

## Supporting Information for:

# Synthesis of a boratabenzene-(2,3,4,5-tetramethyl-phosphole): towards a planar monophosphole

Guillaume Bélanger-Chabot,<sup>a</sup> Philippe Rioux,<sup>a</sup> Laurent Maron\*<sup>b</sup> and Frédéric-Georges Fontaine\*<sup>a</sup>

<sup>a</sup> Département de chimie, Université Laval, 1045 Avenue de la Médecine  
Cité Universitaire, Québec, Qc, G1V0A6 (Canada). Fax :+1 418 6565140

<sup>b</sup> Université de Toulouse, INSA, UPS, LPCNO, 135 avenue de Rangueil, 31077 Toulouse (France) and  
CNRS, LPCNO, UMR 5215 CNRS-UPS-INSA, 31077 Toulouse (France)

\*Email : [frederic.fontaine@chm.ulaval.ca](mailto:frederic.fontaine@chm.ulaval.ca)

[laurent.maron@irsamc.ups-tlse.fr](mailto:laurent.maron@irsamc.ups-tlse.fr)

### Contents

1. General experimental	S2
a. Synthesis of <b>2</b>	S2
b. Synthesis of <b>3</b>	S3
c. Synthesis of <b>4</b>	S4
2. NMR characterization of <b>2</b> , <b>3</b> , and <b>4</b>	S5
3. Crystallographic structural determination	S11
4. Computational details	S15
5. References	S23

## 1. General experimental

Manipulations were carried out under an atmosphere of dinitrogen, using standard glovebox and Schlenk techniques. Dry, deoxygenated, distilled solvents were used for all manipulations. Toluene, benzene and THF were distilled from sodium/benzophenone. Pentane was distilled from sodium/benzophenone using tetraglyme as a phase transfer agent. Deuterated solvents were dried over NaK, degassed using freeze-pump-thaw cycles and purified by vacuum transfer. Borabenzene-PMe<sub>3</sub> (C<sub>5</sub>H<sub>5</sub>B·PMe<sub>3</sub>)<sup>1</sup> and tetramethylphospholylithium TMEDA (**1**)<sup>2</sup> were synthesized following literature procedures.

NMR spectra were recorded on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (<sup>1</sup>H), 100.580 MHz (<sup>13</sup>C), 128.336 MHz (<sup>11</sup>B), or on a Bruker NMR AC-300 at 300MHz (<sup>1</sup>H), 75.435 MHz (<sup>31</sup>P). <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts are referenced to residual protons in deuterated solvent. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), or overlapping (ov). Chemical shifts are reported in ppm. Coupling constants are reported in Hz.

### a. Synthesis of boratabenzene-(2,3,4,5)tetramethylphosphole lithium TMEDA (**2**)

Borabenzene-PMe<sub>3</sub> (250 mg; 1.6 mmol) and **1** (440 mg; 1.7 mmol) were heated at 90°C in a solution of toluene (20 mL) for 5 days. Every 24 hours, the solution was concentrated under vacuum and the resulting mixture was diluted to the original volume of toluene, in order to remove the PMe<sub>3</sub> formed. The orange solution was then filtered and concentrated under vacuum until a fair amount of white precipitate formed. The solution was filtered and the white precipitate was dried under vacuum, yielding 400 mg (80%) of an off-white powder. Crystals of **2** were obtained from a saturated solution in pentane or from a pentane/THF solution.

$\delta_{\text{H}}$  (C<sub>6</sub>D<sub>6</sub>) 1.24 (4H, s, TMEDA), 1.46 (12H, s, TMEDA), 2.06 (6H, s, CMe <sub>$\beta$</sub> ), 2.60 (6H, d, <sup>3</sup>J<sub>H-H</sub> = 10.7, CMe <sub>$\alpha$</sub> ), 6.39 (1H, tt, <sup>3</sup>J<sub>H-H</sub> = 7.3, <sup>4</sup>J<sub>H-H</sub> = 1.4, H4-C<sub>5</sub>H<sub>5</sub>B), 7.15 (2H, ddd, <sup>3</sup>J<sub>H-H</sub> = 10.3, <sup>4</sup>J<sub>H-P</sub> = 4.4, <sup>4</sup>J<sub>H-H</sub> = 1.4, H2,6-C<sub>5</sub>H<sub>5</sub>B), 7.40 (2H, ddd, <sup>3</sup>J<sub>H-H</sub> = 10.3, <sup>3</sup>J<sub>H-H</sub> =

7.3,  $^4J_{\text{H-P}} = 2.9$ , H3,5- $C_5H_5B$ ).  $\delta_{\text{C}}$  ( $C_6D_6$ ) 14.1 (d,  $^3J_{\text{C-P}} = 4.0$ ,  $CMe_{\beta}$ ), 15.3 (d,  $^2J_{\text{C-P}} = 27.9$ ,  $CMe_{\alpha}$ ), 44.9 (s, TMEDA), 55.5 (s, TMEDA), 110.2 (s, C4- $C_5H_5B$ ), 127.4 (br, C2,6- $C_5H_5B$ ), 132.5 (d,  $^3J_{\text{C-P}} = 8.8$ , C3,5- $C_5H_5B$ ), 134.9 (d,  $^3J_{\text{C-P}} = 3.8$ ,  $CMe_{\beta}$ ), 136.1 (d,  $^2J_{\text{C-P}} = 10.0$ ,  $CMe_{\alpha}$ ).  $\delta_{\text{P}}$  ( $C_6D_6$ ) 0.70 (bs).  $\delta_{\text{B}}$  ( $C_6D_6$ ) 32.3 (s). The compound degrades in time, preventing the possibility of elemental analysis.

**b. Synthesis of 2-trimethylsilyl-boratabenzene-2,3,4,5-tetramethylphosphole lithium TMEDA (3)**

**1** (320 mg; 1.2 mmol) was dissolved in 20 mL of toluene. A solution of 2-trimethylsilyl-chloroboracyclohexadiene (110 mg; 0.56 mmol) in 5 mL of toluene was then quickly added to the phospholyl solution, resulting in a bright yellow solution. The mixture was agitated for few minutes during which a white precipitate formed while the bright color changed into a very pale yellow solution. The mixture was filtered and the filtrate was evaporated to dryness. The resulting milky oil was washed with two portions of ether, yielding 20 mg (9%) of a white powder having as impurity excess of **1**. Some crystals were isolated from a pentane solution of **1** and impurities. Some less pure product could be obtained from the ether solutions and include as known side products, **2** and tetramethylphospholyl-trimethylsilyl.

$\delta_{\text{H}}$  ( $C_6D_6$ ) 0.75 (9H, s,  $SiMe_3$ ), 1.26 (4H, s, TMEDA), 1.49 (12H, s, TMEDA), 2.13 (6H, s,  $CMe_{\beta}$ ), 2.36 (6H, d,  $^3J_{\text{H-H}} = 10.5$ ,  $CMe_{\alpha}$ ), 6.44 (1H, tt, ,  $^3J_{\text{H-H}} = 7.3$ ,  $^4J_{\text{H-H}} = ^5J_{\text{H-P}} = 1.4$ , H4- $C_5H_5B$ ), 6.47 (1H, ddd,  $^3J_{\text{H-H}} = 10.3$ ,  $^4J_{\text{H-P}} = 4.4$ ,  $^4J_{\text{H-H}} = 1.2$ , H6- $C_5H_5B$ ), 7.21 (1H, dd,  $^3J_{\text{H-H}} = 10.3$ ,  $^3J_{\text{H-H}} = 7.1$ , H5- $C_5H_5B$ ), 7.74 (1H, dd,  $^3J_{\text{H-H}} = 7.1$ ,  $^4J_{\text{H-P}} = 4.7$ , H3- $C_5H_5B$ ).  $\delta_{\text{C}}$  ( $C_6D_6$ ) 3.0 (d,  $^4J_{\text{C-P}} = 5.7$ ,  $SiMe_3$ ), 14.2 (d,  $^3J_{\text{C-P}} = 2.3$ ,  $CMe_{\beta}$ ), 15.2 (d,  $^2J_{\text{C-P}} = 22.6$ ,  $CMe_{\alpha}$ ), 45.2 (s, TMEDA), 55.7 (s, TMEDA), 112.1 (s, C4- $C_5H_5B$ ), 133.8 (d,  $^3J_{\text{C-P}} = 3.9$ ,  $CMe_{\beta}$ ), 137.1 (d,  $^3J_{\text{C-P}} = 7.9$ , C3- $C_5H_5B$ ); 138.0 (s, C5- $C_5H_5B$ ); 138.3 (d,  $^3J_{\text{C-P}} = 6.2$ ,  $CMe_{\beta}$ ).  $\delta_{\text{P}}$  ( $C_6D_6$ ) -5.9 (bs).  $\delta_{\text{B}}$  ( $C_6D_6$ ) 35.8 (s). The C2,6- $C_5H_5B$  were not located. The compound degrades in time, preventing the possibility of elemental analysis.

