Supporting Information

The neutral boron [(L$_{1-3}$)BPh$_2$] and cationic charged boron [(L$_{1a-3a}$)BPh$_2$] complexes for chemical CO$_2$ conversion to obtain cyclic carbonates at ambient conditions

Ahmet KILIC$^a$, Eyyup YASAR$^a$, Emine AYTAR$^a$

* Harran University, Chemistry Department, Art and Science Faculty, 63290, Sanliurfa, Turkey

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1. Experimental

* To whom correspondence should be addressed: Harran University, Chemistry Department, TR-63190 Sanliurfa, Turkey. Tel: +90 414 318 3587, Fax: +90 414 318 3541, e-mail: kilica63@harran.edu.tr; kilica63@hotmail.com; http://orcid.org/0000-0001-9073-4339 (A. Kilic);
**General considerations**

All chemical solvents, starting materials and other chemicals used for synthesis were purchased from Sigma-Aldrich, TCI Chemicals, Fluka, or Alfa Aesar and used without further purification. $^1$H (at 400 MHz) and $^{13}$C (at 100 MHz) Nuclear magnetic resonance spectra (NMR-spectra) were recorded using an Agilent Technologies 400 MHz spectrometer in DMSO-$d_6$ with tetramethylsilane as internal standard. $^{11}$B NMR spectra were acquired at 192.5 MHz in DMSO-$d_6$ and at 23 °C temperature. $^{31}$P NMR spectra were recorded at 242.9 MHz in DMSO-$d_6$. The example was allowed to equilibrate for at least 20 min at room temperature before the $^{31}$P NMR spectrum was obtained. Chemical shifts are given in parts per million (ppm). Coupling constants are given in Hertz (Hz). FT-IR spectra were recorded using a Perkin-Elmer Two UATR-FT spectrophotometer in the range of 4000 to 400 cm$^{-1}$ at 25 °C with equipped ATR accessory. UV-Vis spectra were recorded on a Perkin-Elmer model Lambda 25 spectrophotometer in the range of 200 to 1100 nm using quartz cuvettes at room temperature. The EtOH and DMF have been selected as solvents for electronic spectra. Thermal analyses were performed with a SHIMADZU DTG-60H and simultaneous DTA-TG apparatus systems up to 800 °C (10 °C min$^{-1}$) under a dynamic nitrogen atmosphere (15 ml min$^{-1}$). Elemental analyses of C, H, and N were carried out on a LEKO CHNS 932 model elemental analyzer. The mass spectra (LC-MS) were obtained through using an Agilent LC-MS/MS spectrometer by ESI technique. Melting points were measured with an Electrothermal 9100 and are uncorrected. Catalytic experiments were carried out in a PARR 4560 50 mL stainless steel high-pressure reactor. CO$_2$ with a purity of 99.999 % was commercially available and used without further purification. GC analysis was performed on an Agilent 7820A model for conversion and selectivity of the mixture. The mixture was separated by centrifugation, and the liquid phase was subjected to GC analysis with ethylene glycol dibutyl ether as an internal standard and hydrogen as the carrier gas.
2. **Synthesis of the neutral salen ligands (L₁₋₃)**

The neutral salen ligands (L₁₋₃) were synthesized as given procedure: (2.0 g, 12.8 mmol) of 4-amino-2,2,6,6-tetramethylpiperidine for ligand L₁, (2.1 g, 12.8 mmol) of N,N-Diethyl-p-phenylenediamine for ligand L₂ and (2.9 g, 12.8 mmol) of 2-Aminoethyl diphenylborinate for ligand L₃ was dissolved in EtOH (30 mL) at room temperature and put into a trinecked-flask, equipped with a nitrogen (N₂) connection. The three mixtures were warmed and then the key starting material 5-chloromethyl salicylaldehyde (2.2 g, 12.8 mmol) was added to each reaction balloon in the presence of two drops formic acid as catalyst. The reaction mixture was heated to reflux temperature for 4 h with continuous stirring and then the mixture cooled slowly to room temperature. The solvent was removed and the solid was washed three times with diethyl ether with n-hexane, successively, and dried under vacuum. Finally, re-crystallization from CH₂Cl₂/C₂H₅OH (1:2) by slow evaporation afforded pure (L₁₋₃) ligands.

