

Rare-Earth-Mediated Catalytic-Like Conversion of P₄ into Organic P₁ and norbornane-P₇ Compounds**

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Table of Contents

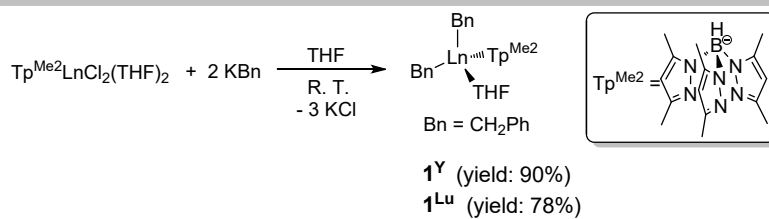
Table of Contents.....	1
Experimental Procedures.....	1
2. Synthesis and characterization of Complexes 1-3 and I, II	2
3. X-ray Crystallographic Analysis of Complexes 2, 3 , and I	6
4. References	23

Experimental Procedures

All manipulations involving air- and moisture-sensitive compounds were carried out with rigorous exclusion of air and water, using standard Schlenk techniques or a Vigor glovebox under an atmosphere of dinitrogen. THF, toluene and hexane were purified using an Mbraun SPS-800 Solvent Purification System, dried over fresh Na chips and stored in the glovebox in the glovebox. C₆D₆ and THF-*d*₈ were obtained from Cambridge Isotope and dried over Na/K alloy prior to use. (Tp^{Me2})YBn₂(THF) and KBn were prepared according to literature procedure^[1,2]. (CH₃)₃SiCl, CH₃OH, ¹Pr₂NH, and HPPH₂ were purchased from J&K and dried with 4Å sieves. Other commercially available reagents were purchased and used without purification. P₄ was prepared by sublimation of red phosphorus at 450 °C in quartz tube under vacuum condition and stored in the refrigerator of the glovebox. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. ¹H NMR, ¹³C NMR and ³¹P NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer (FT, 400 MHz for ¹H; 100 MHz for ¹³C; 161 MHz for ³¹P) at room temperature. Chemical shifts for ¹H and ¹³C NMR were quoted in ppm referenced to the residual resonance of the deuterated solvents. H₃PO₄ (85%) sealed in a capillary was used as an external standard in the ³¹P NMR analysis. Elemental analyses for C, H and N were carried out on a Vario EL III elemental analyzer. *The resonances of B-H bond in the Tp^{Me2} ligand are too broad to be observed in their ¹H NMR spectra.* **Caution:** P₄ is light-sensitive and highly flammable upon exposure to air. It should be handled carefully.

2. Synthesis and characterization of complexes 1-3 and compound I and II.

2.1 Synthesis and characterization of (Tp^{Me2})LnBn₂(THF)₂ (1^{Ln}).



1^Y: The known complexes.^[1]

1^{Lu}: The 20 mL THF solution of KBn (2.600 g, 20.00 mmol) was added slowly to a 30 mL THF solution of Tp^{Me}₂LuCl₂(THF) (3.576 g, 10 mmol). After stirring for 24 h, the thick, pale-red solution was evaporated to dryness under vacuum and toluene (30 mL) was added to the residue. After stirring for 30 min, the mixture was filtered through celite and the filtrate was concentrated to about 10 mL and then layered with n-hexane to afford compound **1^{Lu}** as colorless powder. Yield: 5.665 g (78%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) 1.07 (s, 4H, THF), 2.06 (s, 6H, CH₃-Tp^{Me}₂), 2.10 (s, 6H, CH₃-Tp^{Me}₂), 2.21 (s, 3H, CH₃-Tp^{Me}₂), 2.30 (s, 3H, CH₃-Tp^{Me}₂), 2.44 (s, 4H, CH₂Ph), 3.47 (s, 4H, THF), 5.45 (s, 1H, 4-H-Tp^{Me}₂), 5.55 (s, 2H, 4-H-Tp^{Me}₂), 6.77-6.81 (m, 2H, CH₂Ph), 7.15-7.23 (m, 8H, CH₂Ph); ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) 13.0 (CH₃-Tp^{Me}₂), 14.4 (CH₃-Tp^{Me}₂), 25.1 (THF), 60.4 (CH₂Bn), 71.4 (THF), 106.4 (4-C-Tp^{Me}₂), 117.7 (CH₂Ph), 125.2 (CH₂Ph), 128.3 (CH₂Ph), 145.4 (Tp^{Me}₂), 155.5 (Tp^{Me}₂). Elemental Analysis Calcd for C₃₃H₄₄BN₆OLu (726.31): C, 54.56; H, 6.10; N, 11.57. Found: C, 54.42; H, 6.17; N, 11.48.