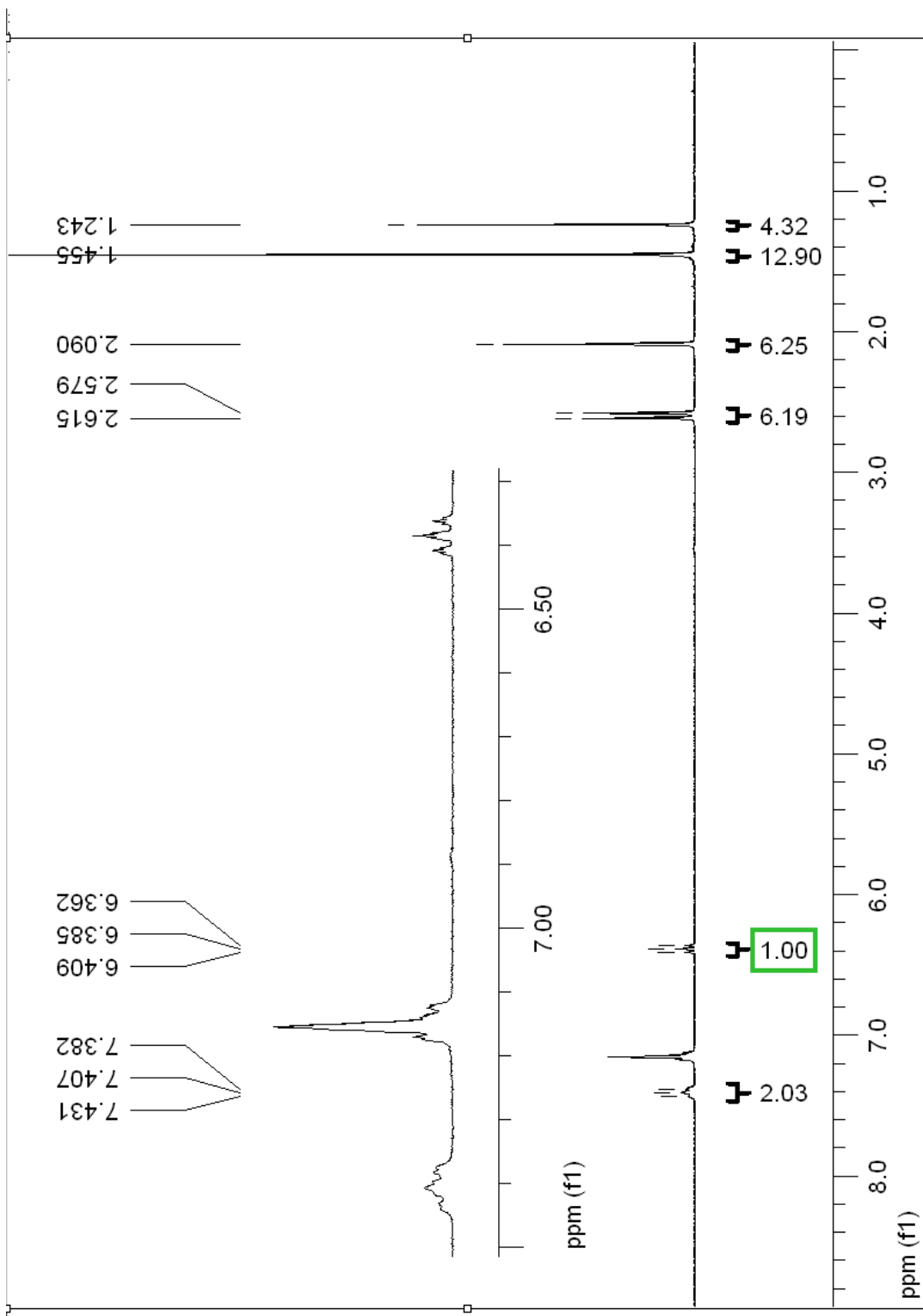
c. Synthesis of bis(boratabenzene-2,3,4,5-tetramethylphosphole)Fe(II)

**2** (195 mg; 0.60 mmol) was added to FeCl<sub>2</sub> (38 mg; 0.30 mmol) in THF (7 mL) for 2 hours. The resulting red solution was evaporated to dryness and extracted with toluene in order to remove LiCl. The toluene solution was evaporated to dryness, yielding a sticky red solid. Several washes with pentane yield an orange powder (114 mg, 78%). Crystals can be obtained by recrystallization in pentane.

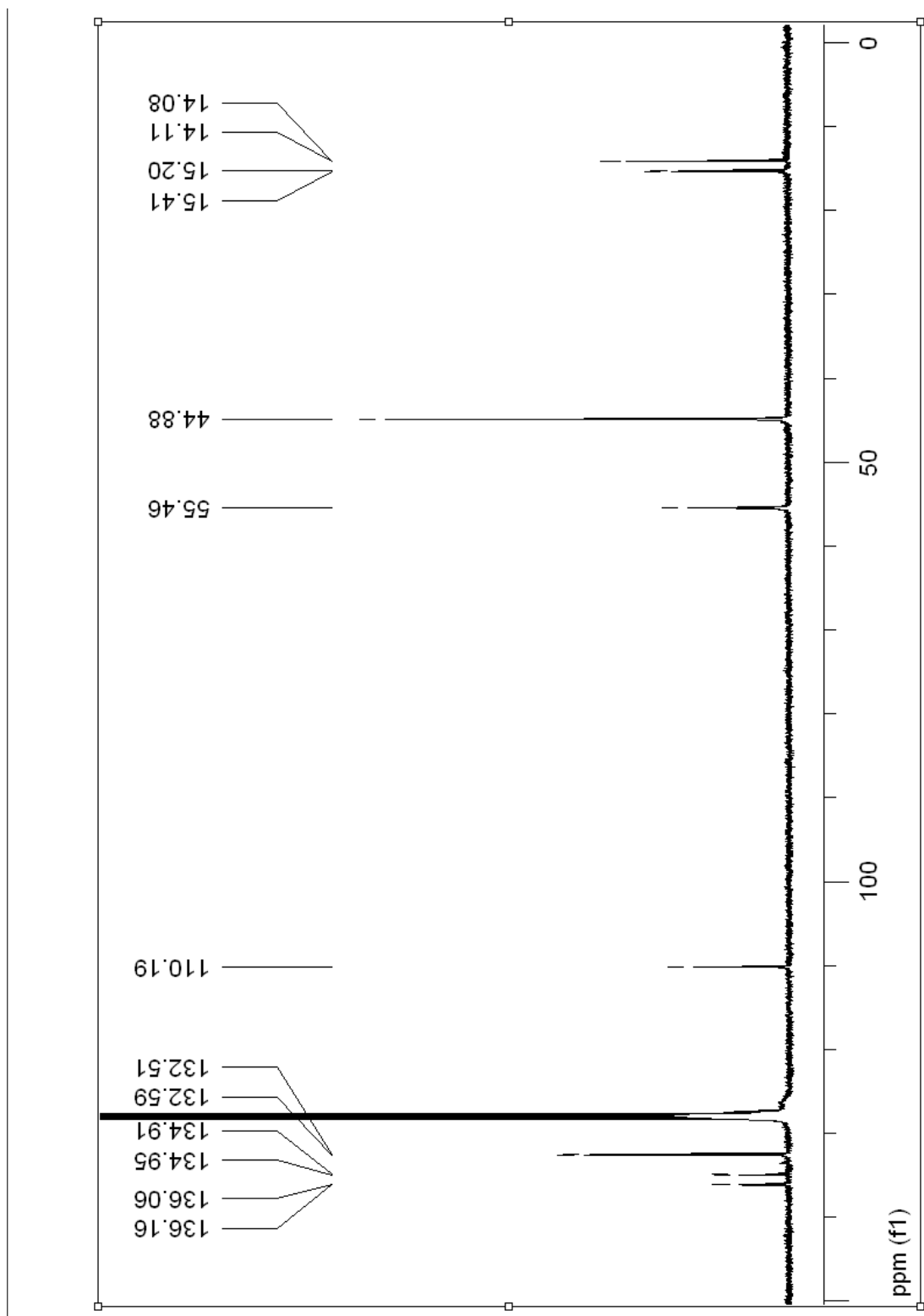
$\delta_{\text{H}}$  (C<sub>6</sub>D<sub>6</sub>) 2.00 (12H, s, CMe $\beta$ ), 2.41 (12H, d, <sup>3</sup>J<sub>H-P</sub> = 10.7, CMe $\alpha$ ), 4.47 (4H, ddd, <sup>3</sup>J<sub>H-H</sub> = 9.0, <sup>3</sup>J<sub>H-P</sub> = 3.3, <sup>4</sup>J<sub>H-H</sub> = 0.7, H2,6-C<sub>5</sub>H<sub>5</sub>B), 4.89 (4H, ddd, <sup>3</sup>J<sub>H-H</sub> = 9.0 = 5.8, <sup>3</sup>J<sub>H-P</sub> = 1.4, H3,5-C<sub>5</sub>H<sub>5</sub>B), 5.09 (2H, td, <sup>3</sup>J<sub>H-H</sub> = 5.8, <sup>4</sup>J<sub>H-H</sub> = 0.7, H4-C<sub>5</sub>H<sub>5</sub>B).  $\delta_{\text{C}}$  (C<sub>6</sub>D<sub>6</sub>) 14.0 (d, <sup>3</sup>J<sub>C-P</sub> = 3.1, CMe $\beta$ ), 15.3 (d, <sup>2</sup>J<sub>C-P</sub> = 22.2, CMe $\alpha$ ); 79.8 (s, C4-C<sub>5</sub>H<sub>5</sub>B), 82.6 (br, C2,6-C<sub>5</sub>H<sub>5</sub>B), 92.5 (d, <sup>3</sup>J<sub>C-P</sub> = 6.5, C3,5-C<sub>5</sub>H<sub>5</sub>B), 133.3 (d, <sup>2</sup>J<sub>C-P</sub> = 3.2, CMe $\beta$ ), 139.3 (d, <sup>2</sup>J<sub>C-P</sub> = 10.0, CMe $\alpha$ ).  $\delta_{\text{P}}$  (C<sub>6</sub>D<sub>6</sub>) -11.5 (bs).  $\delta_{\text{B}}$  (C<sub>6</sub>D<sub>6</sub>) 18.4 (s). m/z (ESI-electrospray) 487.1763 (M+H<sup>+</sup> requires 487.1744).

