

## Supporting Information (14 pages)

### Interaction of Carbene and Olefin Donors with $[\text{Cl}_2\text{PN}]_3$ : Exploration of a Reductive Pathway toward $(\text{PN})_3$

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## Experimental Section

**General.** All the reactions were performed using standard Schlenk line techniques under an atmosphere of nitrogen or in an inert atmosphere glove box (Innovative Technology, Inc.). Solvents were dried using Grubbs-type solvent purification system<sup>1</sup> manufactured by Innovative Technology, Inc., degassed (freeze-pump-thaw method) and stored over molecular sieves under nitrogen atmosphere prior to use. Phosphonitric chloride trimer [Cl<sub>2</sub>PN]<sub>3</sub>, HCl (2.0 M solution in Et<sub>2</sub>O), BH<sub>3</sub>•THF (1.0 M solution) and elemental sulfur were purchased from Aldrich and used as received. 1,3-Bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr),<sup>2</sup> 1,3-Bis-(2,6-diisopropylphenyl)-2-methyleneimidazoline (IPr=CH<sub>2</sub>)<sup>3</sup> were prepared following literature procedures. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P NMR spectra were recorded on a Varian iNova-400 spectrometer and referenced externally to SiMe<sub>4</sub> (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) and 85 % H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P{<sup>1</sup>H}). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Mass spectra were obtained on a Agilent 6220 spectrometer. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

**X-ray Crystallography.** Crystals of suitable quality for X-ray crystallography were removed from a vial in glove box and coated immediately with thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was picked and mounted on glass fiber and then quickly placed in a low temperature stream of nitrogen on the X-ray diffractometer.<sup>4</sup> All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using either Mo K $\alpha$  radiation or Cu K $\alpha$  (compound **2**), with the crystals cooled to -100 °C. The data were corrected for absorption<sup>5</sup> through Gaussian integration from the indexing of the crystal faces. Structures were solved using

direct methods programs SHELXS-97, and refined using SHELXS-97.<sup>6</sup> Hydrogen atoms were assigned positions based on  $sp^2$  or  $sp^3$  hybridization geometries of their attached carbon atoms, and were given thermal parameters 20 % greater than those of their parent atoms.

### Synthetic Procedures.

**Synthesis of [IPr•PN(Cl<sub>2</sub>PN)<sub>2</sub>] (1).** To a mixture of IPr (280 mg, 0.72 mmol), phosphonitric chloride trimer [Cl<sub>2</sub>PN]<sub>3</sub> (100 mg, 0.29 mmol) and sodium (15 mg, 0.65 mmol) was added 15 mL of a 1:1 mixture of toluene/THF mixture. The reaction was then stirred overnight to give a pale green slurry. The precipitate was allowed to settle and the mother liquor was then filtered through Celite to yield a green solution. The volatiles were removed from the filtrate and the resulting solid was then washed with 5 mL of hexanes and dried to give a pale green powder. Crystals (colorless blocks) suitable for X-ray crystallography were grown by cooling a saturated toluene solution layered with hexanes to -35 °C for 7 days (103 mg, 55 % yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz): δ 0.94 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.45 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.63 (septet, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.17 (s, 2H, N-CH-), 7.05 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 4H, ArH), 7.15 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.5 MHz): δ 23.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 121.6 (-N-CH-), 123.7 (ArC), 124.6 (ArC), 129.1 (ArC), 139.1 (ArC), 146.3 (N-C-N). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 161 MHz): δ 6.1 (d, -Cl<sub>2</sub>P=N, <sup>2</sup>J<sub>PP</sub> = 86.9 Hz), 101.4 (t, IPr-P=N, <sup>2</sup>J<sub>PP</sub> = 86.9 Hz). Repeated attempts to obtain satisfactory elemental analysis consistently led to low analyses values for N (> 3 % lower). Mp (°C): 153-155 (dec.), 225-227 (melts).

**Alternate synthesis of [IPr•PN(Cl<sub>2</sub>PN)<sub>2</sub>] (1) in the absence of Na metal.** To a mixture of IPr (0.41 g, 1.1 mmol), phosphonitrilic chloride trimer, [Cl<sub>2</sub>PN]<sub>3</sub> (0.18 g, 0.53 mmol) was added 15 mL of toluene. The reaction mixture was stirred overnight at room temperature to give a thick brown slurry. The insoluble fraction was allowed to settle and the mother liquor was then filtered through Celite to yield a pale brown solution. Removal of the volatiles from the filtrate afforded a brown oil. The oil was dissolved in 12 mL of toluene, layered with hexanes and cooled to -35 °C for 10 days to give **1** as a colorless crystalline solid (45 mg, 13 % yield).