**Ligand (L₁):** Color: yellow, yield (%): 84, M.p.: >300 °C, Elemental Analysis (calculated for C₁₇H₂₅ClN₂O) (F.W: 309.0 g/mol) (%): C, 66.11; H, 8.16; N, 9.07. Found: C, 66.07; H, 8.11; N, 9.02. LC-MS (Scan ES⁺): m/z = 309.0 [M]⁺. FT-IR (ATR, v max-cm⁻¹): 3497-2416 u(O-H…∙∙∙N), 3018 u(Ar-CH), 2976-2855 u(aliph-CH), 1630 u(C=N), 1583-1442 u(C=C), and 1158 u(C-O). ¹H-NMR (DMSO-d₆): δ (ppm) = 12.92 (s, 1H, OH, D-exchangeable), 8.55 (s, 1H, H=C=N), 7.43-6.70 (m, 3H, Ar-CH), 3.86 (s, 2H, Cl-CH₂), 3.66 (s, 1H, N-CH), 1.85 (s, 1H, N-H), 1.71 (s, 2H, CH-CH₂), 1.60 (s, 2H, CH-CH₂), 1.31 (s, 6H, C-CH₃), 1.07 (s, 6H, C-CH₃). ¹³C-NMR (DMSO-d₆): δ (ppm) = 165.82 (H-C=N), 159.61, 141.08, 132.98, 132.70, 118.57 and 116.73 (Ar-CH), 57.69 (C-CH₃), 57.24 (N-CH), 56.37 (CH-CH₂), 42.37 (Cl-CH₂), 30.26 and 25.05 (C-CH₃). UV-Vis (λ max/(nm), * = shoulder peak): 222, 258, 326 and 419* (C₂H₅OH); 237, 266, 325 and 420* (DMF).
**Ligand (L₂):** Color: dark brown, yield (%): 81, M.p.: 100 °C, Elemental Analysis (calculated for C₁₈H₂₁ClN₂O) (F.W: 317.0 g/mol) (%): C, 68.24; H, 6.68; N, 8.84. Found: C, 68.20; H, 6.61; N, 8.82. LC-MS (Scan ES⁺): m/z = 353.0 [M+2NH₄]⁺. FT-IR (ATR, ν_max cm⁻¹): 3517-2347 υ(O-H∙∙∙∙N), 3133 and 3051 υ(Ar-CH), 2979-2848 υ(aliph-CH), 1652 υ(C=N), 1600-1445 υ(C=C), and 1183 υ(C-O). ¹H-NMR (DMSO-d₆): δ (ppm) = 13.06 (s, 1H, OHy, D-exchangeable), 8.81 (s, 1H, HCN), 7.61-7.12 (m, 7H, Ar-CH), 3.86 (s, 2H, Cl-C₂H₅), 1.64 (d, 2H, J = 6.4 Hz, N-C₂H₅), 1.44 (d, 2H, J = 6.4 Hz, N-C₂H₅), and 0.92 (s, 6H, CH₂-C₃H₇). ¹³C-NMR (DMSO-d₆): δ (ppm) = 161.65 (HC=N), 158.27, 144.11, 138.75, 131.67, 129.49, 128.56, 126.94, 126.05, 124.44, 121.20, 115.96 and 113.23 (Ar-CH), 56.37 (N-C₂H₅), 52.57 (Cl-CH₂), and 10.51 (CH₂-C₃H₇). UV-Vis (λ_max/(nm), * = shoulder peak): 224*, 260, 346 and 423* (C₂H₅OH); 237, 271, 332 and 406 (DMF).