## 2. NMR characterization

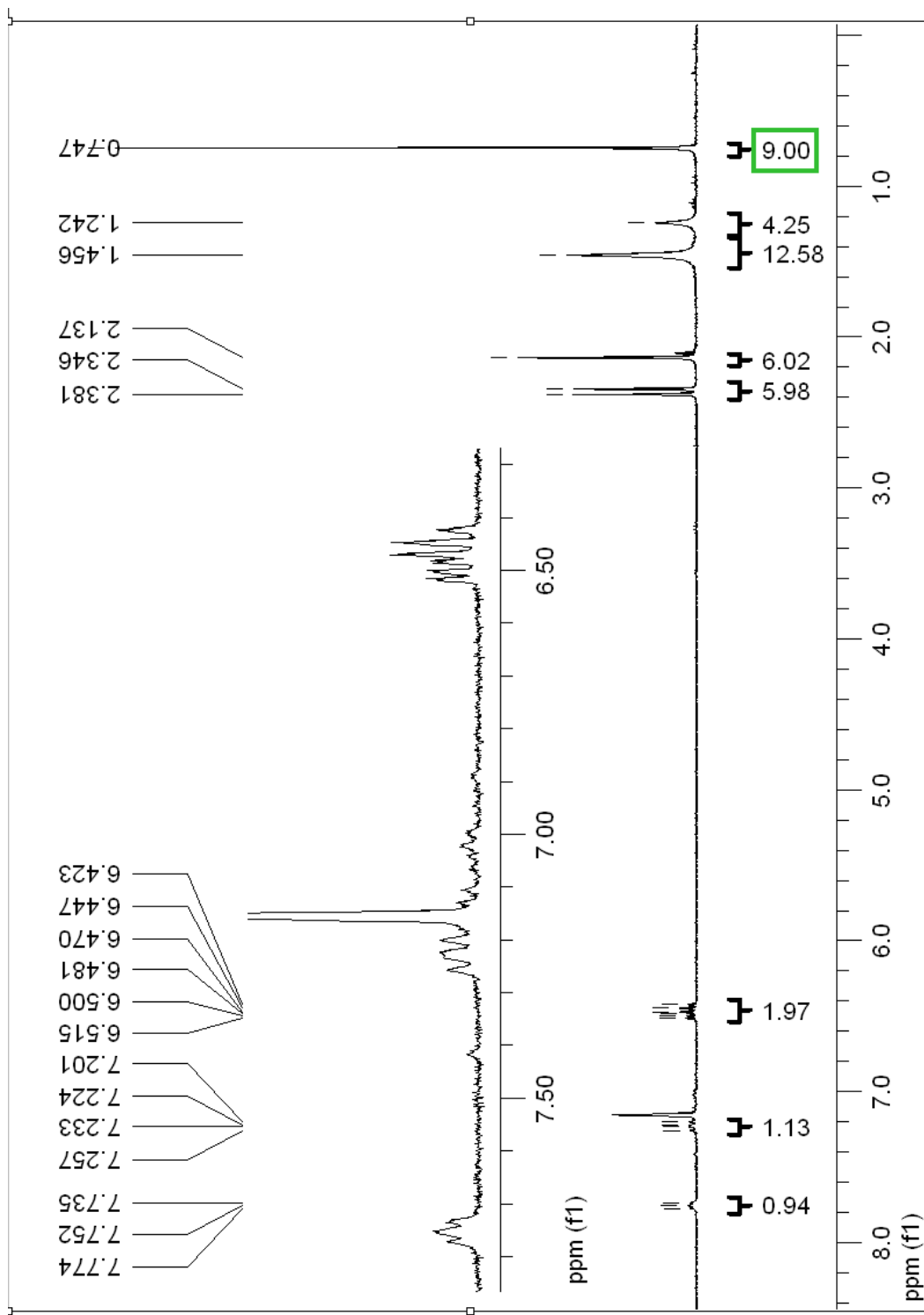
### a. $^1\text{H}$ NMR of **2** ( $\text{C}_6\text{D}_6$ , 300 MHz)



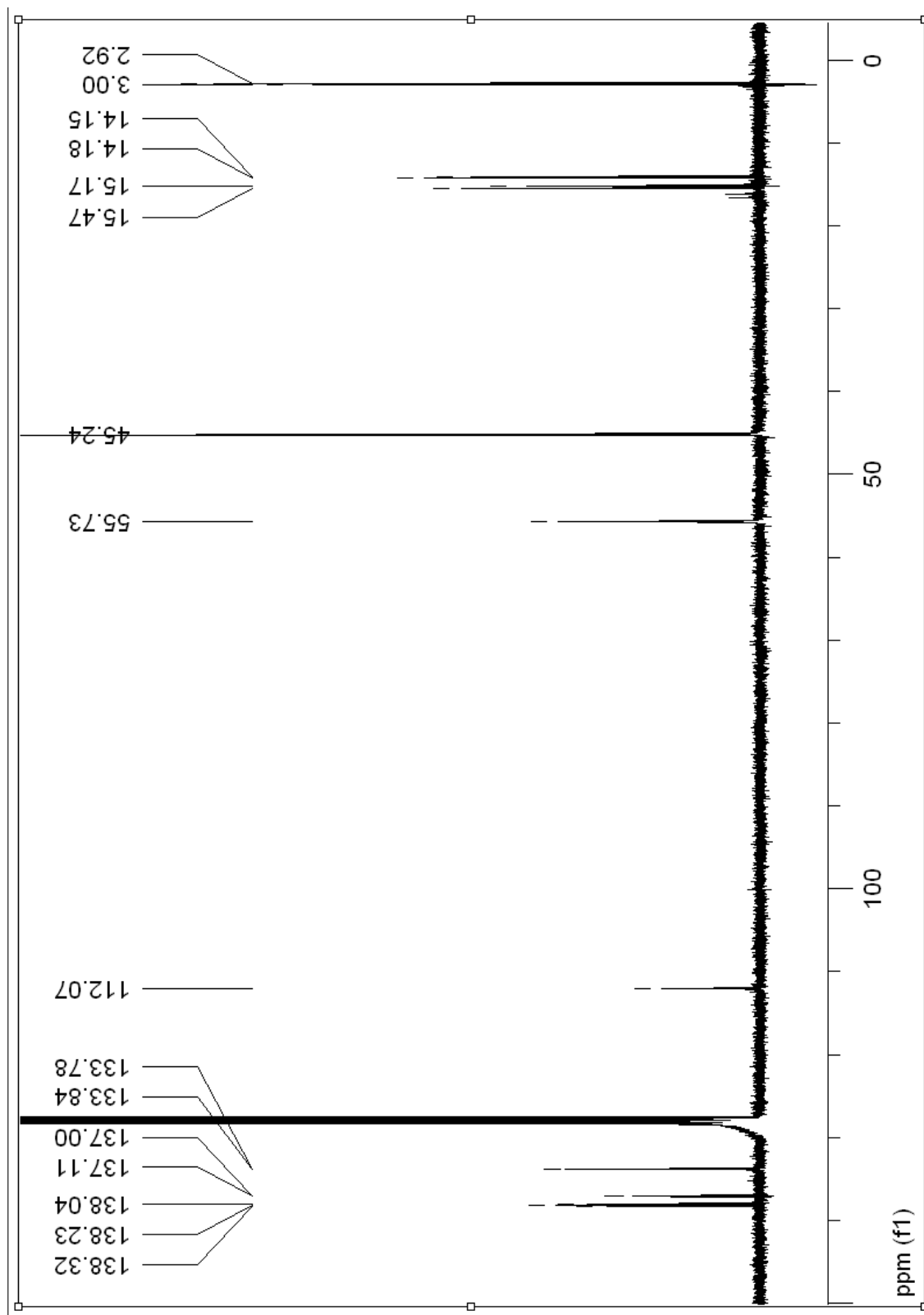
b.  $^{13}\text{C}\{^1\text{H}\}$  of **2** ( $\text{C}_6\text{D}_6$ , 128 MHz)



c.  $^1\text{H}$  NMR of **3** ( $\text{C}_6\text{D}_6$ , 300 MHz)