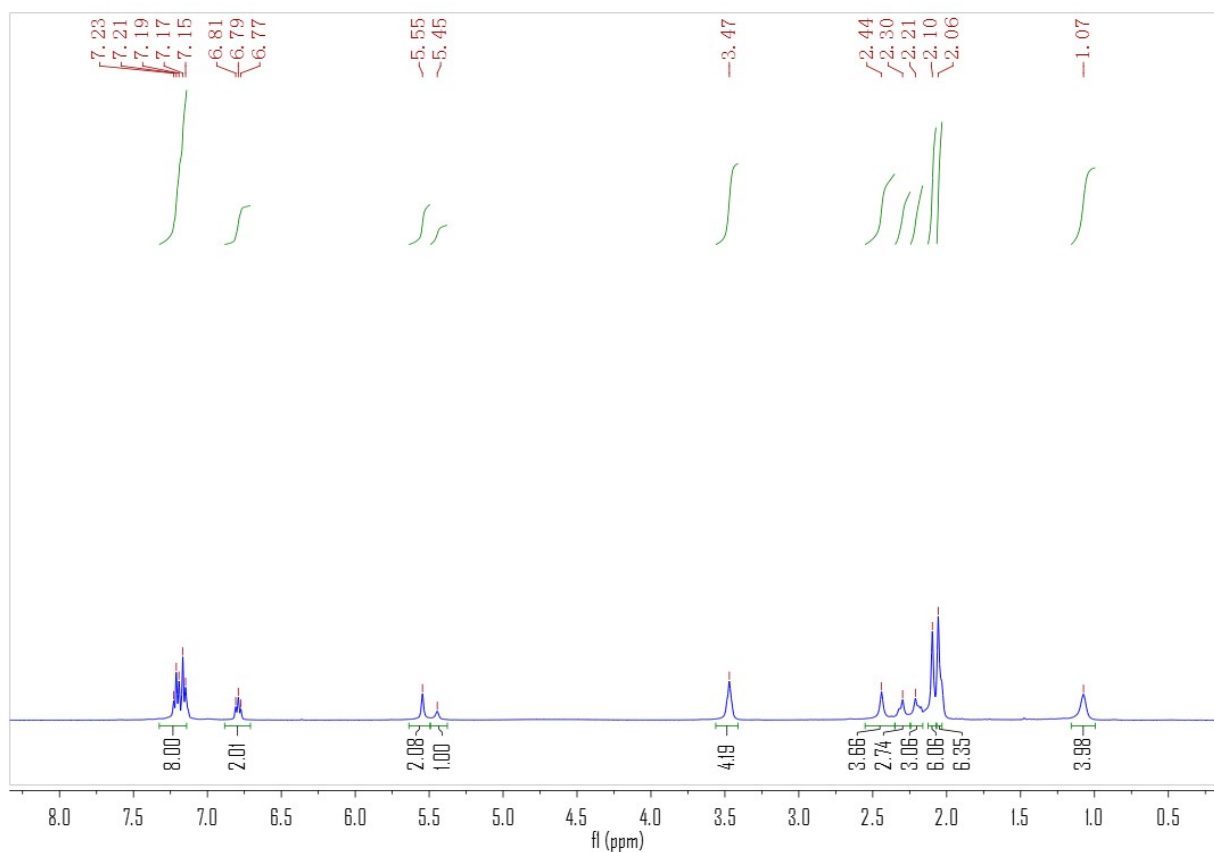


Figure S1. ¹H NMR spectrum of complex **1^{Lu}** in C₆D₆ at room temperature.

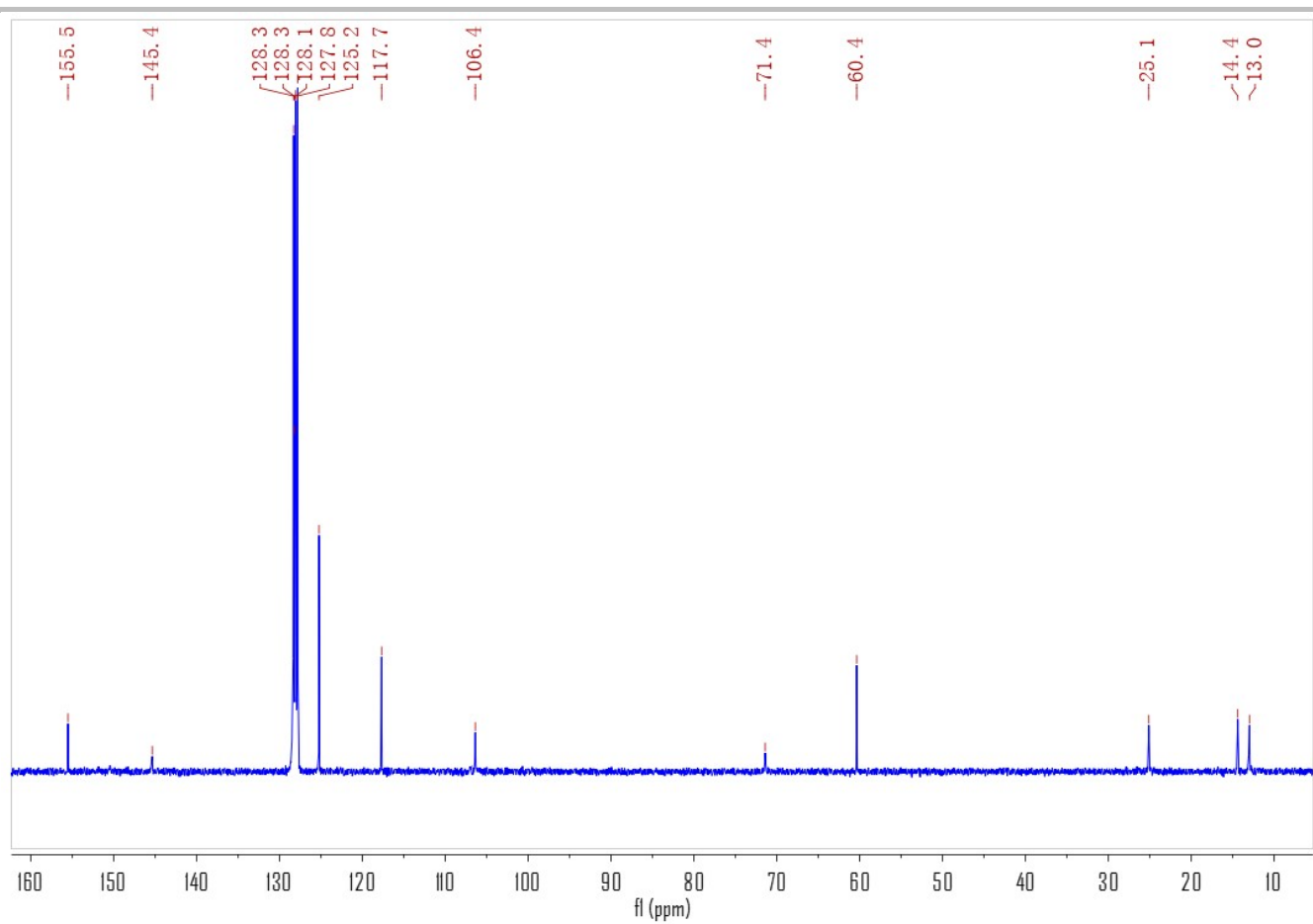
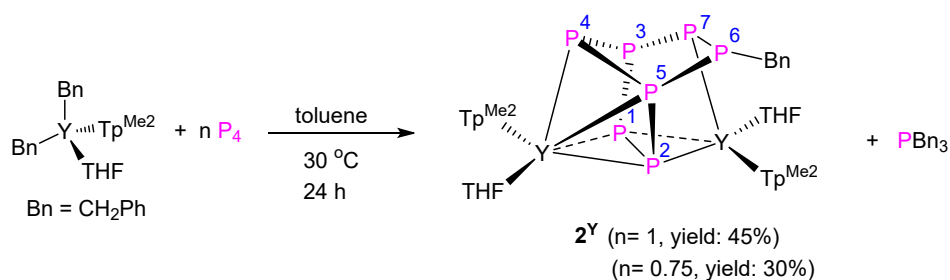


