Supplementary Material

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

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Dedicated to Professor Rainer Beckert on the Occasion of his 60th Birthday

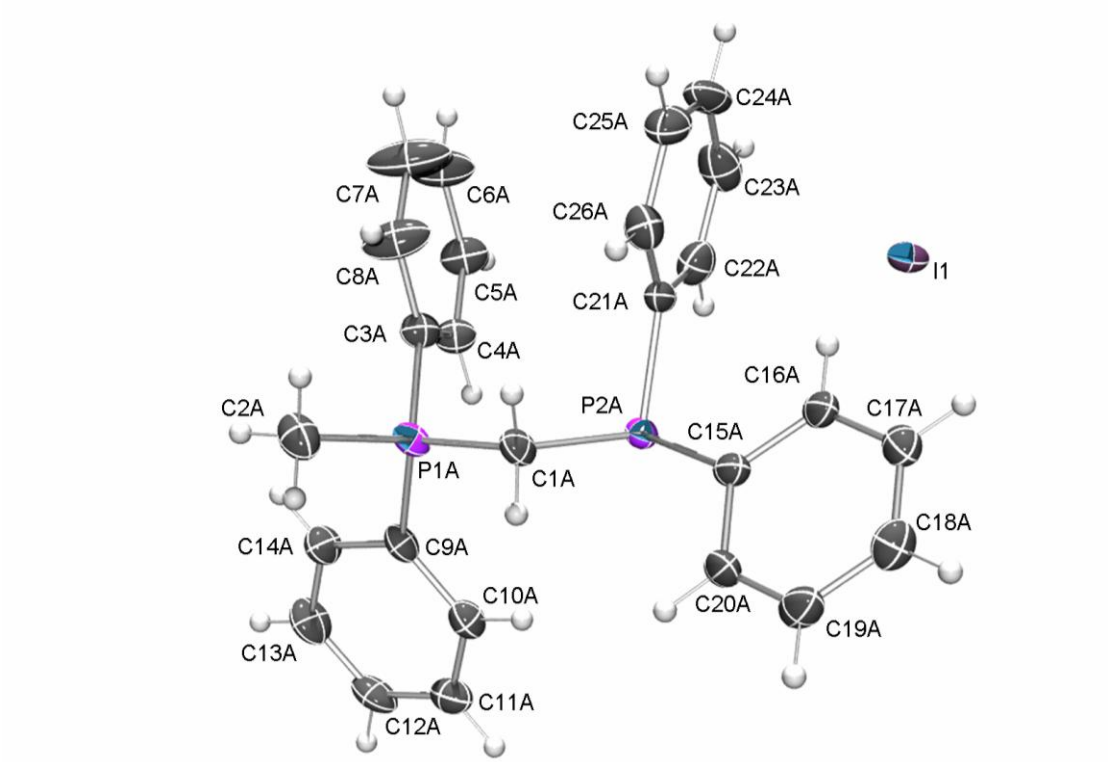

Figure S1. Molecular structure and numbering scheme of **1a**·2$CHCl_3$ (molecule A of two independent molecules). Co-crystallized $CHCl_3$ and a disorder of P2A are omitted for clarity. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.