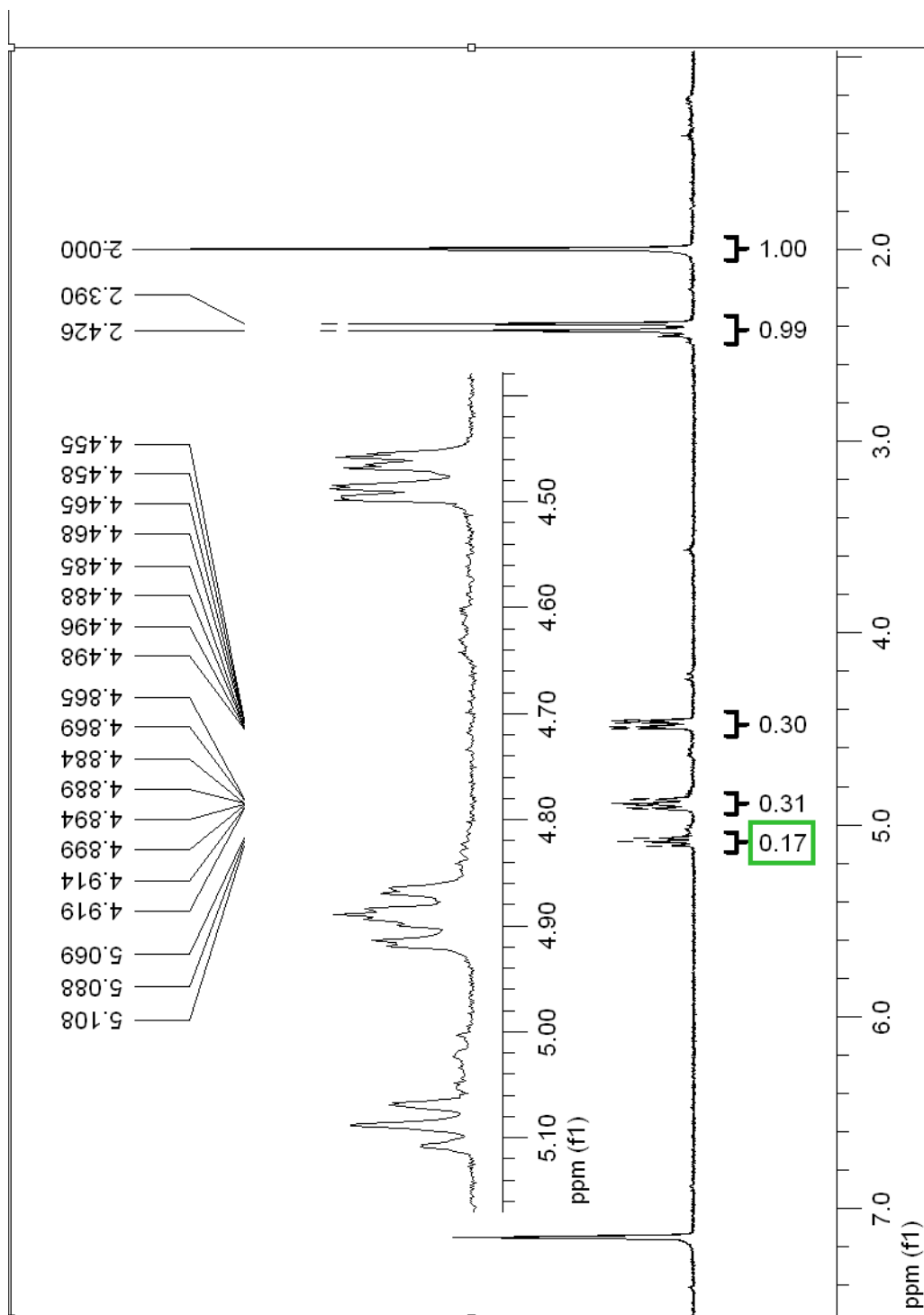


d.  $^{13}\text{C}\{^1\text{H}\}$  of **3** ( $\text{C}_6\text{D}_6$ , 128 MHz)

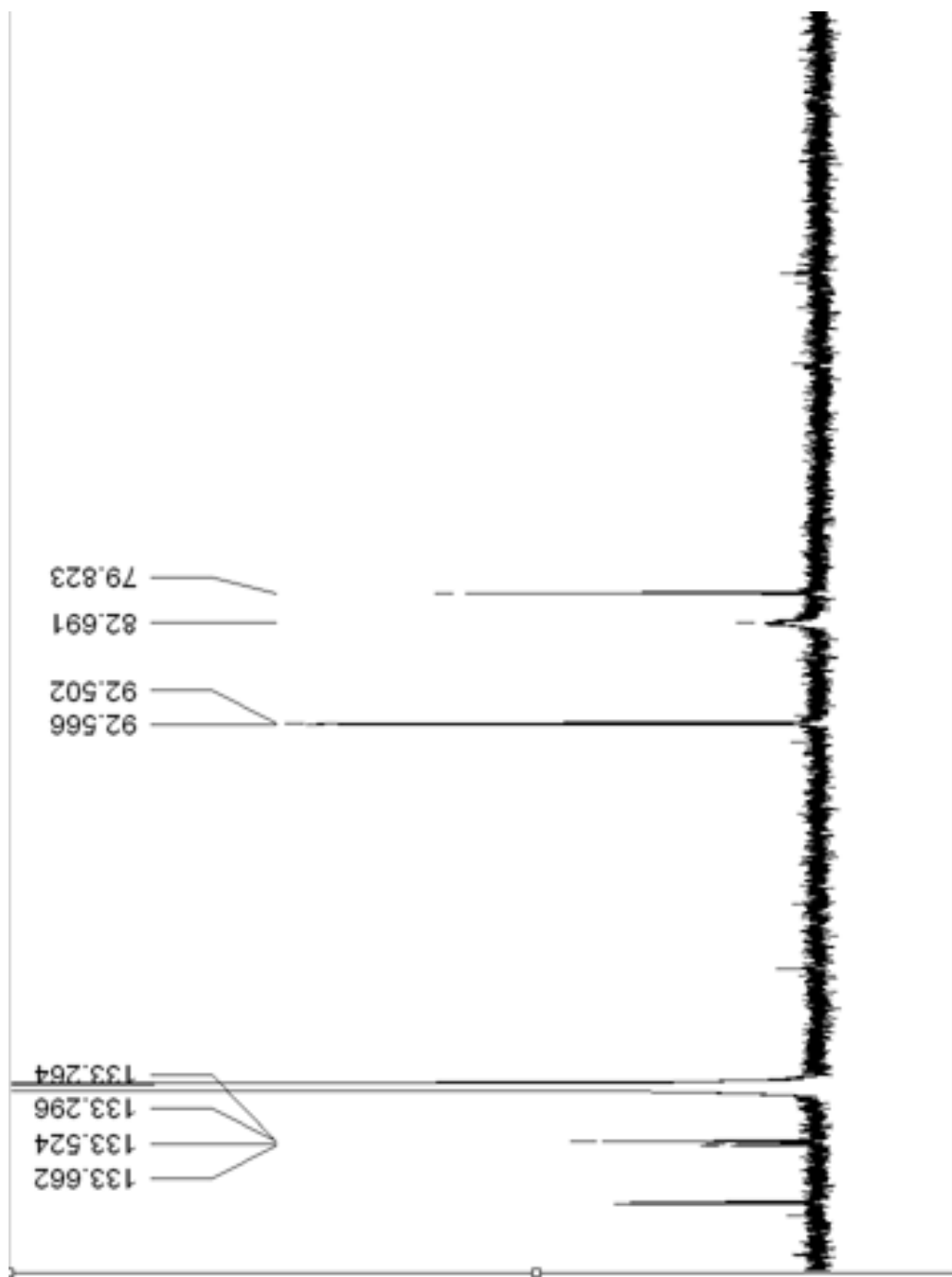




e.  $^1\text{H}$  NMR of **4** ( $\text{C}_6\text{D}_6$ , 300 MHz)



f.  $^{13}\text{C}\{^1\text{H}\}$  of **2** ( $\text{C}_6\text{D}_6$ , 128 MHz)