**Reaction of 1 with S<sub>8</sub>: Synthesis of [IPr•(S)PN(Cl<sub>2</sub>PN)<sub>2</sub>] (2).** To a mixture of **1** (72 mg, 0.11 mmol) and sulfur (3.5 mg, 0.11 mmol) was added 10 mL of toluene. The reaction was stirred overnight at room temperature to give a slightly cloudy mixture. Filtration of the resulting mixture through Celite gave a colorless filtrate. Removal of the volatiles from the filtrate yielded a colorless crystalline solid (67 mg, 88 % yield). X-ray quality crystals of **2** were grown by cooling a saturated toluene solution to -35 °C for 2 days. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz): δ 0.93 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.50 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.79 (septet, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.15 (d, <sup>4</sup>J<sub>HP</sub> = 1.5 Hz, 2H, N-CH-), 7.04 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 4H, ArH), 7.13 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz): δ 23.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 124.5 (-N-CH-), 124.6 (ArC), 127.6 (ArC), 131.4(ArC), 134.0 (ArC), 145.2 (N-C-N). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 161 MHz): δ 13.4 (d, -Cl<sub>2</sub>P=N, <sup>2</sup>J<sub>PP</sub> = 26.7 Hz), 23.9 (t, IPr-P=N, <sup>2</sup>J<sub>PP</sub> = 26.7 Hz). Anal. Calcd. for C<sub>27</sub>H<sub>36</sub>Cl<sub>4</sub>N<sub>5</sub>P<sub>3</sub>S: C, 46.50; H, 5.20; N, 10.40; S, 4.60. Found: C, 47.07; H, 5.60; N, 9.75; S, 4.21. Mp (°C): > 260 °C.

**Synthesis of [IPr•(BH<sub>3</sub>)P•N(Cl<sub>2</sub>PN)<sub>2</sub>] (3).** To a solution of **1** (74 mg, 0.11 mmol) in 6 mL of toluene was added dropwise BH<sub>3</sub>•THF (0.11 mL, 0.11 mmol, 1.0 M solution in THF). The reaction mixture turned slightly cloudy after two hours of stirring at room temperature. The solution was then filtered through Celite and the volatiles were removed from the filtrate to yield a crystalline white solid that was identified as **3** (65 mg, 87% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz): δ 0.91 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.51 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.70 (septet, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.17 (s, 2H, N-CH-), 7.03 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 4H, ArH), 7.14 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz): δ 23.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 124.6 (-N-CH-), 125.7 (ArC), 131.6 (ArC), 133.6 (ArC), 136.2 (ArC), 145.2 (N-C-N). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 161 MHz): δ 12.6 (d, -Cl<sub>2</sub>P=N, <sup>2</sup>J<sub>PP</sub> = 6.0 Hz), 72.5 (br, IPr-P=N). <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 128 MHz): δ -30.5 (d, IPr•P•BH<sub>3</sub>, <sup>1</sup>J<sub>BP</sub> = 71.6 Hz). HR-MS ESI (positive mode, m/z): [M+H]<sup>+</sup>; 678.1352 (Δ = 1.39 ppm). Anal. Calcd. for C<sub>27</sub>H<sub>39</sub>BCl<sub>4</sub>N<sub>5</sub>P<sub>3</sub>: C, 47.75; H, 5.79; N, 10.31. Found: C, 47.94; H, 5.82; N, 9.44. Mp (°C): 194-197 (dec.).

**Synthesis of [(IPr=CH)PCIN(Cl<sub>2</sub>PN)<sub>2</sub>] (4).** To a mixture of IPr=CH<sub>2</sub> (140 mg, 0.35 mmol) and phosphonitrilic chloride trimer [Cl<sub>2</sub>PN]<sub>3</sub> (60 mg, 0.17 mmol) was added 15 mL of toluene. The reaction mixture was heated to 60 °C in an oil bath for 30 hrs. resulting in the formation of a pink solution over a white precipitate. The reaction mixture was then filtered through Celite and the volatiles were removed from the filtrate *in vacuo* to yield a pink powder (110 mg, 88 %). Crystals (colorless needles) suitable for X-ray crystallography were grown by cooling a saturated toluene solution layered with hexanes to -35 °C for 5 days. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz): δ 1.06 (d, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (d, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.91 (septet, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.31 (t, 1H, -CH-, <sup>4</sup>J<sub>HP</sub> = 6.0 Hz, confirmed by selective <sup>1</sup>H{<sup>31</sup>P} and <sup>1</sup>H-<sup>31</sup>P

