## **Supporting information**

to the manuscript

# Imino-stabilised phosphinidene (or azaphosphole?) and some of its derivatives

by

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#### **Table of contents**

NMR spectrum	S2
$[2,6-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)_{2}C_{6}H_{3}]P(3)$	
$[\{2-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-^{i}Pr_{2}C_{6}H_{3}N-CH_{2})]C_{6}H_{3}PCl(10)$	
$[\{2,6-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)_{2}C_{6}H_{3}\}PBr][Br_{3}]$ (11)	
$[2,6-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)_{2}C_{6}H_{3}]P-S_{3}$ (12)	
$[\{2-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-^{i}Pr_{2}C_{6}H_{3}N-CH_{2})]C_{6}H_{3}PH(13)$	
$[\{2-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-^{i}Pr_{2}C_{6}H_{3}N(H)CH_{2})]C_{6}H_{3}P(14)$	
$[\{2-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-^{i}Pr_{2}C_{6}H_{3}N-CH_{2})]C_{6}H_{3}PCH_{3}(15)$	
$[\{2-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-^{i}Pr_{2}C_{6}H_{3}N-CH_{2})]C_{6}H_{3}P-PPh_{2}(16)$	
$[\{2-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-^{i}Pr_{2}C_{6}H_{3}N-CH_{2})]C_{6}H_{3}P-OC(O)H(17)$	
$[\{2-(2,6-{}^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-{}^{i}Pr_{2}C_{6}H_{3}N-CH_{2})]C_{6}H_{3}PCl(O) (18)$	
Table SI.1 <sup>31</sup> P NMR peaks of phosphorus compounds	S24
Mass spectroscopy	S25
IR spectroscopy	S27
X-ray diffraction analyses	S28





.55 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20

<sup>31</sup>P{<sup>1</sup>H} NMR spectrum



Figure SI1. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of  $\mathbf{3}$  in C<sub>6</sub>D<sub>6</sub>





Figure SI2. <sup>1</sup>H, <sup>1</sup>H $\{^{31}P\}$ , <sup>13</sup>C $\{^{1}H\}$ , and <sup>31</sup>P $\{^{1}H\}$  NMR spectra of 10 in C<sub>6</sub>D<sub>6</sub>



<sup>1</sup>H{<sup>31</sup>P} NMR spectrum







Figure SI3.  ${}^{1}H$ ,  ${}^{1}H{}^{31}P$ ,  ${}^{13}C{}^{1}H$ , and  ${}^{31}P{}^{1}H$  NMR spectra of 11 in CD<sub>2</sub>Cl<sub>2</sub>







Figure SI4.  ${}^{1}H$ ,  ${}^{1}H{}^{31}P$ ,  ${}^{13}C{}^{1}H$ , and  ${}^{31}P{}^{1}H$  NMR spectra of 12 in CD<sub>2</sub>Cl<sub>2</sub>



# <sup>13</sup>C{<sup>1</sup>H} NMR spectrum









Figure SI5.  ${}^{1}H$ ,  ${}^{1}H{}^{31}P$ ,  ${}^{13}C{}^{1}H$ ,  ${}^{31}P{}^{1}H$ , and  ${}^{31}P$  NMR spectra of 13 in C<sub>6</sub>D<sub>6</sub>



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S13

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1.5

2.0

1.0

# <sup>13</sup>C{<sup>1</sup>H} NMR spectrum



<sup>1</sup>H-<sup>1</sup>H COSY spectrum



Figure SI6.  ${}^{1}H$ ,  ${}^{1}H{}^{31}P$ ,  ${}^{13}C{}^{1}H$ , and  ${}^{31}P{}^{1}H$ ,  ${}^{1}H{}^{-1}H$  COSY NMR spectra of 14 in C<sub>6</sub>D<sub>6</sub>







Figure SI7.  ${}^{1}H$ ,  ${}^{1}H{}^{31}P$ ,  ${}^{13}C{}^{1}H$ , and  ${}^{31}P{}^{1}H$ NMR spectra of 15 in C<sub>6</sub>D<sub>6</sub>



<sup>13</sup>C{<sup>1</sup>H} NMR spectrum



160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20

<sup>31</sup>P{<sup>1</sup>H} NMR spectrum



Figure SI8.  ${}^{1}H$ ,  ${}^{1}H{}^{31}P$ ,  ${}^{13}C{}^{1}H$ , and  ${}^{31}P{}^{1}H$ NMR spectra of 16 in C<sub>6</sub>D<sub>6</sub>