**Ligand (L₃):** Color: orange, yield (%): 82, M.p.: 145 °C, Elemental Analysis (calculated for C₂₂H₂₁BCINO₂) (F.W: 378.0 g/mol) (%): C, 69.96; H, 5.60; N, 3.71. Found: C, 69.91; H, 5.54; N, 3.67. LC-MS (Scan ES⁺): m/z = 378.0 [M⁺]. FT-IR (ATR, ν_max cm⁻¹): 3531-2413 υ(O-H∙∙∙∙N), 3064 and 3040 υ(Ar-CH), 2976-2875 υ(aliph-CH), 1644 υ(C=N), 1591-1481 υ(C=C), 1181 υ(B-O) and 1178 υ(C-O). ¹H-NMR (DMSO-d₆): δ (ppm) = 13.12 (s, 1H, OH, D-exchangeable), 8.63 (s, 1H, HCN), 7.67-6.80 (m, 13H, Ar-CH), 4.28 (s, 2H, Cl-CH₂), 3.54 (t, 2H, J = 7.2 Hz, N-CH₂), and 3.01 (t, 2H, J = 7.2 Hz, O-CH₂). ¹³C-NMR (DMSO-d₆): δ (ppm) = 163.76 (HC=N), 160.29, 136.33, 134.50, 133.19, 131.11, 130.43, 129.68, 128.76, 127.77, 123.99, 117.69, and 115.68 (Ar-CH), 70.74 (N-CH₂), 57.88 (O-CH₂), and 41.63 (Cl-CH₂). UV-Vis (λ_max/(nm), * = shoulder peak): 220, 238*, 282 and 381 (C₂H₅OH); 238, 251, 280 and 382 (DMF).

3. **Synthesis of the cationic-charged salen ligands (L₁a-3a)**
The cationic-charged salen ligands \((L_{1a-3a})\) were synthesized as are given procedure: A mixture of triphenylphosphine (1.7 g, 6.5 mmol) in 50 mL toluene, ligand \(L_1\) (2.0 g, 6.5 mmol), ligand \(L_2\) (2.1 g, 6.5 mmol), and ligand \(L_3\) (2.5 g, 6.5 mmol) was added under reflux in a round bottom flask (100 mL) for 24 h in a \(N_2\) atmosphere with continuous stirring. Then, the mixtures were cooled down and subject to filtration at room temperature and the various color solids for each ligand were washed three times with diethyl ether, followed by drying at 60 °C for 12 h in vacuum to give a pure cationic-charged salen ligands \((L_{1a-3a})\).

**Ligand \((L_{1a})\):** Color: yellow, yield (%): 79, M.p.: 210 °C, Elemental Analysis (calculated for C\(_{35}\)H\(_{40}\)ClN\(_2\)OP) (F.W: 571.0 g/mol) (%): C, 73.60; H, 7.06; N, 4.91. Found: C, 73.55; H, 7.01; N, 4.88. LC-MS (Scan ES\(^+\)): m/z = 571.0 [M]\(^+\). FT-IR (ATR, \(\nu_{max}\)-cm\(^{-1}\)): 3470-2368 \(\nu\)(O-H\(\cdot\cdot\cdot\)N), 3059 \(\nu\)(Ar-CH), 2975-2819 \(\nu\)(aliph-CH), 1633 \(\nu\)(C=N), 1586-1437 \(\nu\)(C=C), and 1166 \(\nu\)(C-O). \(^1\)H-NMR (DMSO-d\(_6\)): \(\delta\) (ppm) = 13.03 (s, 1H, O\(\cdot\)H, D-exchangeable), 8.68 (s, 1H, H\(\cdot\)C=N), 7.37-6.82 (m, 18H, Ar-C\(\cdot\)H), 3.94 (s, 2H, Cl-C\(\cdot\)H\(_2\)), 3.48 (s, 1H, N\(\cdot\)H), 2.26 (s, 1H, N\(\cdot\)H), 1.84 (d, 2H, J = 6.8 Hz, CH-C\(\cdot\)H\(_2\)), 1.71 (d, 2H, J = 6.8 Hz, CH-C\(\cdot\)H\(_2\)), 1.44 (s, 6H, C-C\(\cdot\)H\(_3\)) and 1.15 (s, 6H, C-C\(\cdot\)H\(_3\)). \(^{13}\)C-NMR (DMSO-d\(_6\)): \(\delta\) (ppm) = 160.28 (H\(\cdot\)C\(=\)N), 159.66, 137.13, 133.78, 133.58, 131.86, 130.39, 129 43, 129.33, 129.25, 129.18, 128.63, 125.74 and 118.61 (Ar-C\(\cdot\)H), 57.76 (C-C\(\cdot\)H\(_3\)), 57.27 (N-C\(\cdot\)H), 56.40 (CH-C\(\cdot\)H\(_2\)), 42.41 (Cl-C\(\cdot\)H\(_2\)), 30.27 and 25.08 (C-C\(\cdot\)H\(_3\)). \(^{31}\)P-NMR (242.9 MHz, DMSO-d\(_6\)): \(\delta\) (ppm) 25.51. UV-Vis (\(\lambda_{max}\)/(nm), * = shoulder peak): 224, 256, 328 and 415* (C\(_2\)H\(_4\)OH); 241, 270, 324 and 421* (DMF).