### 3. Crystallographic Structural Determination

Crystallographic data are reported in Table S1 and the ORTEP are represented in Figures S2 to S5. Single crystals were coated with Paratone-N oil, mounted using a glass fibre and frozen in the cold nitrogen stream of the goniometer. The data for **2-Mo** and **3** were collected on a Bruker SMART APEX II diffractometer with a MoK $\alpha$  radiation and the data for **2-Cu** and **4** were collected on a Bruker Microstar with a CuK $\alpha$  radiation. The data were reduced (SAINT)<sup>3</sup> and corrected for absorption (SADABS).<sup>4</sup> The structure was solved and refined using SHELXS-97 and SHELXL-97.<sup>5</sup> All non-H atoms were refined anisotropically. The hydrogen atoms were placed at idealized positions. Neutral atom scattering factors were taken from the International Tables for X-Ray Crystallography.<sup>6</sup> All calculations and drawings were performed using the SHELXTL package.<sup>7</sup> The crystal structure gave a satisfactory checkcif report and the data have been deposited with CCDC (CCDC No. 780139 (**2-Cu**), 780141 (**2-Mo**), 780140 (**3**), and 780138 (**4**)). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk, or via the internet at [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

The rotation out of plane ( $\theta$ ) is compared to the perfect orientation that would be expected if efficient orbital overlap would occur between the lone pair on phosphorous and the  $p_z$  orbital on boron (see Fig. S1A), where a mirror plane is passing through the phosphole and boratabenzene moieties. Using the assumption that the boratabenzene ring is always perfectly planar (which is close to reality), the value  $\theta$  was calculated using the average of the torsion angles C $\alpha$ 1-P-B-C2 and C $\alpha$ 2-P-B-C6.

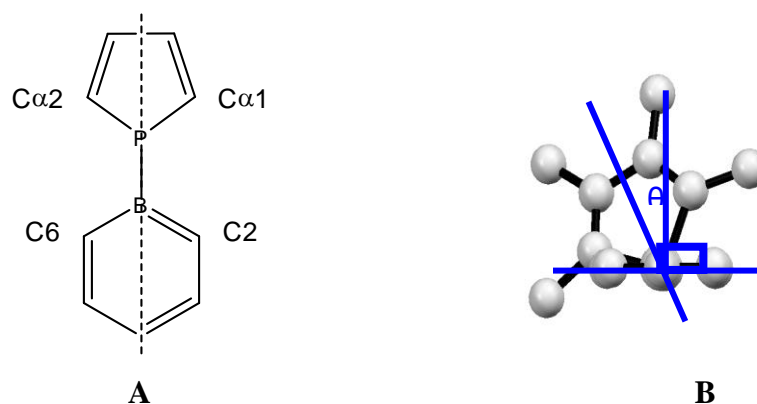


Fig. S1. Illustration of the perfect orientation for the formation of a P-B double bond (A) and of the rotation observed in boratabenzene-phosphole (B).

**Table S1.** Crystal data and structure refinement for **2**, **3**, and **4**.

	<b>2<sup>a</sup></b>	<b>2<sup>b</sup></b>	<b>3</b>	<b>4</b>
formula	C <sub>19</sub> H <sub>33</sub> LiBN <sub>2</sub> P	C <sub>19</sub> H <sub>33</sub> LiBN <sub>2</sub> P	C <sub>22</sub> H <sub>41</sub> LiBN <sub>2</sub> PSi	C <sub>26</sub> H <sub>34</sub> B <sub>2</sub> P <sub>2</sub> Fe
fw	338.19	338.19	410.38	485.94
size(mm)	0.14 x 0.04 x 0.03	0.11 x 0.18 x 0.22	0.60 x 0.20 x 0.09	0.20 x 0.08 x 0.08
cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	P2(1)/n	P2(1)/n	P2(1)/c	P2(1)/c
a (Å)	8.766(3)	8.7343(5)	10.345(2)	7.0954(2)
b (Å)	18.191(7)	8.1187(9)	14.114(3)	13.2891(3)
c (Å)	13.428(5)	13.3941(7)	18.403(4)	13.6815(3)
α. β. γ (deg)	90 95.435(6) 90	90 95.630(3) 90	90 100.889(3) 90	90 103.061(1) 90
V (Å <sup>3</sup> )	2131.6(14)	2109.45(19)	2638.7(9)	1256.68(5)
Z	4	4	4	2
wavelength (Å)	0.71073	1.54178	0.71073	1.54178
D <sub>calc</sub> (g·cm <sup>-3</sup> )	1.054	1.065	1.033	1.284
F <sub>000</sub>	736	736	896	512
Temp (K)	200(2)	150(2)	200(2)	296(2)
no. of unique/total reflns	3440/19893	3932/24605	4264/24522	2481/16308
GOF	1.007	0.907	1.000	1.033
R <sub>int</sub>	0.1355	0.0791	0.1957	0.0518
final R indices [I > 2σ(I)]	0.0583	0.0597	0.0697	0.0378

<sup>a</sup> Study of **2** using a KαMo radiation. <sup>b</sup> Study of **2** using a KαCu radiation.

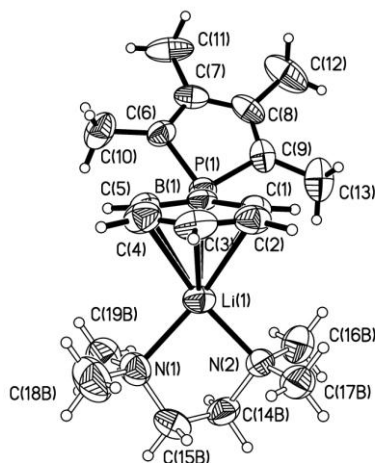


Fig. S2 – ORTEP diagram of **2-Mo**. Ellipsoids are represented at 50% probability. One of the two disordered TMEDA molecules is represented (85% occupation). Selected bond lengths (Å) and angles (deg): B(1)-P(1) 1.939(4); B(1)-C(1) 1.493(5); C(1)-C(2) 1.392(5); C(2)-C(3) 1.388(5); C(3)-C(4) 1.380(5); C(4)-C(5) 1.383(5); B(1)-C(5) 1.505(5); P(1)-C(6) 1.774(4); C(6)-C(7) 1.351(5); C(7)-C(8) 1.443(5); C(8)-C(9) 1.363(5); P(1)-C(9) 1.779(4); C(6)-P(1)-C(9) 91.68(18); C(6)-P(1)-B(1) 109.93(18); C(9)-P(1)-B(1) 111.69(18); C(1)-B(1)-C(5) 114.3(3); C(1)-B(1)-P(1) 124.4(3); C(5)-B(1)-P(1) 121.0(3); C(1)-B(1)-P(1)-C(9) -30.9(4); C(5)-B(1)-P(1)-C(6) 55.1(3).

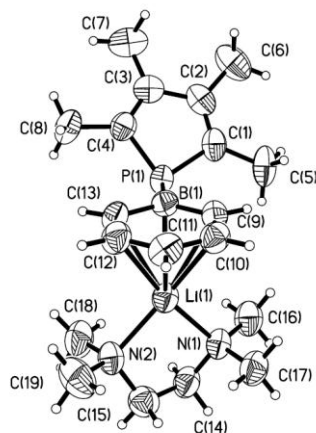


Fig. S3 – ORTEP diagram of **2-Cu**. Ellipsoids are represented at 50% probability. Selected bond lengths (Å) and angles (deg): B(1)-P(1) 1.953(3); B(1)-C(9) 1.485(4); C(9)-C(10) 1.387(4); C(10)-C(11) 1.402(4); C(11)-C(12) 1.389(4); C(12)-C(13) 1.380(4); B(1)-C(13) 1.502(4); P(1)-C(1) 1.777(3); C(1)-C(2) 1.345(4); C(2)-C(3) 1.474(4); C(3)-C(4) 1.354(4); P(1)-C(4) 1.782(3); C(1)-P(1)-C(4) 91.35(14); C(1)-P(1)-B(1) 111.55(13); C(4)-P(1)-B(1) 109.67(13); C(9)-B(1)-C(13) 115.4(3); C(9)-B(1)-P(1) 124.3(2); C(13)-B(1)-P(1) 120.2(2); C(9)-B(1)-P(1)-C(1) -30.0(3); C(13)-B(1)-P(1)-C(4) 55.7(3).