gHSQC experiments), 5.96 (s, 2H, N-CH-), 7.06 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 4H, ArH), 7.20 (t,  $^3J_{\text{HH}} = 8.0$  Hz, 2H, ArH).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125 MHz):  $\delta$  23.3 ( $\text{CH}(\text{CH}_3)_2$ ), 24.9 ( $\text{CH}(\text{CH}_3)_2$ ), 29.1 ( $\text{CH}(\text{CH}_3)_2$ ), 53.4 (doublet of triplets, -CH-P,  $^1J_{\text{CP}} = 231.4$  Hz,  $^3J_{\text{CP}} = 16.1$  Hz), 118.5 (-N-CH-), 124.9 (ArC), 130.0 (ArC), 132.9 (ArC), 147.1 (ArC), 152.0 (d, N-C-N,  $^2J_{\text{CP}} = 15.2$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 201 MHz):  $\delta$  18.8 (d,  $-\text{Cl}_2\text{P}=\text{N}-$ ,  $^2J_{\text{PP}} = 17.5$  Hz), 25.6 (t,  $-\text{HC}-\text{ClP}=\text{N}-$ ,  $^2J_{\text{PP}} = 17.5$  Hz). Anal. Calcd. for  $\text{C}_{28}\text{H}_{37}\text{Cl}_5\text{N}_5\text{P}_3$ : C, 47.11; H, 5.22; N, 9.81. Found: C, 47.70; H, 5.32; N, 9.66. Mp ( $^\circ\text{C}$ ):  $> 260$   $^\circ\text{C}$ .

**Reaction of  $[(\text{IPr}=\text{CH})\text{PClN}(\text{Cl}_2\text{PN})_2]$  with HCl.** To a solution of **4** (85 mg, 0.12 mmol) in 10 mL of toluene was added a solution of HCl (0.120 mL, 0.24 mmol, 2.0 M solution in  $\text{Et}_2\text{O}$ ). The reaction mixture clouded immediately and was stirred for 2 hours to give a white slurry. The slurry was allowed to settle and the white precipitate was isolated by filtration.  $^{31}\text{P}\{^1\text{H}\}$  NMR analysis (toluene, 161 MHz) of the filtrate revealed the quantitative formation of free phosphonitric chloride trimer,  $[\text{Cl}_2\text{PN}]_3$ .<sup>7</sup> The precipitate was dried *in vacuo* to give a white powder (51 mg, 97 % yield) which was identified as  $[\text{IPr}-\text{CH}_3]\text{Cl}$ .

Data for  $[\text{IPr}-\text{CH}_3]\text{Cl}$ :  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.17 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.27 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 2.07 (s, 3H,  $-\text{CH}_3$ ), 2.32 (septet,  $^3J_{\text{HH}} = 7.0$  Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 7.36 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 4H, ArH), 7.60 (t,  $^3J_{\text{HH}} = 8.0$  Hz, 2H, ArH), 8.53 (s, 2H, N-CH-).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  10.8 (s,  $-\text{CH}_3$ ), 23.5 ( $\text{CH}(\text{CH}_3)_2$ ), 24.9 ( $\text{CH}(\text{CH}_3)_2$ ), 29.1 ( $\text{CH}(\text{CH}_3)_2$ ), 125.4 (-N-CH-), 127.1 (ArC), 129.2 (ArC), 132.5 (ArC), 144.5 (ArC), 145.1 (N-C-N). MS-ESI (positive mode, m/z):  $[\text{IPr}-\text{CH}_3]^+$ ; 403.3. Anal. Calcd. for  $\text{C}_{28}\text{H}_{39}\text{ClN}_2$ : C, 76.59; H, 8.95; N, 6.38;. Found: C, 76.56; H, 8.87; N, 6.56.

**Table S1.** Crystallographic Experimental Details for [IPr•PN(Cl<sub>2</sub>PN)<sub>2</sub>] (**1**)*A. Crystal Data*

formula	C <sub>34</sub> H <sub>44</sub> Cl <sub>4</sub> N <sub>5</sub> P <sub>3</sub>
formula weight	757.45
crystal dimensions (mm)	0.50 × 0.35 × 0.09
crystal system	triclinic
space group	<i>P</i> $\bar{1}$
unit cell parameters <sup>a</sup>	
<i>a</i> (Å)	9.9329(3)
<i>b</i> (Å)	12.3748(4)
<i>c</i> (Å)	16.5363(5)
α (deg)	86.1689(3)
β (deg)	76.2264(3)
γ (deg)	80.9368(3)
<i>V</i> (Å <sup>3</sup> )	1948.60(10)
<i>Z</i>	2
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.291
μ (mm <sup>-1</sup> )	0.458