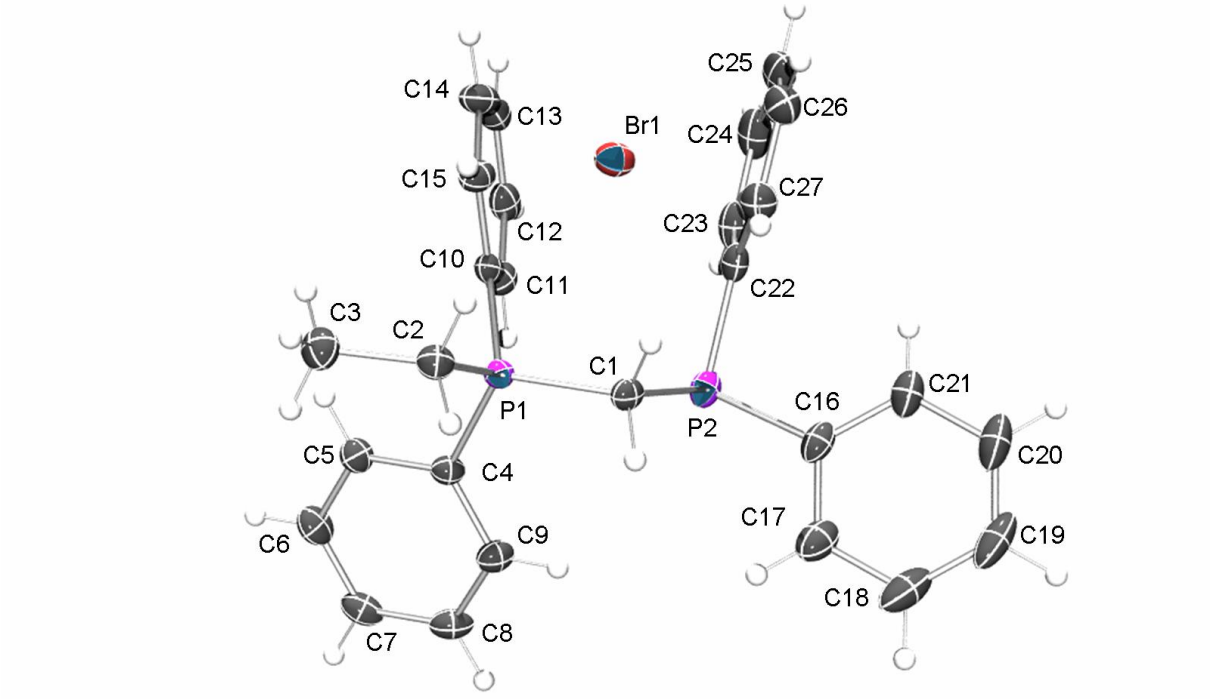

Figure S2. Molecular structure and numbering scheme of **1b**·toluene. Co-crystallized toluene is omitted for clarity. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.

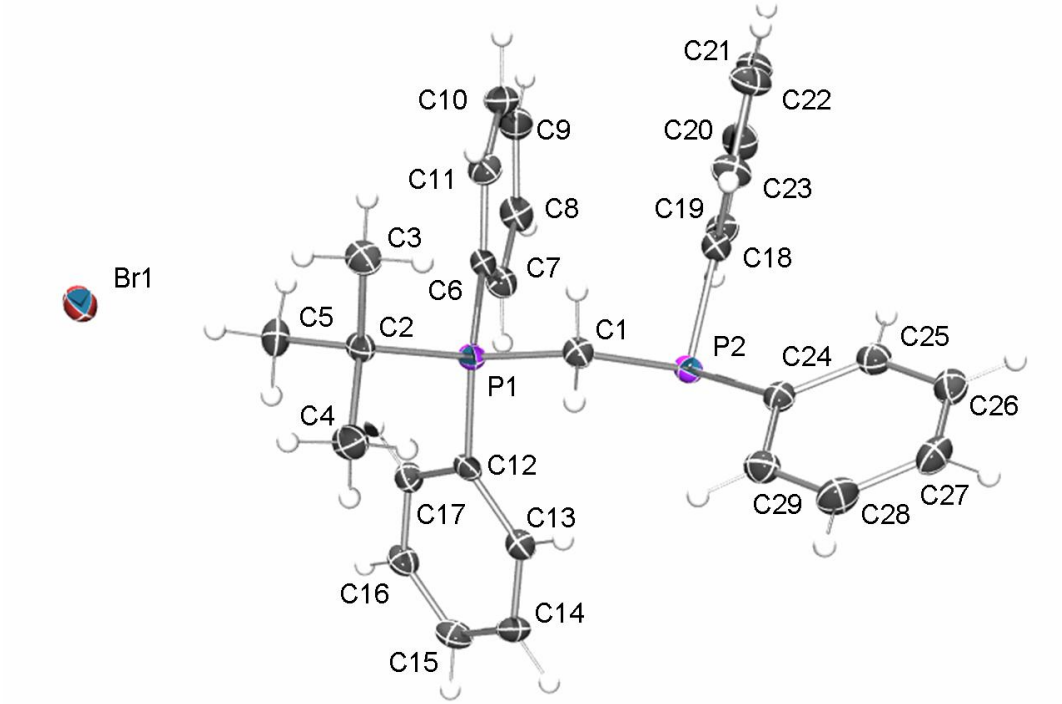

Figure S3. Molecular structure and numbering scheme of **1e**·2CH_2Cl_2. Co-crystallized CH_2Cl_2 is omitted for clarity. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.

