Supporting Information for

A Hybrid Lithium Oxalate-Phosphinate Salt

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Experimental:

General Considerations: Boric acid, lithium hydroxide and propylene carbonate were purchased from Aldrich. Diphenylchlorophosphine was purchased from Strem Chemicals. n-Butyllithium and oxalic acid was purchased from Acros Organics. Pentane, hexanes, tetrahydrofuran, hydrogen peroxide, sodium hydroxide, and toluene were purchased from Fisher. Dimethylsulfoxide-d6 was purchased from Jade Scientific. All reagents were used without further purification. ^1H , ^{11}B , and ^{13}C NMR data was obtained on a 600 MHz Inova NMR spectrometer at 599.9126, 192.4691, and 150.1853 MHz respectively. ^{31}P NMR data were obtained on a 400 MHz Inova NMR spectrometer at 161.910 MHz. ^1H NMR shifts were given relative to $(\text{CHD}_2)\text{S}(\text{O})\text{CD}_3$ (2.50 ppm) and ^{13}C NMR shifts were given relative to $(\text{CD}_3)_2\text{SO}$ (39.5 ppm). $^{11}\text{B}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were externally referenced to H_3BO_3 in D_2O and H_3PO_4 in D_2O respectively. The IR data was obtained using a Midac M2000 spectrometer. Melting point was measured using a capillary Mel-temp apparatus and was not corrected. Elemental analysis was performed by Robertson Microlit Laboratories, Madison, New Jersey. TGA experiments were performed on a Perkin Elmer DSC 7. Diphenylphosphinic acid and lithium diphenylphosphinide were prepared as described in the literature.^{1,2}

Li(THF)[(C₂O₄)B(O₂PPh₂)₂] (1):

Method A: Boric acid (0.114 g, 1.85 mmol), diphenylphosphinic acid (0.808 g, 3.70 mmol), lithium hydroxide (0.044 g, 1.85 mmol) and oxalic acid (0.167 g, 1.85 mmol) were added to a mortar, ground into a homogeneous powder, transferred to a round bottom flask, and placed under vacuum. The flask was heated for 4 hours at 200°C. Tetrahydrofuran (15 mL) was added and the slurry was filtered to remove insoluble materials. The solution was concentrated by evaporation and layered with pentane. Colorless crystals were collected and dried under vacuum (0.203 g, 20.3%).

Method B: Boric acid (0.057 g, 0.93 mmol), diphenylphosphinic acid (0.202 g, 0.926 mmol), lithium diphenylphosphinide (0.208 g, 0.926 mmol) and oxalic acid (0.083 g, 0.93 mmol) were added to a mortar, ground into a homogeneous powder, transferred to a round bottom flask, and placed under vacuum. The flask was heated for 4 hours at 200°C. Tetrahydrofuran (15 mL) was added and the slurry was filtered to remove insoluble materials. The solution was concentrated by evaporation and layered with pentane. Colorless crystals were collected and dried under vacuum to yield **1**•0.5THF (0.094 g, 19%); mp 161-166°C; ¹H NMR (600 MHz): δ 7.61-7.64 (m, 16H), 7.46-7.48 (m, 8H), 7.37-7.40 (m, 16H), 3.59-3.61 (m, 12H), 1.74-1.77 (m, 12H); ¹³C{¹H} NMR: δ 159.0, 135.2 (d, ¹J_{PC} = 137.6 Hz), 131.0 (d, ⁴J_{PC} = 2.4 Hz), 130.7 (d, ³J_{PC} = 10.0 Hz), 128.1 (d, ²J_{PC} = 12.6 Hz), 66.9, 25.1; ³¹P{¹H} NMR: δ 20.9; ¹¹B{¹H} NMR: δ 7.99; FTIR (KBr): 3077 (w), 3057 (w), 3014 (w), 2982 (w), 2877 (w), 1813 (m), 1801 (m), 1773 (w), 1593 (w), 1486 (w), 1316 (s), 1218 (s), 1187 (s), 1133 (s), 1075 (s), 1048 (s), 1025 (m), 995 (s), 955 (s), 890 (w), 755 (w), 730 (m), 695 (s); Anal. Calcd for C₆₀H₅₆B₂Li₂O₁₈P₄ · C₄H₈O: C, 59.28; H, 4.99. Found: C, 59.22; H, 5.09.

TGA: 6.63800 mg of **1** was placed on a platinum pan and inserted into the oven. Under a N₂ flow of 40.0 mL/min, the oven was heated from 23.8700°C to 991.3019°C at a continuous ramp of 20.00 °C/min. The data were analyzed and plotted with Origin 8.1 software.