165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20





Figure SI9.  ${}^{1}H$ ,  ${}^{1}H{}^{31}P$ ,  ${}^{13}C{}^{1}H$ , and  ${}^{31}P{}^{1}H$  NMR spectra of 17 in C<sub>6</sub>D<sub>6</sub>



### <sup>13</sup>C NMR spectrum



<sup>31</sup>P{<sup>1</sup>H} NMR spectrum



Figure SI10.  ${}^{1}H$ ,  ${}^{1}H{}^{31}P$ ,  ${}^{13}C{}^{1}H$ , and  ${}^{31}P{}^{1}H$  NMR spectra of 18 in C<sub>6</sub>D<sub>6</sub>

 Table SI.1 <sup>31</sup>P NMR peaks of phosphorus compounds

Compounds	<sup>31</sup> P{ <sup>1</sup> H} (ppm)
$[2,6-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)_{2}C_{6}H_{3}]P(3)$	178.2
$[\{2-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-^{i}Pr_{2}C_{6}H_{3}N-CH_{2})]C_{6}H_{3}PCl(10)$	134.1
$[\{2,6-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)_{2}C_{6}H_{3}\}PBr][Br_{3}] (11)$	67.3
$[2,6-(2,6-Pr_2C_6H_3N=CH)_2C_6H_3]P-S_3$ (12)	120.7
$[\{2-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-^{i}Pr_{2}C_{6}H_{3}N-CH_{2})]C_{6}H_{3}PH(13)$	19.9
$[\{2-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-^{i}Pr_{2}C_{6}H_{3}N(H)CH_{2})]C_{6}H_{3}P(14)$	174.7
$[\{2-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-^{i}Pr_{2}C_{6}H_{3}N-CH_{2})]C_{6}H_{3}PCH_{3}(15)$	61.0
$[\{2-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-^{i}Pr_{2}C_{6}H_{3}N-CH_{2})]C_{6}H_{3}P-PPh_{2}(16)$	80.8/9.4
$[\{2-(2,6-{}^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-{}^{i}Pr_{2}C_{6}H_{3}N-CH_{2})]C_{6}H_{3}P-OC(O)H(17)$	124.6
$[\{2-(2,6-^{i}Pr_{2}C_{6}H_{3}N=CH)-6-(2,6-^{i}Pr_{2}C_{6}H_{3}N-CH_{2})]C_{6}H_{3}PCl(O) (18)$	29.1

#### Mass spectroscopy



Figure SI11. ESI<sup>+</sup> mass spectrum (MeOH/DCM) of  $\bf 3$ 





The middle and bottom spectra are theoretical isotope models of C32H39BrPN2(OH)2 and C32H39BrPN2(H2O)2, respectively.

**Figure SI12**. ESI<sup>+</sup> mass spectrum (MeOH/DCM) of **11** (a and b, top) and theoretical modes with OH<sup>-</sup> (b, middle) and H<sub>2</sub>O (b, bottom). The MS data is consistent with theoretical modes of  $[(dimph)PBr]^+$  cation with two  $[OH]^-$  moiety. It's approximately 1.5 mins from when sample vial was open to when sample got into the MS analyzer. Two  $[OH]^-$  moiety are presented due to exposing the sample to air during the process of preparation.



Figure SI13. ESI<sup>-</sup> mass spectrum (MeOH/DCM) of 12

#### **IR** spectroscopy



Figure SI14. IR spectrum of 14

X-ray diffraction analyses. Crystals of compounds 3, 14, and 18, suitable for X-ray diffraction analysis, were obtained from toluene solutions at -30°C, whereas crystals of compound 17 were grown from a toluene/THF mixture at -30°C. The crystals were coated in a film of perfluoropolyether oil and mounted on a glass fibre and transferred to a diffractometer. Intensity data were collected on a transferred to a diffractometer. Prior to data collection crystals were cooled to 200 K. Data were collected on a Bruker APEX II single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) and APEX II CCD detector. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.<sup>[i]</sup> Diffraction data for all four samples were collected with a sequence of  $0.5^{\circ} \omega$  scans at 0, 120, and 240° in  $\varphi$ . Initial unit cell parameters were determined from 36 data frames with 0.5°  $\omega$  scan each, collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.<sup>[ii]</sup> The structural model was refined with full set of anisotropic thermal displacement coefficient for all non-hydrogen atoms. All hydrogen atom positions were calculated based on the geometry of related non-hydrogen atoms. All hydrogen atoms were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.<sup>[iii]</sup> Crystal and structure refinement data are garnered in Table SI1.

The molecule of **3** is bisected by a crystallographically imposed mirror plane running through the C1-C4 axis, resulting in averaging of two non-equivalent aldimine parts. Because the phosphorus atom lies outside the crystallographic mirror plane, its position is disordered with equal occupancy of both sides. The crystal of compound **18** (Figure SI15) was twinned, with the contribution of the second component totalling 0.42, which resulted in a relatively low accuracy.