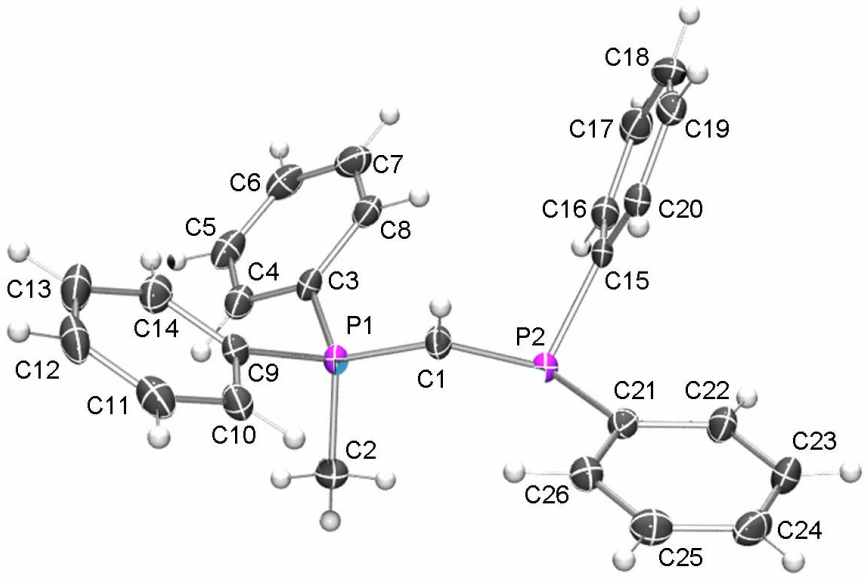

Figure S4. Molecular structure and numbering scheme of **2a**. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.

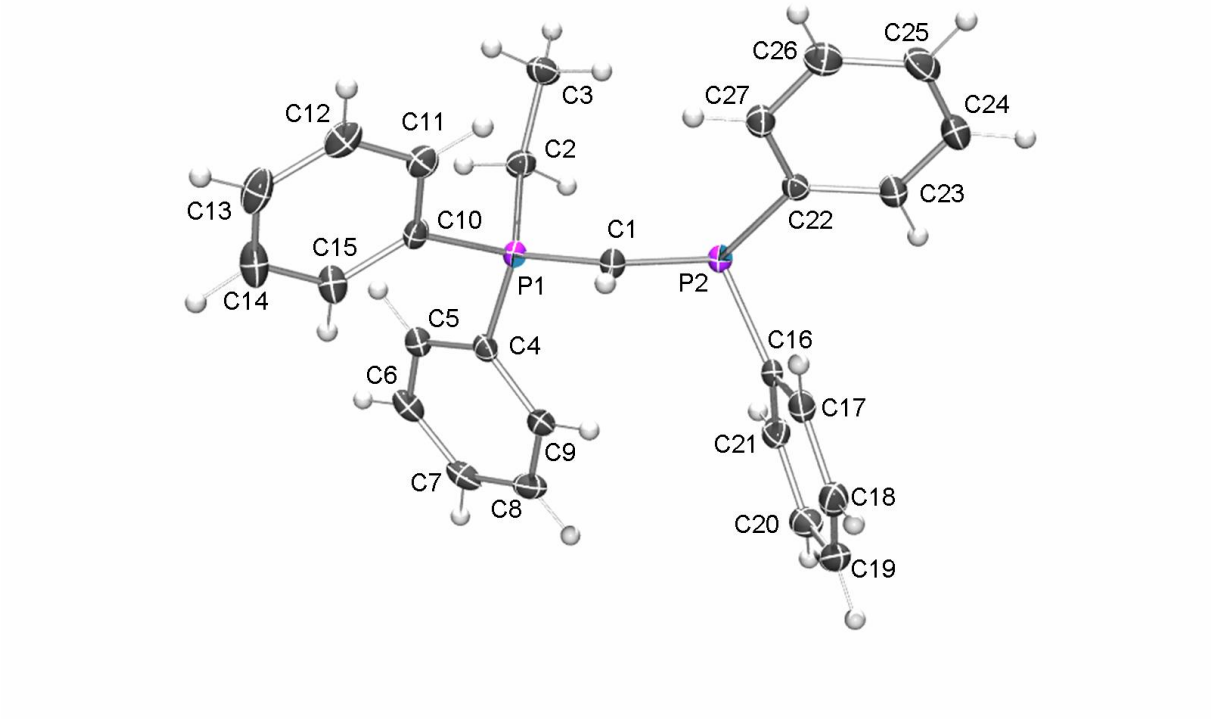

Figure S5. Molecular structure and numbering scheme of **2b**. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.