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex 1^{Lu} in C_6D_6 at room temperature.

2.2 Synthesis and characterization of $(\text{Tp}^{\text{Me}_2})_2\text{Y}_2\text{P}_7\text{Bn}(\text{THF})_2$ (2^{Y}).



P_4 (124.2 mg, 1 mmol) was added to a stirred toluene solution (2 mL) of $\text{Tp}^{\text{Me}_2}\text{YBn}_2(\text{THF})$ (640.5 mg, 1 mmol) at ambient temperature. Then the reaction mixture was taken out from the glovebox and stirring at 30 °C. The reaction mixture gradually changed from light yellow to reddish brown. Accompanied by stirring, a pale solid began to precipitate out. Keeping stirring for 24 h, the precipitation was filtered under reduced pressure and washed by 2 mL toluene and dried under vacuum to give 2^{Y} as a pale-yellow powder (275.5 mg, 45% yield based on Y). Yellow crystals of 2^{Y} suitable for X-ray single crystal diffraction analysis were obtained by gas phase diffusion of t-BuOMe into the THF solution (ca 2 mL) of 2^{Y} . ^1H NMR (400 MHz, $\text{THF-}d_6$, 25 °C): δ (ppm) 1.77 (m, 4H, $\text{O}(\text{CH}_2\text{CH}_2)_2$), 1.83 (brs, 1H, CH_2Ph), 2.35 (s, 9H, $\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 2.36 (s, 9H, $\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 2.52 (s, 1H, CH_2Ph), 2.67 (s, 9H, $\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 2.70 (s, 9H, $\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 3.62 (m, 4H, $\text{O}(\text{CH}_2\text{CH}_2)_2$), 5.69 (s, 3H, 4- $H\text{-Tp}^{\text{Me}_2}$), 5.73 (s, 3H, 4- $H\text{-Tp}^{\text{Me}_2}$), 6.93-6.96 (m, 1H, CH_2Ph), 7.04-7.10 (m, 4H, CH_2Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{THF-}d_6$, 25 °C): δ (ppm) 13.0 ($\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 13.0 ($\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 16.5 ($\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 18.5 ($\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 26.2 (THF), 46.5 (d, $^1J_{\text{PC}} = 45.73$ Hz, CH_2Ph), 68.0 (THF), 106.7 (4- $\text{C-Tp}^{\text{Me}_2}$), 124.8 (CH_2Ph), 127.8 (CH_2Ph), 130.1 (CH_2Ph), 140.5 (CH_2Ph), 145.0 (Tp^{Me_2}), 145.5 (Tp^{Me_2}), 151.5 (Tp^{Me_2}), 151.5 (Tp^{Me_2}); ^{31}P NMR (160 MHz, $\text{THF-}d_6$, 25 °C): δ (ppm) -117.3 (t, 1P, $^1J_{\text{PP}} = 280.59$ Hz,), -90.4 (t, 1P, $^1J_{\text{PP}} = 249.82$ Hz), -36.6 (t, 1P, $^1J_{\text{PP}} = 333.56$ Hz), -10.8 (t, 1P, $^1J_{\text{PP}} = 243.66$ Hz), 45.3 (t, 1P, $^1J_{\text{PP}} = 329.35$ Hz), 68.5 (q, 1P, $^1J_{\text{PP}} = 299.16$ Hz), 77.3 (q, 1P, $^1J_{\text{PP}} = 334.43$ Hz). Elemental Analysis Calcd for $\text{C}_{45}\text{H}_{67}\text{B}_2\text{N}_{12}\text{O}_2\text{P}_7\text{Y}_2$ (1224.34): C, 44.14; H, 5.52; N, 13.73. Found: C, 44.22; H, 5.54; N, 13.64.

