

## Supplementary Material

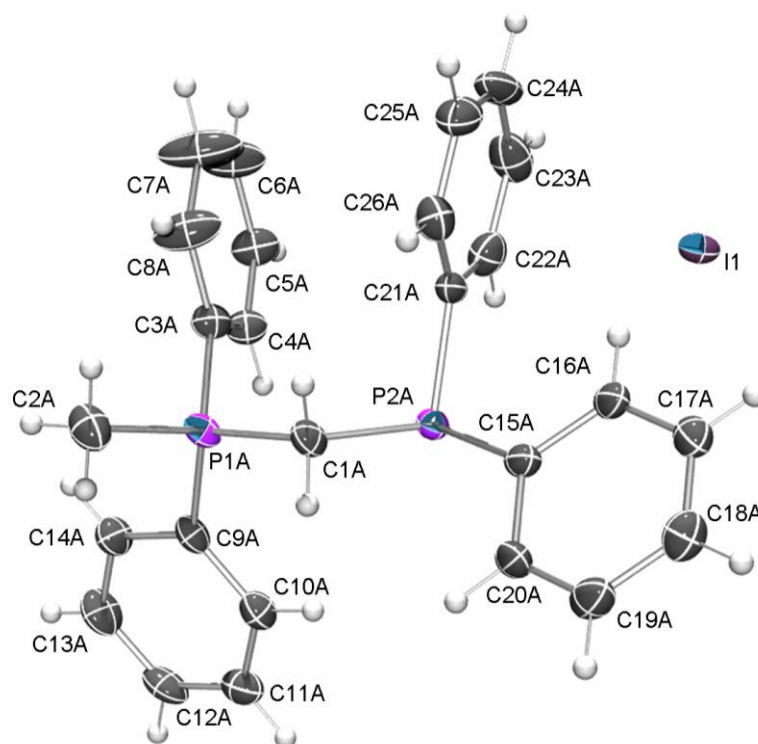
### Dppm-derived phosphonium salts and ylides as ligand precursors for s-block organometallics

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and Matthias Westerhausen

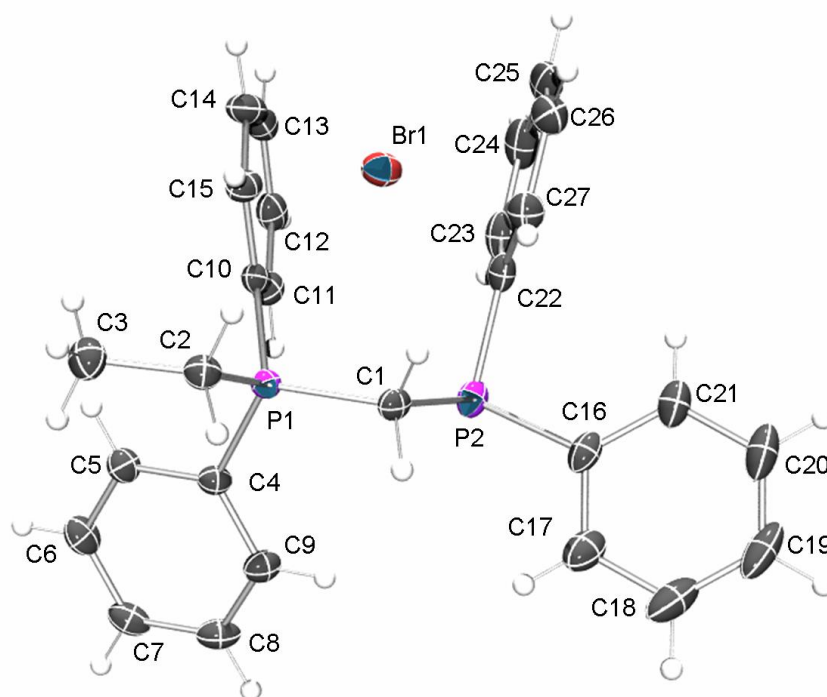
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**Dedicated to Professor Rainer Beckert on the Occasion of his 60<sup>th</sup> Birthday**