**Ligand \((L_{2a})\):** Color: dark brown, yield (%): 76, M.p.: 95 °C, Elemental Analysis (calculated for C\(_{36}\)H\(_{36}\)ClN\(_2\)OP) (F.W: 579.0 g/mol) (%): C, 74.66; H, 6.27; N, 4.84. Found: C, 74.62; H, 6.23; N, 4.80. LC-MS (Scan ES\(^+\)): m/z = 579.0 [M]\(^+\). FT-IR (ATR, \(\nu_{max}\)-cm\(^{-1}\)): 3582-2546 \(\nu\)(O-H\(\cdot\cdot\cdot\)N), 3055 \(\nu\)(Ar-CH), 2967-2872 \(\nu\)(aliph-CH), 1660 \(\nu\)(C=N), 1610-1441 \(\nu\)(C=C), and 1182 \(\nu\)(C-O). \(^1\)H-NMR (DMSO-d\(_6\)): \(\delta\) (ppm) = 13.72 (s, 1H, O\(\cdot\)H, D-exchangeable), 8.65 (s, 1H, H\(\cdot\)C=N), 7.61-6.79 (m, 22H, Ar-C\(\cdot\)H), 4.27 (s, 2H, Cl-C\(\cdot\)H\(_2\)), 3.41-3.53 (q, 4H, N-C\(\cdot\)H\(_2\)), 2.54 (s, 6H, C-C\(\cdot\)H\(_3\)) and 1.15 (s, 6H, C-C\(\cdot\)H\(_3\)).
and 1.08 (t, 6H, J = 7.0 Hz, CH₂-CH₃). ¹³C-NMR (DMSO-d₆): δ (ppm) = 161.10 (HC=N), 161.00, 144.33, 138.71, 132.49, 132.46, 131.96, 131.86, 129.13, 129.25, 129.13, 118.06 and 116.54 (Ar-CH), 59.12 (N-CH₃), 51.92 (Cl-CH₂), and 34.52 (CH₂-CH₃). ³¹P-NMR (242.9 MHz, DMSO-d₆): δ (ppm) 25.58. UV-Vis (λ_max/(nm), * = shoulder peak): 223*, 268, 324* and 403 (C₂H₅OH); 238, 274, 325 and 408 (DMF).

**Ligand (L₃a):** Color: green-yellow, yield (%): 74, M.p.: 120 ºC, Elemental Analysis (calculated for C₄₀H₃₆BClNO₂P) (F.W: 640.0 g/mol) (%): C, 75.07; H, 5.67; N, 2.19. Found: C, 75.03; H, 5.63; N, 2.15. LC-MS (Scan ES⁺): m/z = 640.0 [M]⁺. FT-IR (ATR, υ_max-cm⁻¹): 3547-2419 υ(O-H∙∙∙∙N), 3035 and 3023 υ(Ar-CH), 2981-2875 υ(aliph-CH), 1649 υ(C=N), 1566-1459 υ(C=C), 1184 υ(B-O) and 1180 υ(C-O). ¹H-NMR (DMSO-d₆): δ (ppm) = 13.23 (s, 1H, O-D exchangeable), 8.65 (s, 1H, HC=N), 8.02-6.79 (m, 28H, Ar-CH), 4.27 (s, 2H, Cl-CH₂), 3.55 (t, 2H, J = 7.0 Hz, N-CH₂), and 2.81 (t, 2H, J = 7.0 Hz, O-CH₂). ¹³C-NMR (DMSO-d₆): δ (ppm) = 161.08 (HC=N), 159.13, 136.33, 134.50, 133.19, 131.11, 130.43, 129.79, 129.68, 128.76, 128.65, 128.40, 127.77, 127.24, 124.00, 117.70, and 115.67 (Ar-CH), 70.74 (N-CH₂), 57.88 (O-CH₂), and 41.63 (Cl-CH₂). ³¹P-NMR (242.9 MHz, DMSO-d₆): δ (ppm) 22.66. UV-Vis (λ_max/(nm), * = shoulder peak): 223, 240*, 281 and 380 (C₂H₅OH); 234, 248, 279 and 381 (DMF).