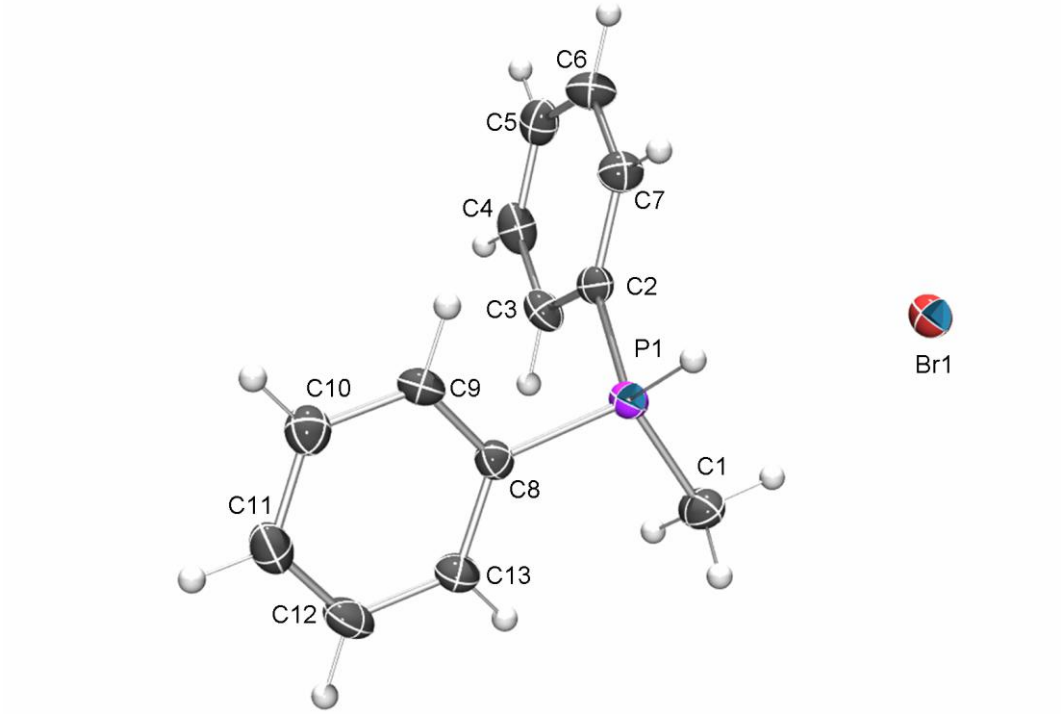

Figure S6. Molecular structure and numbering scheme of **3.** The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.

Structure determinations.

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[S1,S2]