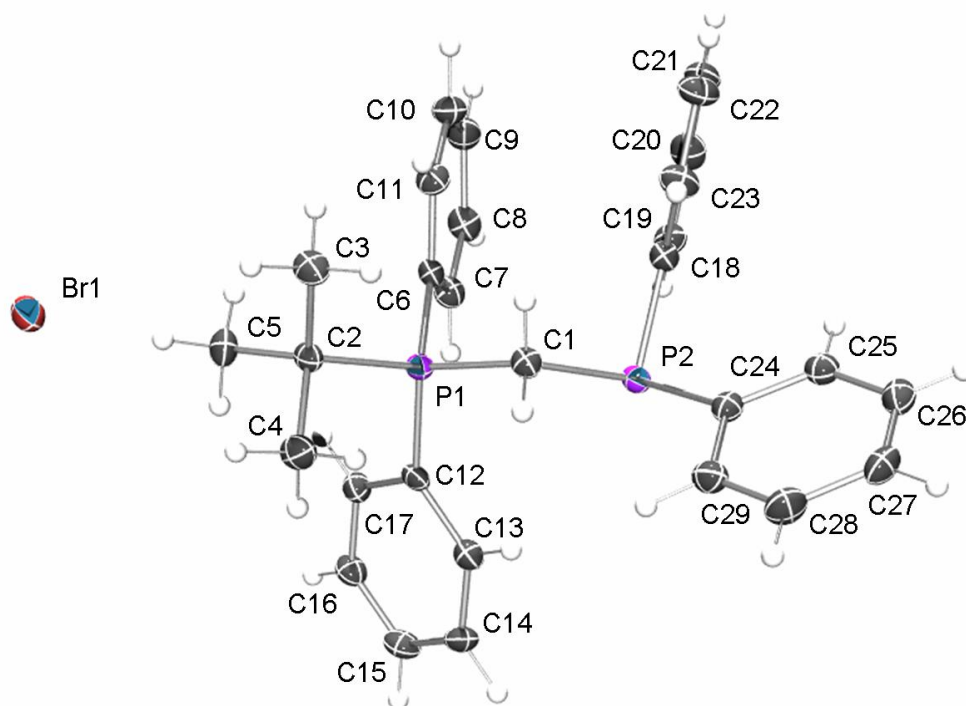
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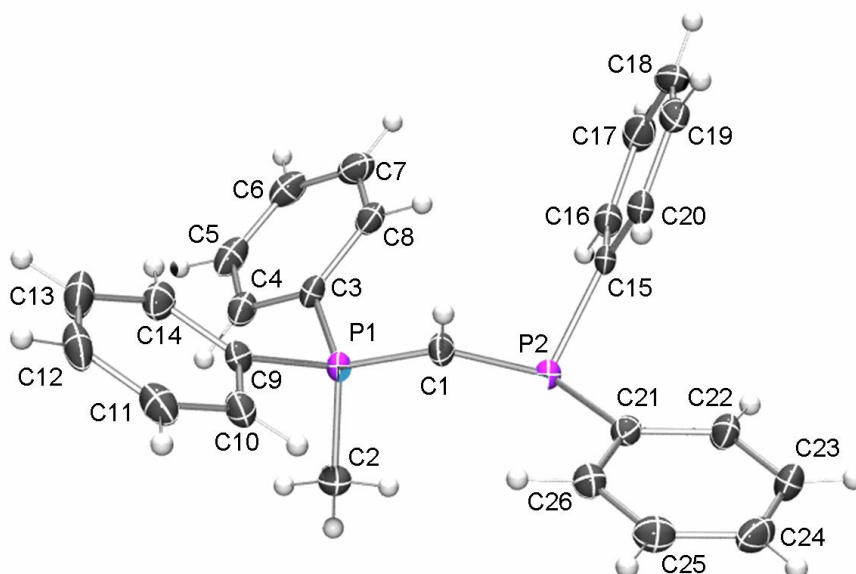
**Figure S1.** Molecular structure and numbering scheme of **1a**·2CHCl<sub>3</sub> (molecule A of two independent molecules). Co-crystallized CHCl<sub>3</sub> and a disorder of P2A are omitted for clarity. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.