4. **Synthesis of the neutral boron [(L₁₃)BPh₂] complexes**

The new neutral boron [(L₁₃)BPh₂] complexes were synthesized using a procedure similar to that described in the literature [1-3]. Firstly, 30 mL anhydrous toluene put into a three-necked-flask equipped with a nitrogen (N₂) connection. Then, to this solution it was added 0.5 g, 1.62 mmol for ligand (L₁), 0.5 g, 1.58 mmol for ligand (L₂), and 0.5 g, 1.32 mmol for ligand (L₃) in 20 mL anhydrous toluene, which was subsequently stirred for 30 min. at room temperature. The three mixtures was warmed and then triphenyl borane (BPh₃) (0.5 g, 2.09 mmol) was added slowly into each reaction balloon and the mixtures was stirred at reflux.
temperature for 24 h. After cooling to room temperature, the solution was filtrated and the products were washed several times by hexane and diethyl ether, successively. The solid product was purified by re-crystallization in a mixture of CHCl₃/hexane (1:2) and the target compounds were obtained in a good yield.

**[L₁BPh₂]**: Color: yellow, yield (%): 70, M.p.: 210 °C, Elemental Analysis (calculated for C₂₉H₃₄BClN₂O) (F.W: 473.0 g/mol) (%): C, 66.11; H, 8.16; N, 9.07. Found: C, 66.07; H, 8.11; N, 9.02. LC-MS (Scan ES⁻): m/z = 512.0 [M+K]⁺. FT-IR (ATR, v_max/cm⁻¹): 3067 and 3042 v(Ar-CH), 2973-2826 v(aliph-CH), 1602 v(C=O), 1578-1484 v(C=C), 1183 v(B-O), 1179 v(C-O), 1026 v(B-N), and 882 v(B-Ph). ¹H-NMR (DMSO-d₆): δ (ppm) = 8.81 (s, 1H, H_C=N), 7.98-6.49 (m, 13H, Ar-C_H), 3.86 (s, 2H, Cl-C_H₂), 3.56 (s, 1H, N-C_H), 1.98 (s, 1H, NH), 1.62 (d, 4H, J = 6.4 Hz, CH-C_H₂), 1.33 (s, 6H, C-C_H₃) and 0.92 (s, 6H, C-C_H₃). ¹³C-NMR (DMSO-d₆): δ (ppm) = 158.26 (H_C=N), 157.77, 135.61, 134.50, 133.34, 131.11, 130.44, 129.79, 129.69, 129.38, 129.23, 128.77, 128.62, 128.48, 127.78, 127.48, 127.14, 124.00, 119.22, and 115.67 (Ar-C_H), 57.71 (C-C_H₃), 57.13 (N-C_H), 56.62 (CH-C_H₂), 42.33 (Cl-C_H₂), 30.21 and 24.99 (C-C_H₃). ¹¹B NMR (DMSO-d₆, 192.5 MHz, 23 °C, δ ppm): 28.85. UV-Vis (λ_max/(nm), *= shoulder peak): 221, 241*, 281 and 391 (C₂H₅OH); 238, 251, 276 and 384 (DMF).