**Figure SI15.** Molecular structure of compound **18**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

	3	14	17	18
empirical formula	$C_{32}H_{39}N_2P$	$C_{32}H_{41}N_2P$	$C_{33}H_{41}N_2O_2P$	$C_{32}H_{40}N_2OClP$
formula weight	482.62	484.64	528.65	535.08
crystal habit	block	block	block	prism
crystal color	orange	red	yellow	white
temperature, K	200(2)	200(2)	200(2)	200(2)
wavelength, Å	0.71073	0.71073	0.71073	0.71073
crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
space group	Pbcn	Cc	P2(1)/n	Cmc2(1)
unit cell dimensions:				
a, Å	21.2829(7)	8.277(5)	10.6711(6)	30.90(4)
b, Å	8.2036(3)	43.32(3)	20.7210(12)	11.407(14)
c, Å	16.1186(6)	8.716(5)	13.5816(7)	17.67(2)
a, °	90	90	90	90

 Table 1. Crystal and structure refinement data

b, °	90	112.867(8)	91.933(3)	90
g, °	90	90	90	90
volume, Å <sup>3</sup>	2814.25(17)	2880(3)	3001.4(3)	6228(13)
Z	4	4	4	8
density (calc), Mg/m <sup>3</sup>	1.139	1.118	1.170	1.141
absorption coeff., $mm^{-1}$	0.120	0.117	0.123	0.199
<i>F</i> (000)	1040	1048	1136	2288
crystal size, mm <sup>3</sup>	0.14 x 0.23 x 0.47	0.19 x 0.11 x 0.08	0.34 x 0.27 x 0.13	0.40 x 0.50 x 0.90
$\theta$ range for data collection	1.91 to 27.91	2.00 to 28.37	1.79 to 30.03	1.90 to 25.25
index ranges	$\begin{array}{l} -28 \leq h \leq 26,  -10 \\ \leq k \leq 10,  -21 \leq 1 \\ \leq 21 \end{array}$	$\begin{array}{l} -10 \leq h \leq 10,  \text{-} \\ 57 \leq k \leq 56,  \text{-}10 \\ \leq l \leq 11 \end{array}$	$\begin{array}{l} \text{-14} \leq h \leq 14,  \text{-21} \\ \leq k \leq 27,  \text{-18} \leq l \leq \\ 18 \end{array}$	$\begin{array}{l} -36 \leq h \leq 36, - \\ 13 \leq k \leq 13, -21 \\ \leq l \leq 2l \end{array}$
reflections collected	30233	14188	32015	25625
independent reflections	$\begin{array}{l} 3370 \; [R_{int} = \\ 0.0508] \end{array}$	$\begin{array}{l} 6151 \; [R_{int} = \\ 0.0585] \end{array}$	$\begin{array}{l} 8168 \; [R_{int} = \\ 0.0584] \end{array}$	5582 [R(int) = 0.0883]
absorption correction	SADABS	SADABS	SADABS	SADABS
max. and min. transmission	0.9458 and 0.9837	0.9779 and 0.9902	0.9595 and 0.9842	0.8409 and 0.9245
refinement method	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$
data / restraints / parameters	3370/0/164	6151 / 3 / 330	8168 / 0 / 343	5582 / 768 / 533
goodness-of-fit on $F^2$	1.022	0.984	1.015	1.236
final <i>R</i> indices [I $> 2\sigma(I)$ ]	R1 = 0.0479, wR2 = 0.1119	R1 = 0.0601, wR2 = 0.1433	R1 = 0.0607 w $R2 = 0.1485$	R1 = 0.1249 w $R2 = 0.2974$
<i>R</i> indices (all data)	R1 = 0.0873, wR2 = 0.1341	R1 = 0.1134, wR2 = 0.1696	R1 = 0.1065, w $R2 = 0.1816$	R1 = 0.1858, w $R2 = 0.3508$
largest diff. peak and hole, e. $A^{-3}$	0.197 and - 0.196	0.715 and - 0.263	0.678 and -0.544	0.337 and - 1.869
absolute structure parameter	-	0.27(19)	-	0.4(4)

<sup>[</sup>i] APEX Software Suite v.2012; Bruker AXS: Madison, WI (2012).

<sup>[</sup>ii] R. H. Blessing, *Acta Crystallogr.* 1995, *A51*, 33-38.
[iii] G. M. Sheldrick, *Acta Crystallogr.* 2008, *A64*, 112-122.