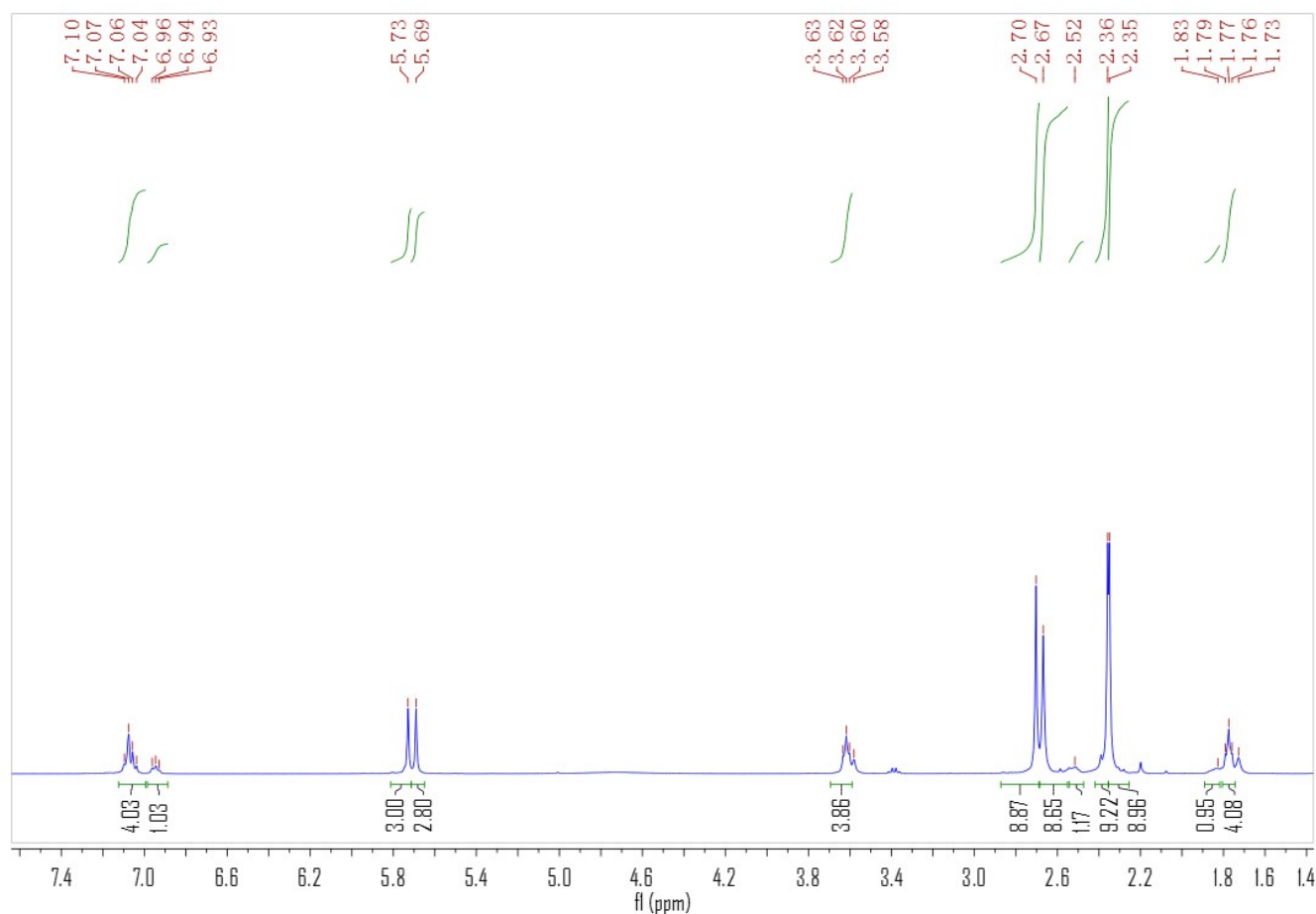


Figure S3. ^1H NMR spectrum of complex 2^{Y} in $\text{THF-}d_6$ at room temperature.