**[L₂BPh₂]**: Color: dark brown, yield (%): 68, M.p.: 160 °C, Elemental Analysis (calculated for C₃₀H₃₀BClN₂O) (F.W: 481.0 g/mol) (%): C, 74.94; H, 6.29; N, 5.83. Found: C, 74.90; H, 6.24; N, 5.80. LC-MS (Scan ES⁻): m/z = 482.0 [M+H]⁺. FT-IR (ATR, v_max/cm⁻¹): 3070 and 3048 v(Ar-CH), 2976-2856 v(aliph-CH), 1611 v(C=N), 1568-1467 v(C=C), 1192 v(B-O), 1181 v(C-O), 1021 v(B-N), and 883 v(B-Ph). ¹H-NMR (DMSO-d₆): δ (ppm) = 8.92 (s, 1H, H_C=N), 7.74-6.54 (m, 17H, Ar-CH), 4.21 (s, 2H, Cl-C_H₂), 3.04 (q, 2H, N-C_H₂), and 0.96 (s, 6H, CH₂-C_H₃). ¹³C-NMR (DMSO-d₆): δ (ppm) = 162.05 (H_C=N), 159.62, 142.10, 139.85, 134.94, 134.47, 130.67, 130.51, 128.48, 121.38, 117.081, 115.91 and 113.28 (Ar-C_H), 53.68 (N-C_H₂), 48.81 (Cl-C_H₂), and 10.49 (CH₂-C_H₃). ¹¹B NMR (DMSO-d₆, 192.5 MHz, 23 °C, δ
ppm): 28.76. UV-Vis ($\lambda_{\text{max}}$/nm), * = shoulder peak): 218, 261, 378 and 397 (C$_2$H$_5$OH); 236, 269, 330* and 414 (DMF).

$[L_3BPh_2]$: Color: brown, yield (%): 72, M.p.: 96 °C, Elemental Analysis (calculated for C$_{34}$H$_{30}$B$_2$ClNO$_2$) (F.W: 542.0 g/mol) (%): C, 75.39; H, 5.58; N, 2.59. Found: C, 75.35; H, 5.53; N, 2.55. LC-MS (Scan ES$^+$): m/z = 565.0 [M+Na]$^+$. FT-IR (ATR, $\nu_{\text{max}}$ cm$^{-1}$): 3067 and 3041 $\nu$(Ar-CH), 2971-2882 $\nu$(aliph-CH), 1624 $\nu$(C=N), 1597-1486 $\nu$(C=C), 1183 and 1168 $\nu$(B-O), 1175 $\nu$(C-O), 1027 $\nu$(B-N), and 883 $\nu$(B-Ph). $^1$H-NMR (DMSO-d$_6$): $\delta$ (ppm) = 8.63 (s, 1H, HC=N), 7.98-6.80 (m, 23H, Ar-CH$_2$), 4.28 (s, 2H, Cl-CH$_2$)$_2$, 3.54 (t, 2H, J = 7.0 Hz, N-CH$_2$), and 3.00 (t, 2H, J = 7.2 Hz, O-CH$_2$). $^{13}$C-NMR (DMSO-d$_6$): $\delta$ (ppm) = 161.08 (HC=N), 158.03, 136.35, 134.49, 133.23, 131.11, 130.43, 129.79, 129.68, 129.37, 128.76, 128.65, 128.50, 127.77, 127.24, 124.00, 119.86, 117.66, and 115.66 (Ar-CH), 65.73 (N-CH$_2$), 57.87 (O-CH$_2$), and 41.62 (Cl-CH$_2$). $^{11}$B NMR (DMSO-d$_6$, 192.5 MHz, 23 °C, $\delta$ ppm): 29.29 and 20.01. UV-Vis ($\lambda_{\text{max}}$/nm), * = shoulder peak): 221, 242*, 284 and 383 (C$_2$H$_5$OH); 236, 253, 276 and 377 (DMF).

5. Synthesis of the cationic charged boron [(L$_{1a-3a}$)BPh$_2$] complexes

The new cationic charged boron [(L$_{1a-3a}$)BPh$_2$] complexes were synthesized using a procedure similar to that described in the literature [1-3]. Firstly, 25 mL anhydrous toluene put into a three-necked-flask equipped with a nitrogen (N$_2$) connection. Then, to this solution it was added 0.3 g, 0.63 mmol for [L$_1$BPh$_2$] complex, 0.3 g, 0.62 mmol for [L$_2$BPh$_2$] complex, and 0.3 g, 0.55 mmol for [L$_3$BPh$_2$] complex in 25 mL anhydrous toluene, which was subsequently stirred for 50 min. at room temperature. Three mixtures was warmed and then triphenyl borane (BPh$_3$) (0.2 g, 0.84 mmol) was added slowly into each reaction balloon and the mixtures was stirred at reflux temperature for 24 h. After cooling to room temperature, the solution was filtrated and the products were washed several times by hexane and diethyl ether, successively.
The solid product was purified by re-crystallization in a mixture of CH$_2$Cl$_2$/hexane (1:2) and the pure compounds were obtained in a good yield.