Li(THF)[(HO(O)PPh₂)(O₂PPh₂)] (2) Diphenylphosphinic acid (0.848 g, 3.89 mmol), boric acid (0.120 g, 1.94 mmol), oxalic acid (0.175 g, 1.94 mmol), and lithium hydroxide (0.093 g, 3.9 mmol) was refluxed in toluene (40 mL) and water was removed by azeotropic distillation using a Dean-Stark Trap apparatus for 4 hours. Solvent was removed and the off-white solid was dissolved in hot tetrahydrofuran (15 mL) and filtered. Slow diffusion of pentane into the tetrahydrofuran solution produced colorless crystals (0.786 g, 79%) suitable for X-ray crystallography; ¹H NMR (600 MHz) δ 7.66-7.71 (m, 16H), 7.35-7.42 (m, 24H), 3.58-3.62 (m, 8H), 1.74-1.77 (m, 8H); ¹³C{¹H} NMR δ 137.2 (d, ¹J_{PC} = 133.0 Hz), 130.9 (d, ³J_{PC} = 9.6 Hz), 130.4, 127.0 (d, ²J_{PC} = 12.2 Hz), 67.0, 25.1; ³¹P{¹H} NMR δ 20.3; Anal. Calcd for C₅₆H₅₈Li₂O₁₀P₄: C, 65.37%; H, 5.69. Found: C, 65.20; H, 5.40.

Crystallography: Summary of crystal data and collection parameters for crystal structure of **1** are provided in Table 1. Detailed descriptions of data collection, as well as data solution, are provided below. ORTEP diagrams were generated with Mercury 2.3 software package. A suitable crystal was mounted on a glass fiber using Paratone-N hydrocarbon oil. The crystal was transferred to a Bruker AXS SMART APEX II diffractometer with a CCD area detector, centered in the X-ray beam, and cooled to 170K using a nitrogen-flow low-temperature apparatus that had been precisely calibrated by a thermocouple placed at the same position as the crystal. An arbitrary hemisphere of data was collected using $0.3^\circ \varphi$ and ω scans, and the data were integrated by the program SAINT. The final unit cell parameters were determined by a least-squares refinement of reflections with $I > 10\sigma(I)$. Data analysis using Siemens XPREP and the successful solution and refinement of the structure determined the space group. Empirical absorption corrections were applied for **1** using the program AXScale. Equivalent reflections were averaged, and the structures were solved by direct methods using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as fixed atoms but not refined for all ordered atoms.

Compound 1. X-ray quality crystals were grown by layering a solution of **1** in tetrahydrofuran with pentane at room temperature. The final cycle of full-matrix least-squares refinement was based on 8248 observed reflections and 433 variable parameters and converged yielding final residuals: $R = 0.0454$, $wR2 = 0.1241$, and $GOF = 1.039$.

Compound 2. X-ray quality crystals were grown by layering a solution of **2** in tetrahydrofuran with pentane at room temperature. The final cycle of full-matrix least-squares refinement was based on 5515 observed reflections and 325 variable parameters and converged yielding final residuals: $R = 0.0490$, $wR2 = 0.1488$, and $GOF = 1.126$.

Figure S1. Structural representation of compound **2**.

Figure S2. Structural representation of inner portion of compound **2** highlighting hydrogen bonding.

Table 1. Crystal Data and Collection Parameters

Compound	1	2
formula	$\text{C}_{60}\text{H}_{56}\text{B}_2\text{Li}_2\text{O}_{18}\text{P}_4 \cdot 2 \text{C}_4\text{H}_8\text{O}$	$\text{C}_{56}\text{H}_{56}\text{Li}_2\text{O}_{10}\text{P}_4$
formula weight	1368.64	1026.77
space group	<i>P</i> -1 (#2)	<i>P</i> -1 (#2)
Temperature (K)	170	170
<i>a</i> (Å)	11.848(2)	10.690(1)
<i>b</i> (Å)	12.601(2)	11.503(1)
<i>c</i> (Å)	13.003(1)	12.199(1)
α (°)	106.611(1)	109.224(1)
β (°)	97.425(1)	107.371(1)
γ (°)	106.470(1)	98.158(1)
<i>V</i> (Å ³)	1736.6(1)	1302.9(2))
<i>Z</i>	1	1
density _{calc} (g/cm ³)	1.309	1.309
diffractometer	Siemens SMART	Siemens SMART
radiation	Mo K α (λ = 0.71073 Å)	Mo K α (λ = 0.71073 Å)
monochromator	graphite	graphite
detector	CCD area detector	CCD area detector
scan type, width	ϕ and ω , 0.3°	ϕ and ω , 0.3°
scan speed (s)	10.0	10.0
no. of reflections measured	hemisphere	hemisphere
2 θ range (°)	3.4-55.0	3.8-53.8
crystal dimensions (mm)	0.30 x 0.22 x 0.17	0.45 x 0.25 x 0.16
no. of reflections measured	21574	14476
no. of unique reflections	8248	5515
no. of observations	6735	4816
no. of parameters	433	325
<i>R</i> , <i>R</i> _w , <i>R</i> _{all}	0.0454, 0.1241, 0.0563	0.0490, 0.1488, 0.0543
GOF	1.039	1.126

References:

1. Wyatt, P.; Eley, H.; Charmant, J.; Daniel, B. J.; Kantacha, A. *Eur. J. Org. Chem.* **2003**, 4216.
2. Strecker, R. A.; Snead, J. L.; Sollott, G. P. *J. Am. Chem. Soc.* **1973**, 95, 210.