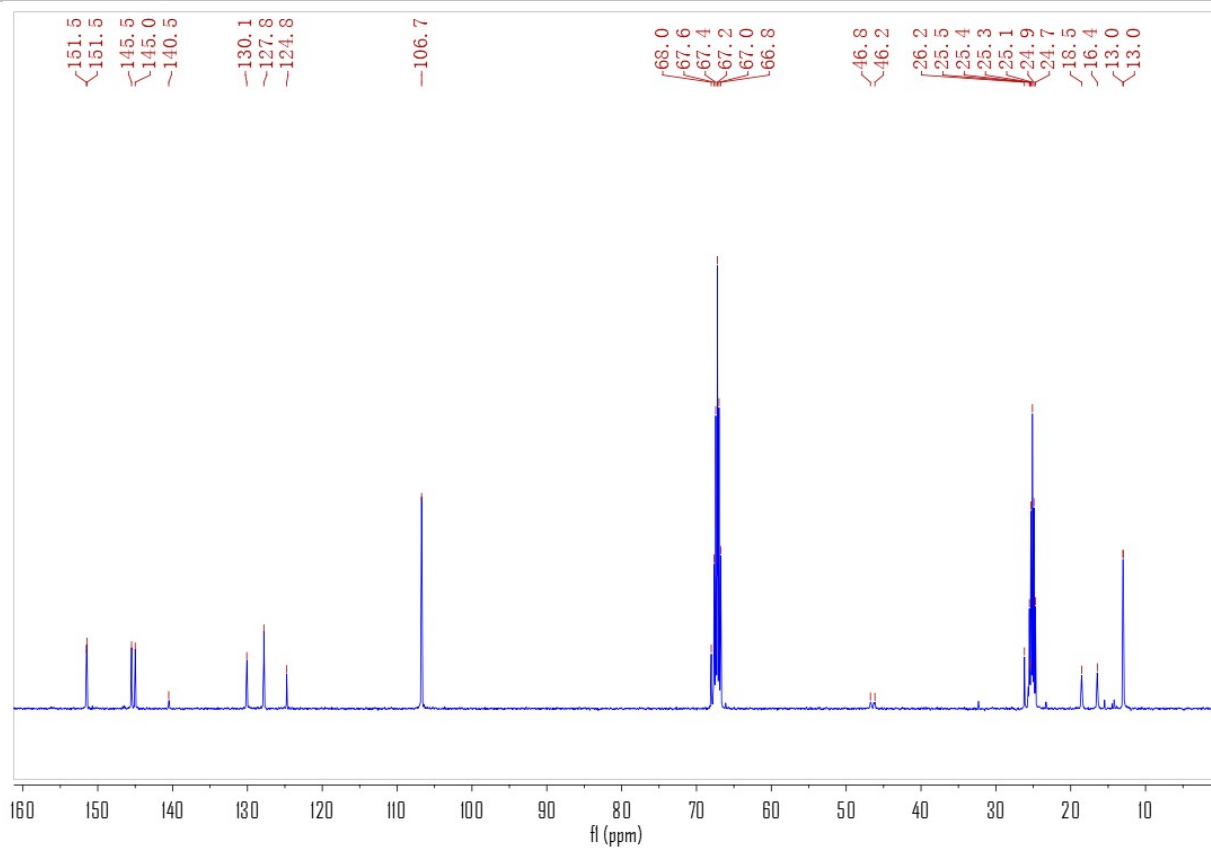


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **2Y** in $\text{THF-}d_8$ at room temperature.