$[L_{1a}BPh_2]$: Color: yellow, yield (%): 65, M.p.: 245 °C, Elemental Analysis (calculated for C$_{47}$H$_{49}$BCl$_2$N$_2$O (F.W: 735.0 g/mol) (%): C, 76.79; H, 6.72; N, 3.81. Found: C, 76.75; H, 6.68; N, 3.78. LC-MS (Scan ES$^+$): m/z = 758.0 [M+Na]$^+$. FT-IR (ATR, $\nu_{max}$-cm$^{-1}$): 3069 $\nu$(Ar-CH), 2990-2885 $\nu$(aliph-CH), 1628 $\nu$(C=N), 1586-1485 $\nu$(C=C), 1185 $\nu$(B-O), 1028 $\nu$(B-N), and 881 $\nu$(B-Ph). $^1$H-NMR (DMSO-d$_6$): $\delta$ (ppm) = 8.81 (s, 1H, H_C=N), 7.98-7.12 (m, 28H, Ar-C$_H$), 4.06 (s, 2H, Cl-C$_H$$_2$), 3.42 (s, 1H, N-C$_H$), 1.64 (d, 2H, $J = 6.4$ Hz, CH-CH$_2$), 1.45 (d, 2H, $J = 6.4$ Hz, CH-CH$_3$), 1.34 (s, 1H, N_H), 1.01 (s, 6H, C-C$_H$$_3$) and 0.92 (s, 6H, C-C$_H$$_3$). $^{13}$C-NMR (DMSO-d$_6$): $\delta$ (ppm) = 159.87 (H_C=C=N), 159.38, 142.86, 138.52, 134.50, 133.68, 132.65, 132.48, 131.98, 131.88, 131.11, 130.44, 129.79, 129.69, 129.27, 129.15, 128.77, 128.65, 127.78, 123.99, 119.22 and 115.67 (Ar-CH), 57.83 (C-C$_H$$_3$), 56.65 (N-C$_H$), 56.55 (CH-CH$_2$), 41.82 (Cl-C$_H$$_2$), 30.21 and 24.98 (C-C$_H$$_3$). $^{31}$P-NMR (242.9 MHz, DMSO-d$_6$): $\delta$ (ppm) 25.51. $^{31}$P-NMR (242.9 MHz, DMSO-d$_6$): $\delta$ (ppm) 25.53. $^{11}$B NMR (DMSO-d$_6$, 192.5 MHz, 23 °C, $\delta$ ppm): 28.85. UV-Vis ($\lambda_{max}$/nm, * = shoulder peak): 221, 245*, 286 and 392 (C$_2$H$_5$OH); 242, 265, 284 and 386 (DMF).

