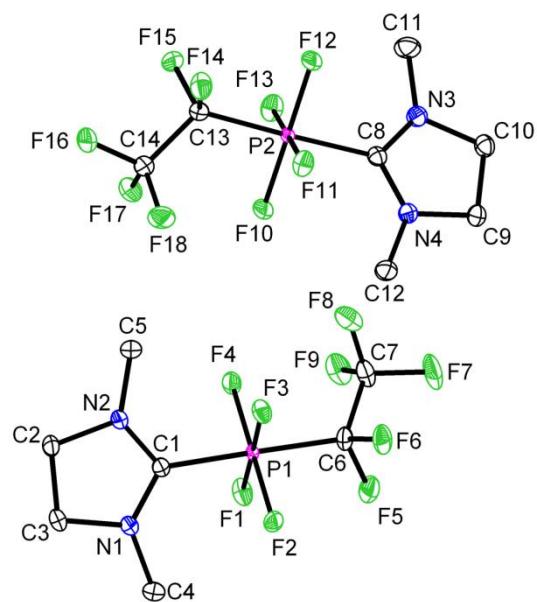
**Figure S2.** Atom labeling for the crystal structure of **1b**.



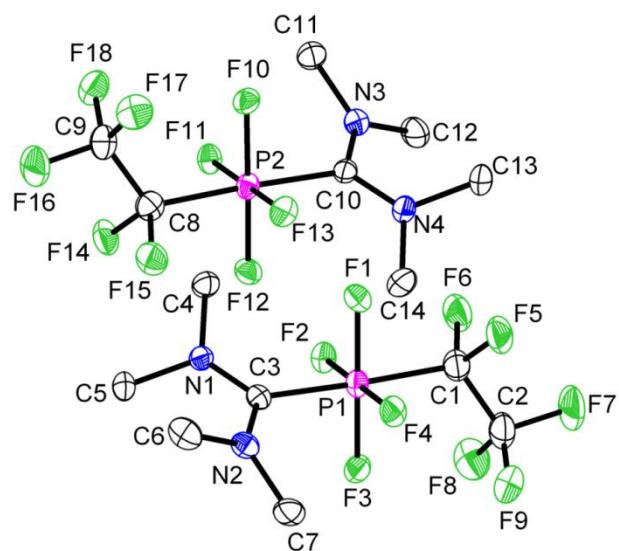
**Figure S3.** Atom labeling for the crystal structure of **2a**.



**Figure S4.** Atom labeling for the crystal structure of **5a**.



**Figure S5.** Atom labeling for the crystal structure of **6a**.



**Figure S6.** Atom labeling for the crystal structure of **6b**.

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