*B. Data Collection and Refinement Conditions*

diffractometer	Bruker D8/APEX II CCD <sup>b</sup>
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	−100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	55.12
total data collected	17249 (−12 ≤ <i>h</i> ≤ 12, −15 ≤ <i>k</i> ≤ 16, −21 ≤ <i>l</i> ≤ 21)
independent reflections	8886 ( <i>R</i> <sub>int</sub> = 0.0117)
number of observed reflections ( <i>NO</i> )	7786 [ <i>F</i> <sub>o</sub> <sup>2</sup> ≥ 2σ( <i>F</i> <sub>o</sub> <sup>2</sup> )]
structure solution method	direct methods ( <i>SHELXS-97</i> <sup>c</sup> )
refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup> ( <i>SHELXL-97</i> <sup>c</sup> )
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9582–0.8018
data/restraints/parameters	8886 / 0 / 415
goodness-of-fit ( <i>S</i> ) <sup>d</sup> [all data]	1.034
final <i>R</i> indices <sup>e</sup>	
<i>R</i> <sub>1</sub> [ <i>F</i> <sub>o</sub> <sup>2</sup> ≥ 2σ( <i>F</i> <sub>o</sub> <sup>2</sup> )]	0.0325
<i>wR</i> <sub>2</sub> [ <i>F</i> <sub>o</sub> <sup>2</sup> ≥ −3σ( <i>F</i> <sub>o</sub> <sup>2</sup> )]	0.0932
largest difference peak and hole	0.473 and −0.397 e Å <sup>-3</sup>

<sup>a</sup>Obtained from least-squares refinement of 9952 reflections with 5.02° < 2θ < 55.04°.

<sup>b</sup>Programs for diffractometer operation, data collection, data reduction and absorption

correction were those supplied by Bruker.

<sup>c</sup>Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

$$dS = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2} \quad (n = \text{number of data}; p = \text{number of parameters varied}; w \\ = [\sigma^2(F_o^2) + (0.0481P)^2 + 0.7296P]^{-1} \text{ where } P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3).$$

$$eR_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}.$$

**Table S2.** Crystallographic Experimental Details for [IPr•(S)PN(Cl<sub>2</sub>PN)<sub>2</sub>] (**2**)*A. Crystal Data*

formula	C <sub>34</sub> H <sub>44</sub> Cl <sub>4</sub> N <sub>5</sub> P <sub>3</sub> S
formula weight	789.51
crystal dimensions (mm)	0.26 × 0.22 × 0.12
crystal system	monoclinic
space group	<i>P2</i> <sub>1</sub> / <i>c</i>
unit cell parameters <sup>a</sup>	
<i>a</i> (Å)	11.5334(2)
<i>b</i> (Å)	13.9851(2)
<i>c</i> (Å)	24.9658(10)
β (deg)	99.5850(10)
<i>V</i> (Å <sup>3</sup> )	3970.66(11)
<i>Z</i>	4
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.321
μ (mm <sup>-1</sup> )	4.586

*B. Data Collection and Refinement Conditions*

diffractometer	Bruker D8/APEX II CCD <sup>b</sup>
radiation (λ [Å])	graphite-monochromated Cu Kα (1.54178)
temperature (°C)	-100
scan type	ω scans (0.5°) (5 s exposures)
data collection 2θ limit (deg)	139.34
total data collected	26061 (-13 ≤ <i>h</i> ≤ 13, -16 ≤ <i>k</i> ≤ 16, -30 ≤ <i>l</i> ≤ 30)
independent reflections	7333 ( <i>R</i> <sub>int</sub> = 0.0220)
number of observed reflections ( <i>NO</i> )	6717 [ <i>F</i> <sub>o</sub> <sup>2</sup> ≥ 2σ( <i>F</i> <sub>o</sub> <sup>2</sup> )]
structure solution method	direct methods ( <i>SHELXS-97</i> <sup>c</sup> )
refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup> ( <i>SHELXL-97</i> <sup>c</sup> )
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.6160–0.3807
data/restraints/parameters	7333 / 15 <sup>d</sup> / 448
goodness-of-fit ( <i>S</i> ) <sup>e</sup> [all data]	1.066
final <i>R</i> indices <sup>f</sup>	
<i>R</i> <sub>1</sub> [ <i>F</i> <sub>o</sub> <sup>2</sup> ≥ 2σ( <i>F</i> <sub>o</sub> <sup>2</sup> )]	0.0392
<i>wR</i> <sub>2</sub> [ <i>F</i> <sub>o</sub> <sup>2</sup> ≥ 3σ( <i>F</i> <sub>o</sub> <sup>2</sup> )]	0.1126
largest difference peak and hole	0.631 and -0.367 e Å <sup>-3</sup>

<sup>a</sup>Obtained from least-squares refinement of 9880 reflections with 7.18° < 2θ < 138.56°.