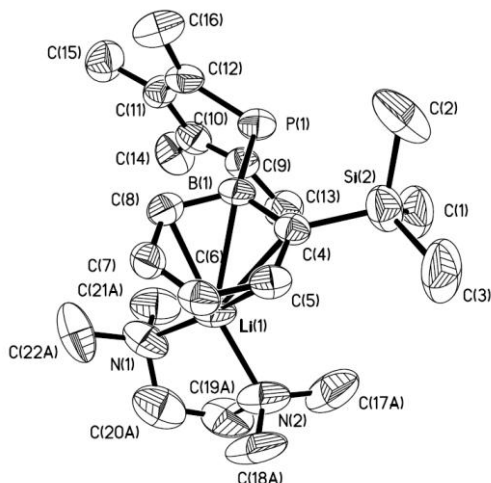


Fig. S4 – ORTEP diagram of **4**. Ellipsoids are represented at 50% probability. Hydrogen atoms were removed for clarity. Selected bond lengths (Å) and angles (deg): B(1)-P(1) 1.975(6); B(1)-C(4) 1.504(7); C(4)-C(5) 1.418(6); C(5)-C(6) 1.391(6); C(6)-C(7) 1.376(6); C(7)-C(8) 1.389(6); B(1)-C(8) 1.482(7); P(1)-C(9) 1.800(5); C(9)-C(10) 1.346(6); C(10)-C(11) 1.449(7); C(11)-C(12) 1.361(6); P(1)-C(12) 1.787(5); C(8)-B(1)-P(1) 120.0(4); C(4)-B(1)-P(1) 122.0(4); C(8)-B(1)-C(4) 118.0(5); C(12)-P(1)-C(9) 90.8(3); C(12)-P(1)-B(1) 104.9(2); C(9)-P(1)-B(1) 105.2(2); C(4)-B(1)-P(1)-C(12) -159.3(4); C(8)-B(1)-P(1)-C(9) -75.3(4).

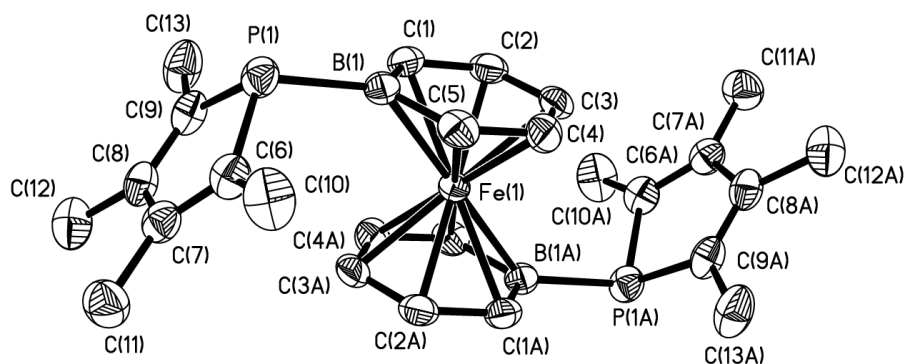


Fig. S5 – ORTEP diagram of **4**. Ellipsoids are represented at 50% probability. Hydrogen atoms were removed for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)-B(1) 2.230(3); Fe(1)-C(1) 2.126(2); Fe(1)-C(2) 2.083(2); Fe(1)-C(3) 2.077(2); Fe(1)-C(4) 2.100(2); Fe(1)-C(5) 2.138(2); B(1)-C(1) 1.507(4); C(1)-C(2) 1.413(3); C(2)-C(3) 1.415(4); C(3)-C(4) 1.416(4); C(4)-C(5) 1.412(4); B(1)-C(5) 1.508(4); B(1)-P(1) 1.942(3); P(1)-C(6) 1.795(3); C(6)-C(7) 1.354(4); C(7)-C(8) 1.460(3); C(8)-C(9) 1.358(4); P(1)-C(9) 1.798(3); C(1)-B(1)-C(5) 114.1(2); C(1)-B(1)-P(1) 122.97(19); C(5)-B(1)-P(1) 122.9(2); C(6)-P(1)-C(9) 91.68(12); C(6)-P(1)-B(1) 109.49(12); C(9)-P(1)-B(1) 108.86(12); C(1)-B(1)-P(1)-C(9) 42.9(2); C(5)-B(1)-P(1)-C(6) -35.5(2).

#### 4. Computational details.

Calculations were carried out using Gaussian 03 package at the DFT level by means of the hybrid density functional B3PW91.<sup>8</sup> For the Fe, P and Si atoms<sup>9</sup>, the Stuttgart-Dresden pseudopotentials were used in combination with their associated basis sets. For the Li, B, C, and H atoms the all electron 6-311G(d,p)<sup>10</sup> basis sets were used. The nature of the optimized stationary point, minima, has been verified by means of analytical frequency calculation at 298.15 K and 1 atm. The geometry optimizations have been achieved without any geometrical constraints. The energy data presented correspond to the free enthalpy in gas phase of the computed compounds in which thermal, vibrational, translational and rotational contributions have been included.

#### Cartesian coordinates of the optimized structures

##### Complex 2\*

57

E: -1227.045635 a.u.

C	4.793042	1.225629	7.433922	C	1.898133	2.352159	9.568799
P	4.206903	2.407546	6.210869	H	1.331537	1.422063	9.697677
C	2.922367	3.005934	7.330895	H	1.176129	3.149116	9.385128
C	2.900588	2.233702	8.455916	H	2.384470	2.561484	10.528820
C	3.953519	1.221295	8.509986	C	4.038087	0.261998	9.662402
B	5.488233	3.879283	6.077371	H	4.905706	-0.395355	9.582300
C	6.815820	3.929995	6.796869	H	3.148447	-0.377389	9.717118
C	7.654856	5.036279	6.635449	H	4.106578	0.788696	10.621046
C	7.339835	6.096177	5.769785	C	5.940298	0.293482	7.181483
C	6.133569	6.091018	5.048725	H	5.619760	-0.632170	6.686491
C	5.220450	5.037009	5.140703	H	6.691181	0.757793	6.534257
C	2.002136	4.130649	6.971953	H	6.445343	0.007972	8.109433
H	1.463038	4.511150	7.843185	H	7.143587	3.161930	7.495091
H	1.255555	3.824574	6.229048	H	8.589640	5.096607	7.192781
H	2.559754	4.969380	6.542169	H	8.018166	6.938775	5.678112

H	5.927266	6.940261	4.397630	H	8.072303	2.460342	0.983805
Li	7.319902	4.141191	4.481046	C	9.338418	3.215262	2.552805
N	6.866199	3.417851	2.460592	H	10.173783	2.569362	2.231963
C	8.025569	2.607598	2.076477	H	9.493922	4.183943	2.068658
N	9.359236	3.435367	4.002960	C	9.536471	2.180494	4.735474
C	5.635796	2.626123	2.397562	C	10.424159	4.369163	4.364861
H	5.433568	2.261112	1.377137	H	4.322013	5.119228	4.528826
H	5.704098	1.770949	3.072400	H	9.503707	2.378606	5.808119
H	4.793146	3.234248	2.728441	H	8.730992	1.480766	4.505895
C	6.732408	4.600707	1.610296	H	10.497314	1.696433	4.492678
H	6.565173	4.329328	0.554529	H	10.402130	4.547176	5.441308
H	7.627039	5.224839	1.666646	H	11.421948	3.986360	4.093692
H	5.887246	5.199364	1.954605	H	10.268511	5.325971	3.861229
H	7.896677	1.613893	2.514475				

### Complex 3\*

69

E: -1349.770406 a.u.

Li	0.345307	9.617516	3.994223	C	1.912451	8.596665	5.375618
C	1.563906	9.798747	6.015720	P	2.584343	12.834577	3.109135
C	1.704915	11.025895	5.373204	C	1.003054	13.420021	2.467152
B	2.301131	11.089249	3.986856	C	0.328128	12.808663	1.276882
C	2.705229	9.773741	3.332366	H	-0.739145	13.049858	1.239740
C	2.470843	8.610976	4.093629	H	0.768514	13.152077	0.333076



H	0.426551	11.718705	1.284286	H	4.510266	7.397720	2.270224
C	0.645436	14.570791	3.113243	H	4.531222	7.663037	0.525012
C	-0.516990	15.445395	2.736124	C	5.323647	10.352027	2.150226
H	-1.117180	15.007508	1.936499	H	5.219704	11.416627	2.374797
H	-1.180484	15.630283	3.588911	H	6.056248	10.232839	1.346447
H	-0.178718	16.427759	2.384587	H	5.718165	9.867368	3.048567
C	1.533620	14.944601	4.210530	H	1.791667	7.650137	5.894359
C	1.295156	16.199786	5.000184	H	2.756897	7.640331	3.690893
H	0.293190	16.216848	5.444528	H	1.169757	9.744589	7.030394
H	1.374024	17.091878	4.366897	H	1.405461	11.917541	5.920815
H	2.018223	16.312665	5.809503	N	-0.771775	8.202709	2.682981
C	2.578500	14.084614	4.399191	C	-2.168511	8.345782	3.111104
C	3.669154	14.185198	5.422379	C	-2.519298	9.783945	3.465849
H	3.339441	14.716552	6.319911	N	-1.666276	10.316064	4.532776
H	4.008566	13.193157	5.735862	C	-0.596963	8.641452	1.297452
H	4.546085	14.715067	5.031211	C	-0.337021	6.811738	2.809182
Si	3.739973	9.634708	1.804187	H	0.456687	8.571442	1.023864
C	3.048466	10.410730	0.357212	H	-1.185367	8.025401	0.597240
H	2.064607	10.043670	0.057418	H	-0.902707	9.682256	1.178867
H	2.993113	11.494888	0.484337	H	0.707177	6.727288	2.504445
H	3.737119	10.224921	-0.475968	H	-0.412607	6.489190	3.850019
C	3.974114	7.870852	1.442658	H	-0.939094	6.131802	2.184290
H	3.000592	7.377635	1.359419	C	-2.029784	9.756558	5.834733