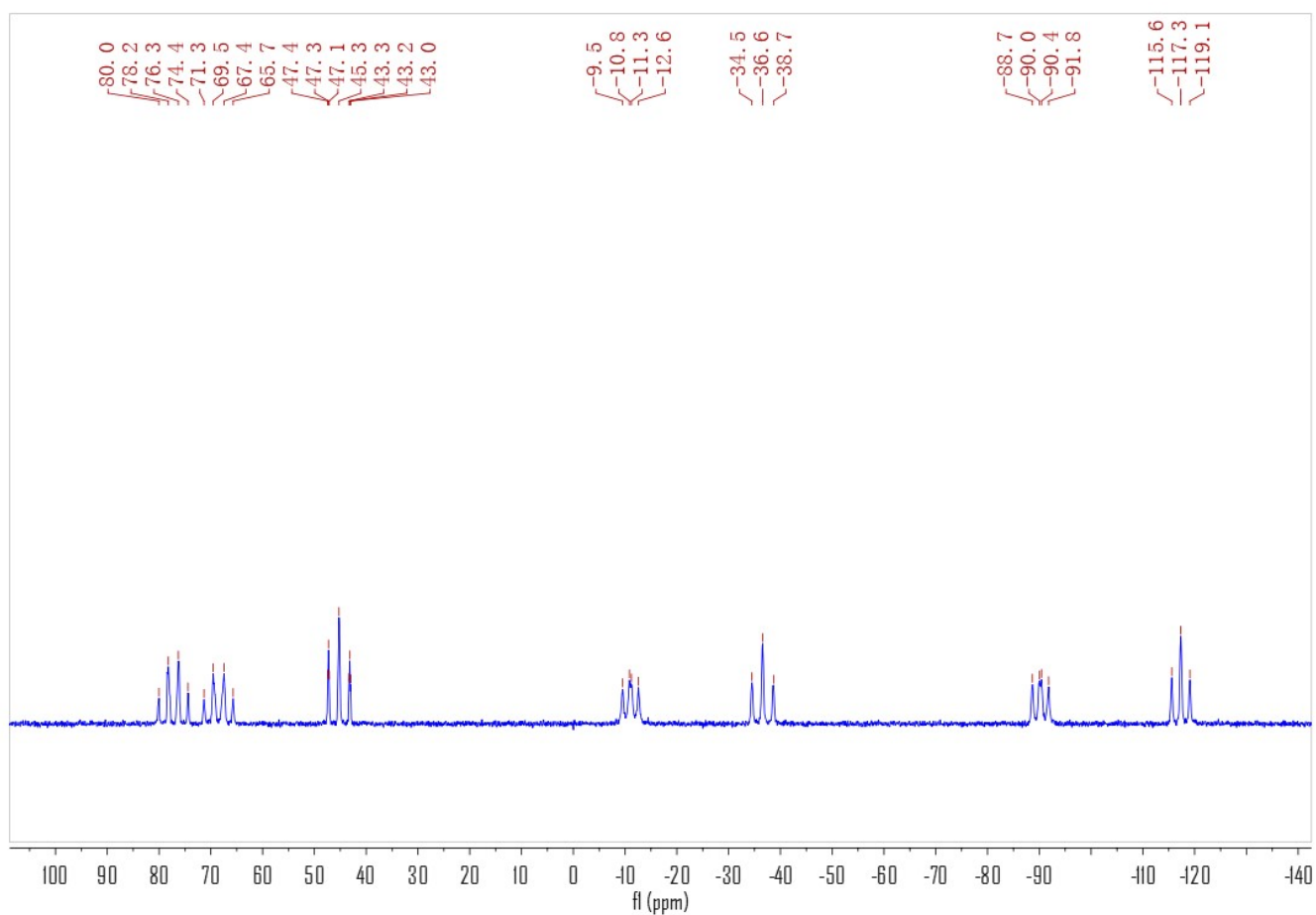


Figure S5. ^{31}P NMR spectrum of complex **2Y** in $\text{THF-}d_8$ at room temperature

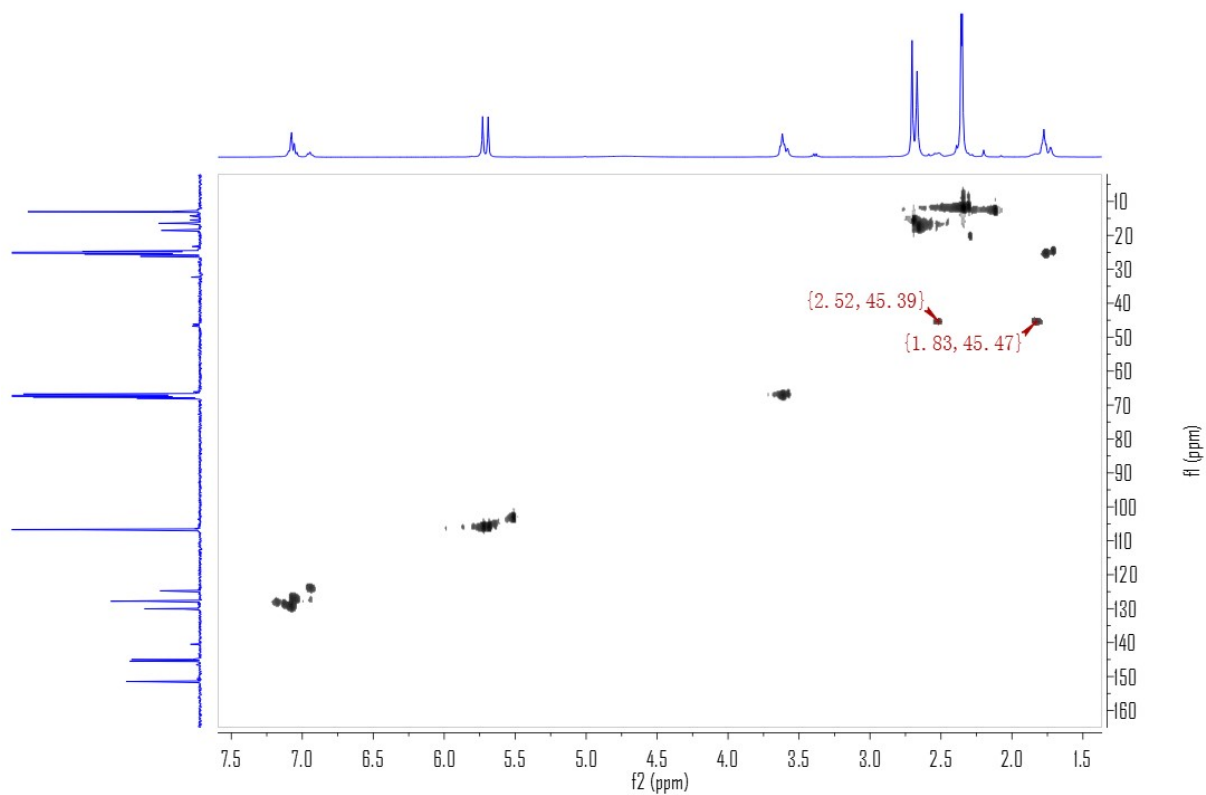


Figure S6. HSQC spectrum of complex **2Y** in THF- d_8 at room temperature.