<sup>b</sup>Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

<sup>c</sup>Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

<sup>d</sup>The geometry of the minor orientation of the disordered toluene solvent molecule was restrained to be the same as that of the major orientation during the refinement by use of the *SHELXL SAME* instruction.

<sup>e</sup> $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$  ( $n$  = number of data;  $p$  = number of parameters varied;  $w = [\sigma^2(F_o^2) + (0.0683P)^2 + 1.6203P]^{-1}$  where  $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$ ).

<sup>f</sup> $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$ .



**Table S3.** Crystallographic Experimental Details for [(IPr=CH)CIPN(Cl<sub>2</sub>PN)<sub>2</sub>] (**4**)*A. Crystal Data*

formula	C <sub>33</sub> H <sub>45</sub> Cl <sub>5</sub> N <sub>5</sub> P <sub>3</sub>
formula weight	805.92
crystal dimensions (mm)	0.64 × 0.17 × 0.15
crystal system	triclinic
space group	<i>P</i> $\bar{1}$
unit cell parameters <sup>a</sup>	
<i>a</i> (Å)	10.5636(4)
<i>b</i> (Å)	11.5438(5)
<i>c</i> (Å)	19.1398(5)
$\alpha$ (deg)	97.4845(5)
$\beta$ (deg)	99.7811(5)
$\gamma$ (deg)	114.9935(4)
<i>V</i> (Å <sup>3</sup> )	2030.64(14)
<i>Z</i>	2
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.318
$\mu$ (mm <sup>-1</sup> )	0.507

*B. Data Collection and Refinement Conditions*

diffractometer	Bruker D8/APEX II CCD <sup>b</sup>
radiation ( $\lambda$ [Å])	graphite-monochromated Mo K $\alpha$ (0.71073)
temperature (°C)	-100
scan type	$\omega$ scans (0.3°) (20 s exposures)
data collection $2\theta$ limit (deg)	54.96
total data collected	18102 ( $-13 \leq h \leq 13$ , $-14 \leq k \leq 14$ , $-24 \leq l \leq 24$ )
independent reflections	9252 ( $R_{\text{int}} = 0.0116$ )
number of observed reflections ( <i>NO</i> )	7954 [ $F_o^2 \geq 2\sigma(F_o^2)$ ]
structure solution method	direct methods ( <i>SHELXD</i> <sup>c</sup> )
refinement method	full-matrix least-squares on $F^2$ ( <i>SHELXL-97</i> <sup>d</sup> )
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9269–0.7380
data/restraints/parameters	9252 / 29 <sup>e</sup> / 525
goodness-of-fit ( $S$ ) <sup>f</sup> [all data]	1.052
final <i>R</i> indices <sup>g</sup>	
<i>R</i> <sub>1</sub> [ $F_o^2 \geq 2\sigma(F_o^2)$ ]	0.0429
<i>wR</i> <sub>2</sub> [ $F_o^2 \geq -3\sigma(F_o^2)$ ]	0.1271
largest difference peak and hole	1.021 and -0.534 e Å <sup>-3</sup>

<sup>a</sup>Obtained from least-squares refinement of 9897 reflections with  $4.40^\circ < 2\theta < 54.90^\circ$ .

<sup>b</sup>Programs for diffractometer operation, data collection, data reduction and absorption

correction were those supplied by Bruker.

<sup>c</sup>Schneider, T. R.; Sheldrick, G. M. *Acta Crystallogr.* **2002**, *D58*, 1772-1779.

<sup>d</sup>Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

<sup>e</sup>The minor orientation of the disordered N<sub>3</sub>P<sub>3</sub>Cl<sub>5</sub> ring was restrained to have the same geometry as that of the major orientation by use of the *SHELXL SAME* instruction.

$fS = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$  ( $n$  = number of data;  $p$  = number of parameters varied;  $w$  =  $[\sigma^2(F_o^2) + (0.0662P)^2 + 1.2274P]^{-1}$  where  $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$ ).

$gR_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$ .

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