$[L_{2a}BPh_2]$: Color: light brown, yield (%): 66, M.p.: 90 °C, Elemental Analysis (calculated for C$_{48}$H$_{45}$BCl$_2$N$_2$O (F.W: 743.0 g/mol) (%): C, 77.58; H, 6.10; N, 3.77. Found: C, 77.54; H, 6.06; N, 3.71. LC-MS (Scan ES$^+$): m/z = 766.0 [M+Na]$^+$. FT-IR (ATR, $\nu_{max}$-cm$^{-1}$): 3051 $\nu$(Ar-CH), 2965-2866 $\nu$(aliph-CH), 1615 $\nu$(C=N), 1556-1442 $\nu$(C=C), 1191 $\nu$(B-O), 1180 $\nu$(C-O), 1024 $\nu$(B-N), and 883 $\nu$(B-Ph). $^1$H-NMR (DMSO-d$_6$): $\delta$ (ppm) = 8.64 (s, 1H, H_C=N), 7.98-7.07 (m, 32H, Ar-C$_H$), 4.82 (s, 2H, Cl-C$_H$$_2$), 2.91-2.82 (q, 4H, N-C$_H$$_2$), and 1.03 (t, 6H, $J = 9.2$ Hz, CH$_2$-CH$_3$). $^{13}$C-NMR (DMSO-d$_6$): $\delta$ (ppm) = 161.23 (H_C=C=N), 159.83, 141.73, 138.80, 134.95, 134.47, 132.61, 131.96, 131.86, 130.51, 128.93, 129.31, 129.19, 127.83, 122.59, 118.79, 118.25 and 116.24 (Ar-CH), 59.38 (N-C$_H$$_2$), 51.90 (Cl-C$_H$$_2$), and 11.53 (CH$_2$-
$^{31}$P-NMR (242.9 MHz, DMSO-d$_6$): $\delta$ (ppm) 26.30. $^{11}$B NMR (DMSO-d$_6$, 192.5 MHz, 23 oC, $\delta$ ppm): 28.61. UV-Vis ($\lambda_{\text{max}}$/nm), * = shoulder peak): 224*, 265 and 408 (C$_2$H$_5$OH); 241, 269 and 406 (DMF).

$[L_{3a}BPh_2]$: Color: dirty white, yield (%): 68, M.p.: 105 °C, Elemental Analysis (calculated for C$_{52}$H$_{45}$B$_2$ClNO$_2$P) (F.W: 804.0 g/mol) (%): C, 77.68; H, 5.64; N, 1.74. Found: C, 77.64; H, 5.59; N, 1.70. LC-MS (Scan ES$^+$): m/z = 844.0 [M+K+H]$^+$. FT-IR (ATR, $\nu_{\text{max}}$/cm$^{-1}$): 3023 $\nu$(Ar-CH), 2963-2836 $\nu$(aliph-CH), 1635 $\nu$(C=N), 1580-1473 $\nu$(C=C), 1186 and 1163 $\nu$(B-O), 1177 $\nu$(C-O), 1031 $\nu$(B-N), and 882 $\nu$(B-Ph). $^1$H-NMR (DMSO-d$_6$): $\delta$ (ppm) = 8.63 (s, 1H, $\text{HC}=$N), 7.98-6.80 (m, 38H, Ar-$\text{CH}$), 4.28 (s, 2H, Cl-$\text{CH}_2$), 3.56 (t, 2H, N-$\text{CH}_2$), and 3.00 (s, 2H, O-$\text{CH}_2$). $^{13}$C-NMR (DMSO-d$_6$): $\delta$ (ppm) = 161.16 (HC$=$N), 159.18, 144.35, 136.28, 134.50, 134.42, 130.63, 130.51, 130.43, 129.99, 128.65, 127.77, 123.99, 118.46, 116.87, and 112.76, (Ar-$\text{CH}$), 57.89 (N-$\text{CH}_2$), 51.06 (O-$\text{CH}_2$), and 41.64 (Cl-$\text{CH}_2$). $^{31}$P-NMR (242.9 MHz, DMSO-d$_6$): $\delta$ (ppm) 22.61. $^{11}$B NMR (DMSO-d$_6$, 192.5 MHz, 23 oC, $\delta$ ppm): 29.06 and 19.58. UV-Vis ($\lambda_{\text{max}}$/nm), * = shoulder peak): 219, 243*, 278 and 376 (C$_2$H$_5$OH); 236, 250, 276 and 374 (DMF).

References


Figure S1. FT-IR spectra of Ligand (L₃)

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Figure S4. FT-IR spectra of $[L_2aBPh_2]$ complex
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Figure S32. LC-MS spectra of ligand (L_{3a})
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Figure S36. LC-MS spectra of the complex $[L_{2a}BPh_2]$. 
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Figure S38. TG-DTA spectra of ligand (L₁)
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Figure S40. TG-DTA spectra of ligand (L_{4a})
Figure S41. TG-DTA spectra of the complex $[L_2BPh_2]$.

Figure S42. TG-DTA spectra of the complex $[L_3BPh_2]$. 