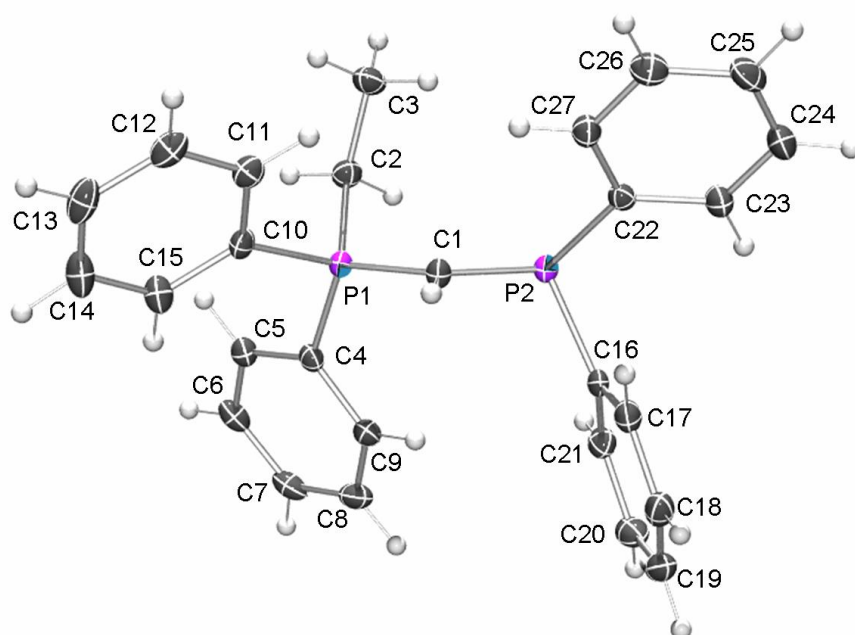
**Figure S2.** Molecular structure and numbering scheme of **1b**-toluene. Co-crystallized toluene is omitted for clarity. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.



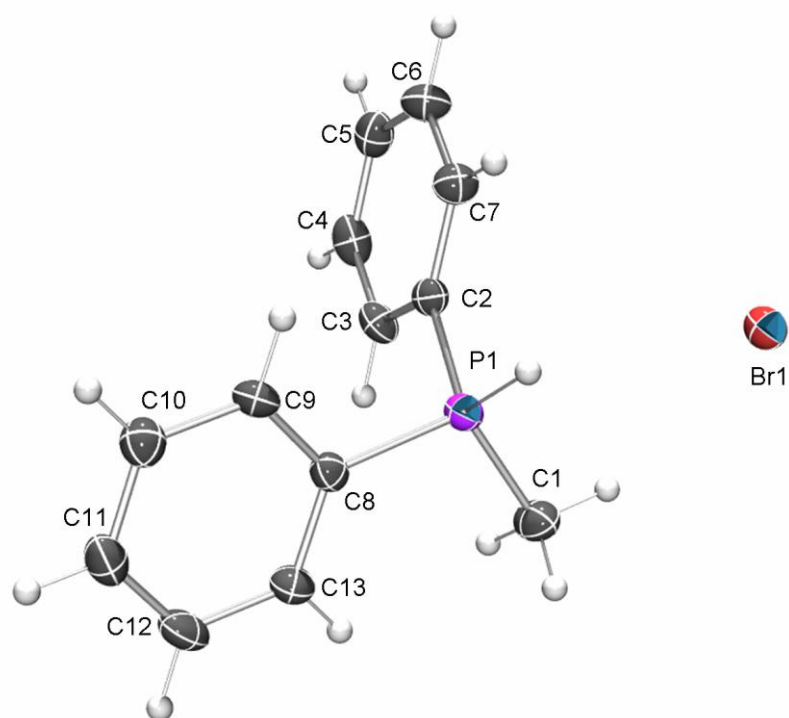
**Figure S3.** Molecular structure and numbering scheme of **1e**·2CH<sub>2</sub>Cl<sub>2</sub>. Co-crystallized CH<sub>2</sub>Cl<sub>2</sub> is omitted for clarity. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.



**Figure S4.** Molecular structure and numbering scheme of **2a**. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.



**Figure S5.** Molecular structure and numbering scheme of **2b**. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.



**Figure S6.** Molecular structure and numbering scheme of **3**. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.

### Structure determinations.

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K $\alpha$  radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.<sup>S1,S2</sup>

The structures were solved by direct methods (SHELXS<sup>S3</sup>) and refined by full-matrix least squares techniques against F<sub>o</sub><sup>2</sup> (SHELXL-97<sup>S3</sup>). All hydrogen atoms of the compounds **1c**, **2a**, **2b** and **2d** and the methylene hydrogen atoms at C1 of **1e** were located by difference Fourier synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically.<sup>S3</sup> Crystallographic data as well as structure solution and refinement details are summarized in Table 4.

### References

[S1] COLLECT, Data Collection Software; Nonius B.V., Netherlands, **1998**.