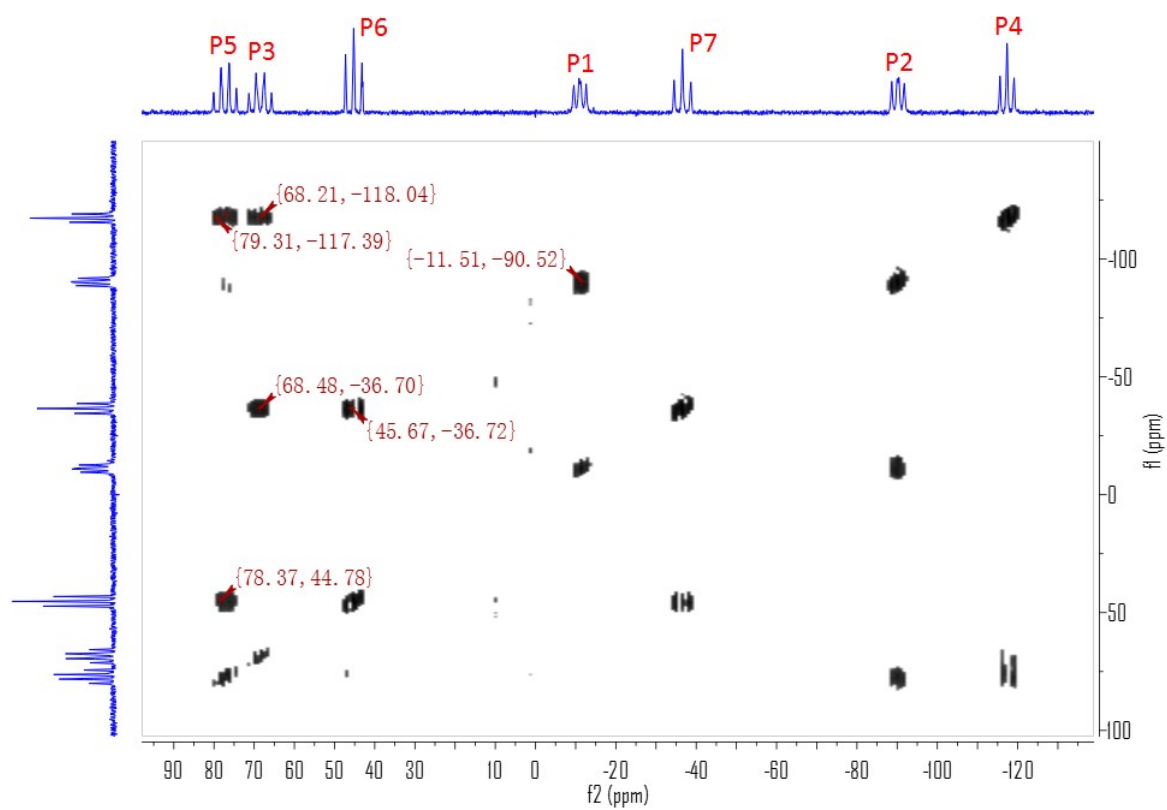
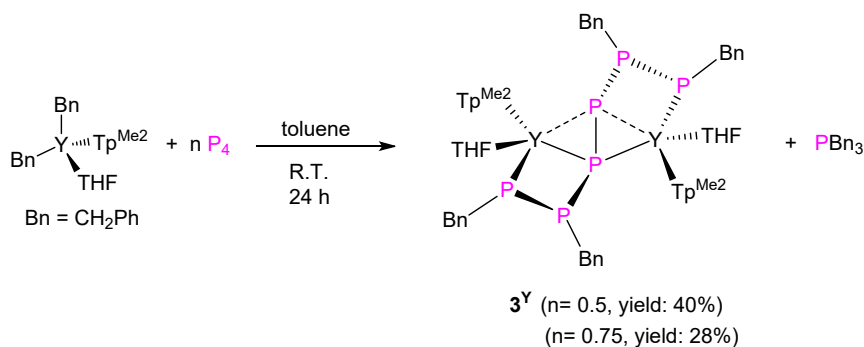


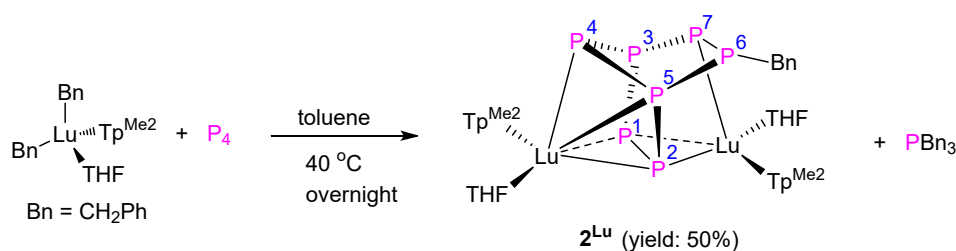
Figure S7. $^{31}\text{P}\{^1\text{H}\}$ COSY spectrum of complex **2Y** in THF- d_8 at room temperature.

2.3 Synthesis and characterization of $(\text{Tp}^{\text{Me}_2})_2\text{Y}_2\text{P}_6(\text{THF})_2$ (3^{Y}).



3^{Y} : P_4 (62.2 mg, 0.5 mmol) was added to a stirred toluene solution (2 mL) of $\text{Tp}^{\text{Me}_2}\text{YBn}_2(\text{THF})$ (640.5 mg, 1 mmol) at ambient temperature. Then the reaction mixture was taken out from the glovebox and stirring at 30 °C. The colour of mixture gradually changed from light yellow to reddish brown. After stirring 24 h, the reddish-brown solution was concentrated close to ca 2 mL under reduced pressure and yellow crystals of 3^{Y} (292.1 mg, 40% yield, based on Y) suitable for X-ray single crystal diffraction analysis were obtained by slow solvent evaporation method from the above-mentioned toluene solution. It is noted that yellow crystals of 3^{Y} were almost undissolved in toluene, and tended to degradation and aggradation once redissolved in THF solvent, prevented its characterization by NMR spectroscopy. Elemental Analysis Calcd for $\text{C}_{66}\text{H}_{82}\text{B}_2\text{N}_{12}\text{O}_2\text{P}_6\text{Y}_2$ (1460.71): C, 54.27; H, 5.66; N, 11.51. Found: C, 54.32; H, 5.73; N, 11.43.