C	-1.762831	11.776659	4.587665	H	-1.913490	8.670992	5.841885
H	-1.421084	12.214253	3.648499	H	-2.392410	10.424979	2.588593
H	-2.793904	12.111779	4.788026	H	-3.587190	9.838382	3.740017
H	-1.111381	12.154316	5.376483	H	-2.863615	7.982171	2.335561
H	-1.368006	10.165343	6.599473	H	-2.318618	7.703947	3.983545
H	-3.071300	9.997282	6.106385				

### Complex 4\*

65

E:-1197.7321191 a.u.

C	-2.275917	-2.716486	0.864351	P	0.085645	0.973315	-0.325968
C	-3.616256	-3.060062	0.593046	C	0.558415	0.314183	1.299389
B	-4.056765	-3.512942	-0.790632	C	1.628159	-0.526222	1.150881
C	-2.951268	-3.424966	-1.831865	C	2.024508	-0.771807	-0.235920
C	-1.632887	-3.071399	-1.478331	C	1.264791	-0.121229	-1.170849
Fe	-2.892758	-1.564646	-0.764657	H	-2.650764	0.395125	1.370737
B	-1.729001	0.383822	-0.737418	H	-4.912077	-0.192214	0.715947
C	-2.168893	-0.069329	-2.121389	H	-5.491090	-0.797613	-1.592617
C	-3.509105	-0.412820	-2.393603	H	-3.789641	-0.811757	-3.365535
C	-4.499670	-0.411951	-1.379080	P	-5.872999	-4.100844	-1.200161
C	-4.153038	-0.057770	-0.051148	H	-0.873942	-2.938267	-2.245696
C	-2.834904	0.295647	0.302927	H	-3.135673	-3.524069	-2.899699

H	-1.994914	-2.317069	1.835933	C	-7.048542	-3.016112	-0.339292
H	-4.316571	-2.878978	1.406119	C	-7.813794	-2.357333	-1.263732
H	-1.467387	-0.250025	-2.933582	C	-7.424791	-2.588741	-2.654559
C	1.448337	-0.153254	-2.661394	C	-6.355064	-3.427137	-2.816629
C	3.200634	-1.654272	-0.551842	C	-7.230569	-2.999649	1.152111
C	2.388590	-1.144049	2.291936	C	-8.990035	-1.481950	-0.929037
C	-0.042864	0.777771	2.596453	C	-8.191978	-1.960279	-3.785213
C	-1.285838	-2.717347	-0.150230	C	-5.758595	-3.876558	-4.120854
H	-0.293791	-2.332871	0.062542	H	-8.287013	-3.057930	1.439337
H	2.506152	-0.180348	-2.946617	H	-6.725031	-3.846040	1.625693
H	0.973316	-1.032626	-3.117811	H	-6.827531	-2.084681	1.607450
H	1.012408	0.730441	-3.136414	H	-8.856266	-0.462175	-1.311271
H	0.723433	1.080321	3.320192	H	-9.917102	-1.863774	-1.375152
H	-0.697459	1.641298	2.448787	H	-9.148292	-1.408104	0.149296
H	-0.642272	-0.006975	3.077734	H	-7.773137	-2.227700	-4.758088
H	1.968204	-0.861441	3.259847	H	-9.244464	-2.271234	-3.780320
H	2.380273	-2.239981	2.237727	H	-8.189606	-0.865151	-3.716703
H	3.442810	-0.839176	2.286169	H	-5.111823	-4.748009	-3.985842
H	3.059685	-2.669149	-0.159264	H	-6.527563	-4.161409	-4.848779
H	3.367826	-1.741782	-1.627699	H	-5.152238	-3.090329	-4.590818
H	4.125088	-1.270821	-0.101828				