[S2] „Processing of X-Ray Diffraction Data Collected in Oscillation Mode“: Otwinowski, Z.; Minor, W. In *Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A*; Carter, C. W.; Sweet, R. M. Eds.; Academic Press, 1997; pp 307-326.

[S3] Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112-122.

**Table S1.** Crystal data and refinement details for the X-ray structure determinations of the compounds **1a- 4a**

Compound	<b>1a</b> ·2CHCl <sub>3</sub>	<b>1b</b> ·0.5 toluene	<b>1b</b> ·toluene	<b>1c</b> ·CHCl <sub>3</sub>
formula	C <sub>26</sub> H <sub>25</sub> P <sub>2</sub> , I, 2 (CHCl <sub>3</sub> )	C <sub>27</sub> H <sub>27</sub> P <sub>2</sub> , Br, 0.5 (C <sub>7</sub> H <sub>8</sub> )	C <sub>27</sub> H <sub>27</sub> P <sub>2</sub> , Br, C <sub>7</sub> H <sub>8</sub>	C <sub>28</sub> H <sub>29</sub> P <sub>2</sub> , I, CHCl <sub>3</sub>
fw (g·mol <sup>-1</sup> )	765.04	539.40	585.47	673.72
<i>T</i> /°C	20(2)	-140(2)	-140(2)	-140(2)
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P 2 <sub>1</sub> /n
<i>a</i> / Å	13.3663(4)	10.8612(5)	11.2927(3)	14.6207(5)
<i>b</i> / Å	15.4789(4)	11.1865(7)	12.1868(3)	11.4279(3)
<i>c</i> / Å	17.3576(6)	11.4441(8)	13.0295(3)	18.8977(6)
$\alpha$ /°	65.360(1)	91.849(3)	66.169(1)	90
$\beta$ /°	87.919(1)	93.243(3)	72.868(1)	106.962(2)
$\gamma$ /°	89.686(2)	106.322(3)	66.193(1)	90
<i>V</i> /Å <sup>3</sup>	3261.88(17)	1330.58(14)	1482.06(6)	3020.14(16)
<i>Z</i>	4	2	2	4
$\rho$ (g·cm <sup>-3</sup> )	1.558	1.346	1.312	1.482
$\mu$ (mm <sup>-1</sup> )	1.589	1.682	1.516	1.448
measured data	20717	8225	8976	17162
data with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	12597	4595	6101	5446
unique data ( <i>R</i> <sub>int</sub> )	14472/0.0224	5939/0.0287	6694/0.0182	6829/0.0517
w <i>R</i> <sub>2</sub> (all data, on <i>F</i> <sup>2</sup> ) <sup>a)</sup>	0.1466	0.1562	0.0813	0.1152
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a)</sup>	0.0595	0.0745	0.0364	0.0526
<i>s</i> <sup>b)</sup>	1.072	1.174	1.027	1.108
Res. Dens./e·Å <sup>-3</sup>	3.329/-1.605	0.687/-0.813	0.390/-0.282	0.771/-0.596
absorpt method	NONE	NONE	NONE	NONE
CCDC No.	842321	842322	847440	842323