The structures were solved by direct methods (SHELXS[S3]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97[S3]). 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.[S3] 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	**1a·2CHCl$_3$**	**1b·0.5 toluene**	**1b·toluene**	**1c·CHCl$_3$**
formula	$C_{26}H_{25}P_2$, I, 2 ($CHCl_3$)	$C_{27}H_{27}P_2$, Br, 0.5 (C_7H_8)	$C_{27}H_{27}P_2$, Br, C_7H_8	$C_{28}H_{29}P_2$, I, $CHCl_3$
fw (g·mol^{-1})	765.04	539.40	585.47	673.72
T/°C	20(2)	-140(2)	-140(2)	-140(2)
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	P ī	P ī	P ī	P 2_1/n
a/ Å	13.3663(4)	10.8612(5)	11.2927(3)	14.6207(5)
b/ Å	15.4789(4)	11.1865(7)	12.1868(3)	11.4279(3)
c/ Å	17.3576(6)	11.4441(8)	13.0295(3)	18.8977(6)
α/°	65.360(1)	91.849(3)	66.169(1)	90
β/°	87.919(1)	93.243(3)	72.868(1)	106.962(2)
γ/°	89.686(2)	106.322(3)	66.193(1)	90
V/Å^3	3261.88(17)	1330.58(14)	1482.06(6)	3020.14(16)
Z	4	2	2	4
ρ (g·cm^{-3})	1.558	1.346	1.312	1.482
μ (mm^{-1})	1.589	1.682	1.516	1.448
measured data	20717	8225	8976	17162
data with I > 2σ(I)	12597	4595	6101	5446
unique data (R_{int})	14472/0.0224	5939/0.0287	6694/0.0182	6829/0.0517
wR_2 (all data, on F^2)[a)]	0.1466	0.1562	0.0813	0.1152
R_1 ($I > 2\sigma(I)$) [a)]	0.0595	0.0745	0.0364	0.0526
s [b)]	1.072	1.174	1.027	1.108
Res. Dens./e·Å^{-3}	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	**1d**	**1e·2CH$_2$Cl$_2$**	**2a**	**2b**
formula	$C_{35}H_{35}BrP_2$	$C_{31}H_{35}BrCl_4P_2$	$C_{26}H_{24}P_2$	$C_{27}H_{26}P_2$
fw (g·mol^{-1})	597.48	691.24	398.39	412.42
T/°C	-140(2)	-140(2)	-140(2)	-140(2)
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	P 2_1/n	P $\bar{1}$	P 2_1/c	P 2_1/c
a/ Å	12.8539(2)	10.1865(5)	14.0787(6)	14.3842(2)
b/ Å	17.2538(3)	12.0944(3)	8.3125(2)	8.5038(1)
c/ Å	13.9988(2)	13.0897(6)	19.3859(8)	19.1582(3)
α/°	90	93.453(2)	90	90
β/°	110.187(1)	95.659(2)	111.060(2)	111.180(1)
γ/°	90	90.983(2)	90	90
V/Å^3	2913.92(8)	1601.44(11)	2117.18(14)	2185.14(5)
Z	4	2	4	4
ρ (g·cm^{-3})	1.362	1.433	1.250	1.254
μ (mm^{-1})	1.544	1.737	0.214	0.210
measured data	17652	9602	12672	13195
data with I > 2σ(I)	5717	6073	3715	4529
unique data (R_{int})	6648/0.0301	7118/0.0270	4805/0.1115	4995/0.0245
wR_2 (all data, on F^2)[a)]	0.0801	0.1105	0.1842	0.0906
R_1 ($I > 2\sigma(I)$) [a)]	0.0342	0.0512	0.0733	0.0347
s [b)]	1.014	1.142	1.097	1.047
Res. dens./e·Å^{-3}	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	**2c·0.5 Et_2O**	**2d**	**3**	**4a·0.5 tmeda**
Formula	$C_{28}H_{28}P_2$, 0.5 ($C_4H_{10}O$)	$C_{35}H_{34}P_2$	$C_{13}H_{14}BrP$	$C_{32}H_{39}LiN_2P_2$, 0.5 ($C_6H_{16}N_2$)
fw ($g \cdot mol^{-1}$)	463.50	516.56	281.12	578.64
T/°C	-140(2)	-140(2)	-140(2)	-140(2)
crystal system	monoclinic	orthorhombic	orthorhombic	triclinic
space group	P 2_1/c	P 2_1 2_1 2_1	P bca	P ī
a/ Å	16.3259(5)	10.5989(1)	15.8039(3)	10.1189(13)
b/ Å	9.0660(2)	15.6582(3)	9.4535(3)	10.9732(14)
c/ Å	18.4623(4)	17.0160(4)	16.4308(4)	16.7403(16)
α/°	90	90	90	105.080(8)
β/°	110.078(2)	90	90	96.475(7)
γ/°	90	90	90	103.303(5)
V/$Å^3$	2566.54(11)	2823.97(9)	2454.80(11)	1716.9(4)
Z	4	4	8	2
ρ ($g \cdot cm^{-3}$)	1.200	1.215	1.521	1.119
μ (mm^{-1})	0.187	0.176	3.444	0.153
measured data	15715	17034	14056	7994
data with I > 2σ(I)	4626	5928	2318	5453
unique data (R_{int})	5866/0.0596	6384/0.0432	2817/0.0549	6097/0.0182
wR_2 (all data, on F^2)[a)]	0.1509	0.1017	0.0821	0.1427
R_1 ($I > 2\sigma(I)$) [a)]	0.0650	0.0431	0.0369	0.0607
s [b)]	1.065	1.105	1.074	1.116
Res. dens./e·$Å^{-3}$	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

[a] Definition of the *R* indices: $R_1 = (\Sigma \| |F_o| - |F_c| \|)/\Sigma |F_o|$;
$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2+bP$; $P = [2F_c^2 + Max(F_O^2]/3$.
[b] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.