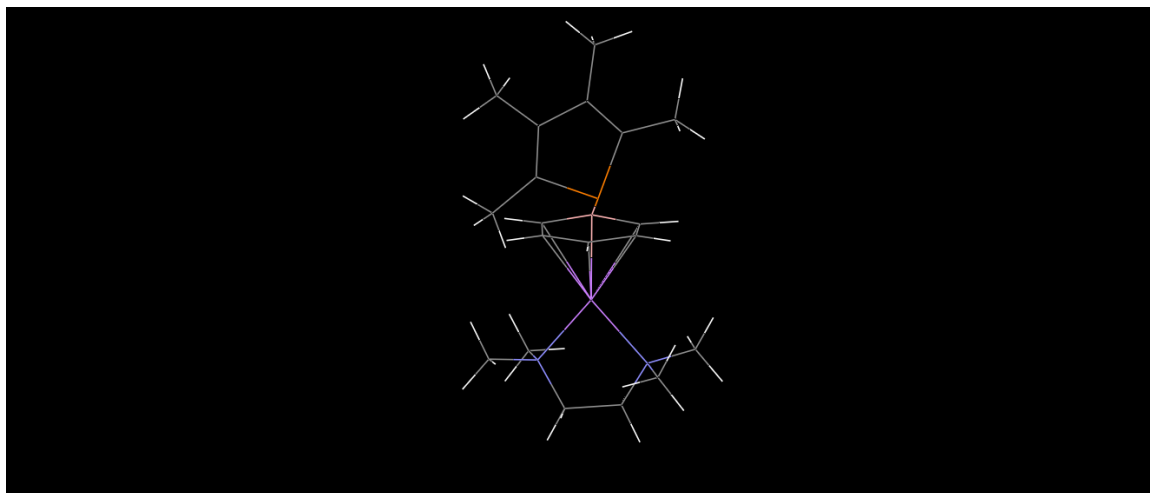


Fig. S6. Molecular representation of the minimized structure of **2\***

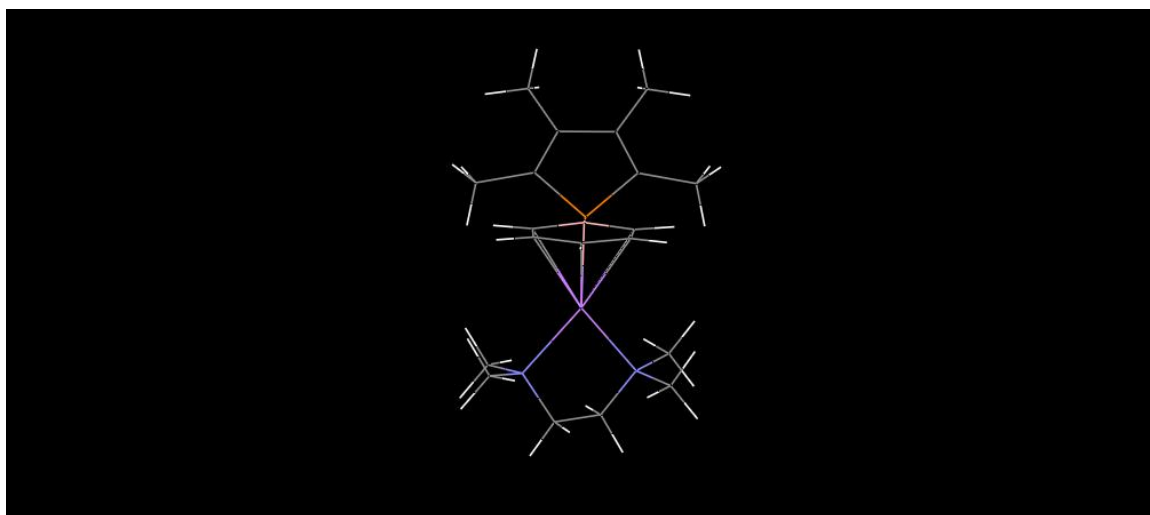


Fig. S7. Molecular representation of the minimized structure of **2'**

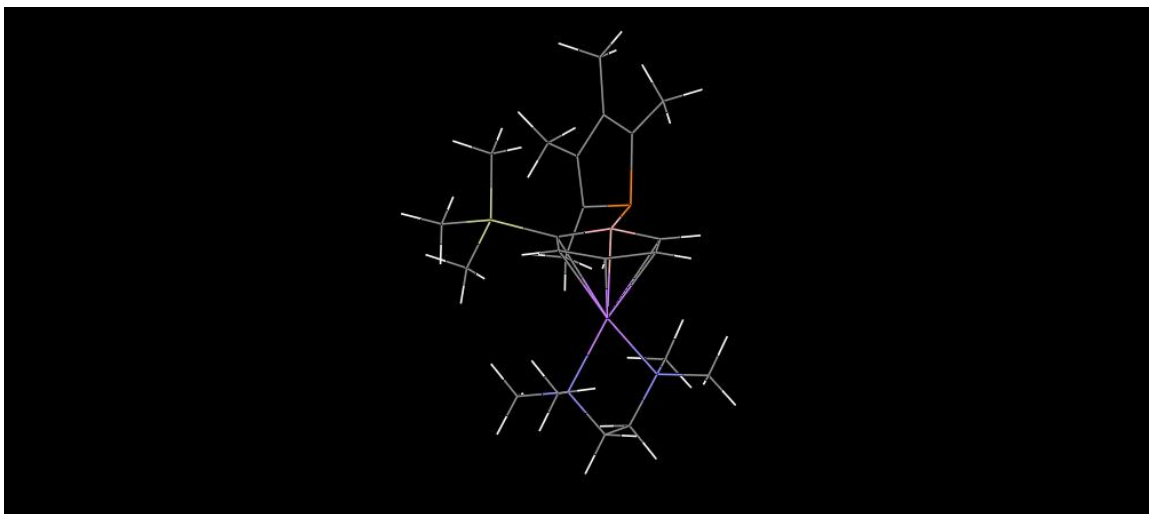


Fig. S8. Molecular representation of the minimized structure of **3\***

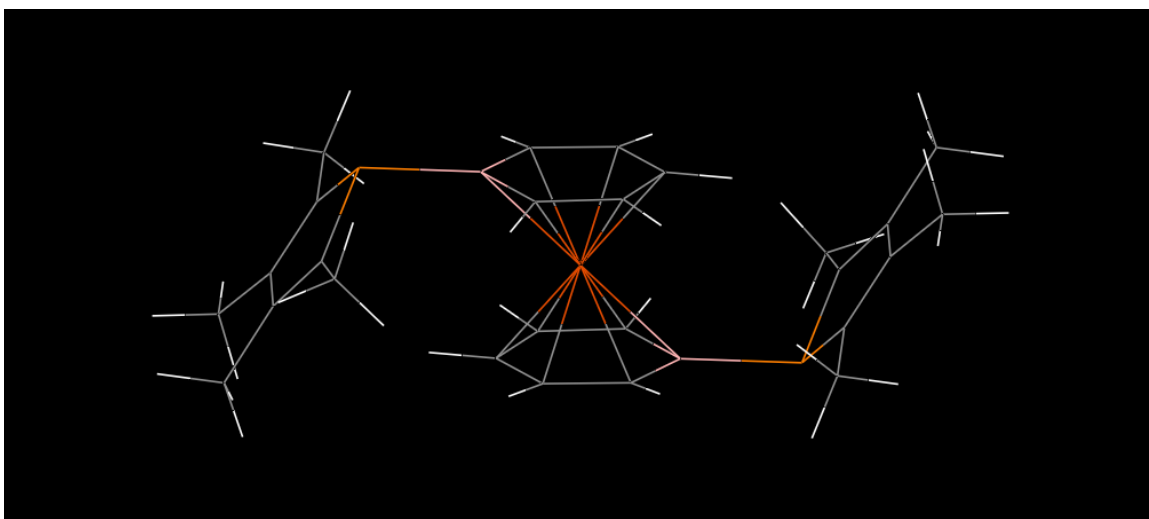


Fig. S9. Molecular representation of the minimized structure of **4\***

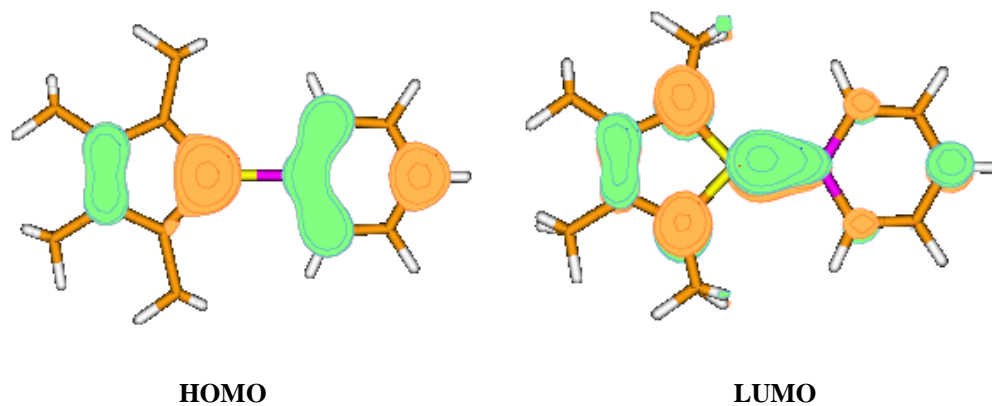


Fig. S10. Molecular representation of the HOMO and the LUMO for the planarized version of the boratabenzene-phosphole **2**.

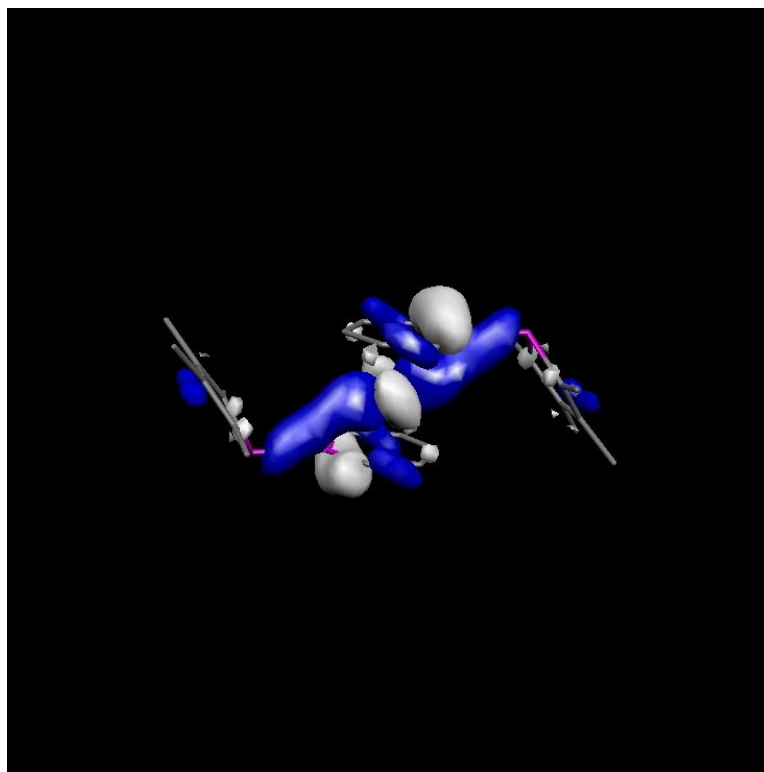


Fig. S11. Molecular representation of the HOMO-4 of **4** where the overlap between the  $d_{xy}$  and the  $p_z$  orbital on boron is represented.

## 5. References

- 
- <sup>1</sup> D. A. Hoic, J. R. Wolf, W. M. Davis, G. C. Fu, *Organometallics*, 1996, **15**, 1315-1318.
- <sup>2</sup> T. Douglas, K. Theopold, *Angew. Chem., Int. Ed.*, 1989, **28**, 1367-1368.
- <sup>3</sup> *SAINTE* Version 7.07a; Bruker AXS Inc.: Madison, WI, 2003. Sheldrick, G. M.
- <sup>4</sup> *SADABS* Version 2004/1; Bruker AXS Inc.: Madison, WI, 2004.
- <sup>5</sup> Sheldrick, G. M. *SHELXS-97 and SHELXL-97. Programs for the refinement of crystal structures*; University of Gottingen: Germany, 1997.
- <sup>6</sup> *International Tables for Crystallography, Vol C.*, Wilson, A. J. C., Ed. Kluwer Academic Publishers: Dordrecht, 1992, pp 219-222 and pp. 500-502.
- <sup>7</sup> *SHELXTL*. Version 6.12; Bruker AXS: Madison, WI, 2001.
- <sup>8</sup> (a) J. P. Perdew, J. A. Chevary, S. H. Vosko, S. H., K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671-6687; (b) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652.
- <sup>9</sup> D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123; (b) J. M. L. Martin, A. Sundermann, *J. Chem. Phys.*, 2001, **114**, 3408; (c) A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.*, 1993, **80**, 1431.
- <sup>10</sup> P. C. Harihara, J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213-222.