**Table S1 (continued)**

Compound	<b>1d</b>	<b>1e·2CH<sub>2</sub>Cl<sub>2</sub></b>	<b>2a</b>	<b>2b</b>
formula	C <sub>35</sub> H <sub>35</sub> BrP <sub>2</sub>	C <sub>31</sub> H <sub>35</sub> BrCl <sub>4</sub> P <sub>2</sub>	C <sub>26</sub> H <sub>24</sub> P <sub>2</sub>	C <sub>27</sub> H <sub>26</sub> P <sub>2</sub>
fw (g·mol <sup>-1</sup> )	597.48	691.24	398.39	412.42
<i>T</i> /°C	-140(2)	-140(2)	-140(2)	-140(2)
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	P 2 <sub>1</sub> /n	P $\bar{1}$	P 2 <sub>1</sub> /c	P 2 <sub>1</sub> /c
<i>a</i> /Å	12.8539(2)	10.1865(5)	14.0787(6)	14.3842(2)
<i>b</i> /Å	17.2538(3)	12.0944(3)	8.3125(2)	8.5038(1)
<i>c</i> /Å	13.9988(2)	13.0897(6)	19.3859(8)	19.1582(3)
$\alpha$ /°	90	93.453(2)	90	90
$\beta$ /°	110.187(1)	95.659(2)	111.060(2)	111.180(1)
$\gamma$ /°	90	90.983(2)	90	90
<i>V</i> /Å <sup>3</sup>	2913.92(8)	1601.44(11)	2117.18(14)	2185.14(5)
<i>Z</i>	4	2	4	4
$\rho$ (g·cm <sup>-3</sup> )	1.362	1.433	1.250	1.254
$\mu$ (mm <sup>-1</sup> )	1.544	1.737	0.214	0.210
measured data	17652	9602	12672	13195
data with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	5717	6073	3715	4529
unique data ( <i>R</i> <sub>int</sub> )	6648/0.0301	7118/0.0270	4805/0.1115	4995/0.0245
w <i>R</i> <sub>2</sub> (all data, on <i>F</i> <sup>2</sup> ) <sup>a)</sup>	0.0801	0.1105	0.1842	0.0906
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a)</sup>	0.0342	0.0512	0.0733	0.0347
<i>s</i> <sup>b)</sup>	1.014	1.142	1.097	1.047
Res. dens./e·Å <sup>-3</sup>	0.354/-0.328	0.792/-0.522	0.700/-0.479	0.310/-0.327
absorpt method	NONE	NONE	NONE	NONE
CCDC No.	842324	856224	842326	842327

Table S1 (continued)

Compound	<b>2c·0.5 Et<sub>2</sub>O</b>	<b>2d</b>	<b>3</b>	<b>4a·0.5 tmeda</b>
Formula	C <sub>28</sub> H <sub>28</sub> P <sub>2</sub> , 0.5 (C <sub>4</sub> H <sub>10</sub> O)	C <sub>35</sub> H <sub>34</sub> P <sub>2</sub>	C <sub>13</sub> H <sub>14</sub> BrP	C <sub>32</sub> H <sub>39</sub> LiN <sub>2</sub> P <sub>2</sub> , 0.5 (C <sub>6</sub> H <sub>16</sub> N <sub>2</sub> )
fw (g·mol <sup>-1</sup> )	463.50	516.56	281.12	578.64
<i>T</i> /°C	-140(2)	-140(2)	-140(2)	-140(2)
crystal system	monoclinic	orthorhombic	orthorhombic	triclinic
space group	P 2 <sub>1</sub> /c	P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P bca	P $\bar{1}$
<i>a</i> /Å	16.3259(5)	10.5989(1)	15.8039(3)	10.1189(13)
<i>b</i> /Å	9.0660(2)	15.6582(3)	9.4535(3)	10.9732(14)
<i>c</i> /Å	18.4623(4)	17.0160(4)	16.4308(4)	16.7403(16)
$\alpha$ /°	90	90	90	105.080(8)
$\beta$ /°	110.078(2)	90	90	96.475(7)
$\gamma$ /°	90	90	90	103.303(5)
<i>V</i> /Å <sup>3</sup>	2566.54(11)	2823.97(9)	2454.80(11)	1716.9(4)
<i>Z</i>	4	4	8	2
$\rho$ (g·cm <sup>-3</sup> )	1.200	1.215	1.521	1.119
$\mu$ (mm <sup>-1</sup> )	0.187	0.176	3.444	0.153
measured data	15715	17034	14056	7994
data with <i>I</i> > 2σ( <i>I</i> )	4626	5928	2318	5453
unique data ( <i>R</i> <sub>int</sub> )	5866/0.0596	6384/0.0432	2817/0.0549	6097/0.0182
w <i>R</i> <sub>2</sub> (all data, on <i>F</i> <sup>2</sup> ) <sup>a</sup>	0.1509	0.1017	0.0821	0.1427
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> )) <sup>a</sup>	0.0650	0.0431	0.0369	0.0607
<i>s</i> <sup>b</sup>	1.065	1.105	1.074	1.116
Res. dens./e·Å <sup>-3</sup>	0.756/-0.366	0.532/-0.250	0.398/-0.319	0.426/-0.270
Flack-parameter	-	-0.04(8)	-	-
absorpt method	NONE	NONE	NONE	NONE
CCDC No.	842328	842329	842325	842330

<sup>a</sup> Definition of the *R* indices:  $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$ ;

$wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$  with  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ ;  $P = [2F_c^2 + \text{Max}(F_o^2)]/3$ .

<sup>b</sup>  $s = \{\sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p)\}^{1/2}$ .