2.4 Synthesis and characterization of $(\text{Tp}^{\text{Me}_2})_2\text{Lu}_2\text{P}_7\text{Bn}(\text{THF})$ (2^{Lu}) and compound I.



P_4 (124.3 mg, 1 mmol) was added to a stirred toluene solution (2 mL) of $\text{Tp}^{\text{Me}_2}\text{LuBn}_2(\text{THF})$ (726.2 mg, 1 mmol) at ambient temperature. Then the reaction mixture was taken out from the glovebox and stirring at 40 °C. The color of mixture gradually changed from milk white to orange. Accompanied by stirring, a yellow solid began to precipitate out. Keeping stirring for 2 days, all the volatiles were removed under vacuum. The residue was extracted by *n*-hexane two times (10 mL \times 2) and dried under vacuum to give orange powder 2^{Lu} . Concentration of the extraction afforded colorless crystals of PBN_3 (**I**) (120.2 mg, 79%). ^1H NMR (400 MHz, C_6D_6 , 25 °C): δ (ppm) 7.12-7.09 (m, 6H, *Ph*), 7.04-7.00 (m, 9H, *Ph*), 2.58 (s, 6H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 25 °C): δ (ppm) 138.32 (d, $^2J_{\text{PC}} = 5.94$ Hz, *Ph*), 129.62 (d, $^3J_{\text{PC}} = 5.78$ Hz, *Ph*), 128.67 (*Ph*), 126.09 (d, $^5J_{\text{PC}} = 2.09$ Hz, *Ph*), 34.79 (d, $^1J_{\text{PC}} = 20.57$ Hz, CH_2); ^{31}P NMR (161 MHz, C_6D_6 , 25 °C): δ (ppm) -12.38; HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{22}\text{P}^+$ 305.1496, found 305.1474. The molecular structure of compound **I** was confirmed by X-ray single crystal diffraction analysis.^[3] Yellow crystals of 2^{Lu} (**a**) and 2^{Lu} (**b**) (617.1 mg, 88% yield) suitable for X-ray single crystal diffraction analysis were obtained respectively by gas phase diffusion of Et_2O or *t*-BuOCH₃ into the THF solution (ca 2 mL) of 2^{Lu} . ^1H NMR (400 MHz, THF-*d*₈, 25 °C): δ (ppm) 1.76-1.79 (m, 4H, $\text{O}(\text{CH}_2\text{CH}_2)_2$), 1.81 (brs, 1H, CH_2Ph), 2.35 (s, 9H, $\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 2.36 (s, 9H, $\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 2.40 (m, 1H, CH_2Ph), 2.73 (s, 9H, $\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 2.77 (s, 9H, $\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 3.62 (m, 4H, $\text{O}(\text{CH}_2\text{CH}_2)_2$), 5.72 (s, 3H, 4-*H*- Tp^{Me_2}), 5.75 (s, 3H, 4-*H*- Tp^{Me_2}), 6.90-6.94 (m, 1H, CH_2Ph), 7.02-7.07 (m, 4H, CH_2Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, THF-*d*₈, 25 °C): δ (ppm) 13.0 ($\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 13.0 ($\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 16.8 ($\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 18.9 ($\text{CH}_3\text{-Tp}^{\text{Me}_2}$), 25.5 (THF), 46.8 (d, $^1J_{\text{PC}} = 44.32$ Hz, CH_2Ph), 68.0 (THF), 107.0 (4-*C*- Tp^{Me_2}), 107.1 (4-*C*- Tp^{Me_2}), 124.5 (CH_2Ph), 127.7 (CH_2Ph), 130.2 (CH_2Ph), 141.1 (CH_2Ph), 145.0 (Tp^{Me_2}), 145.3 (Tp^{Me_2}), 152.0 (Tp^{Me_2}), 152.2 (Tp^{Me_2}); ^{31}P NMR (160 MHz, THF-*d*₈, 25 °C): δ (ppm) -118.8 (dd, 1P, $J_{\text{PP}} = 284.63$ Hz, 188.42 Hz, P2), -100.0 (t, 1P, $^1J_{\text{PP}} = 277.34$ Hz, P4), -48.8 (t, 1P, $^1J_{\text{PP}} = 323.42$ Hz, P7), -15.3 (dd, 1P, $J_{\text{PP}} = 271.44$ Hz, 187.67 Hz, P1), 58.8 (two sets of overlapping multiple peaks, 2P, P3+P6), 68.6 (q, 1P, $^1J_{\text{PP}} = 292.86$ Hz, P5). Elemental Analysis Calcd for $\text{C}_{45}\text{H}_{67}\text{B}_2\text{N}_{12}\text{O}_2\text{P}_7\text{Lu}_2$ (1396.46): C, 38.70; H, 4.84; N, 12.04. Found: C, 38.56; H, 4.88; N, 11.97.

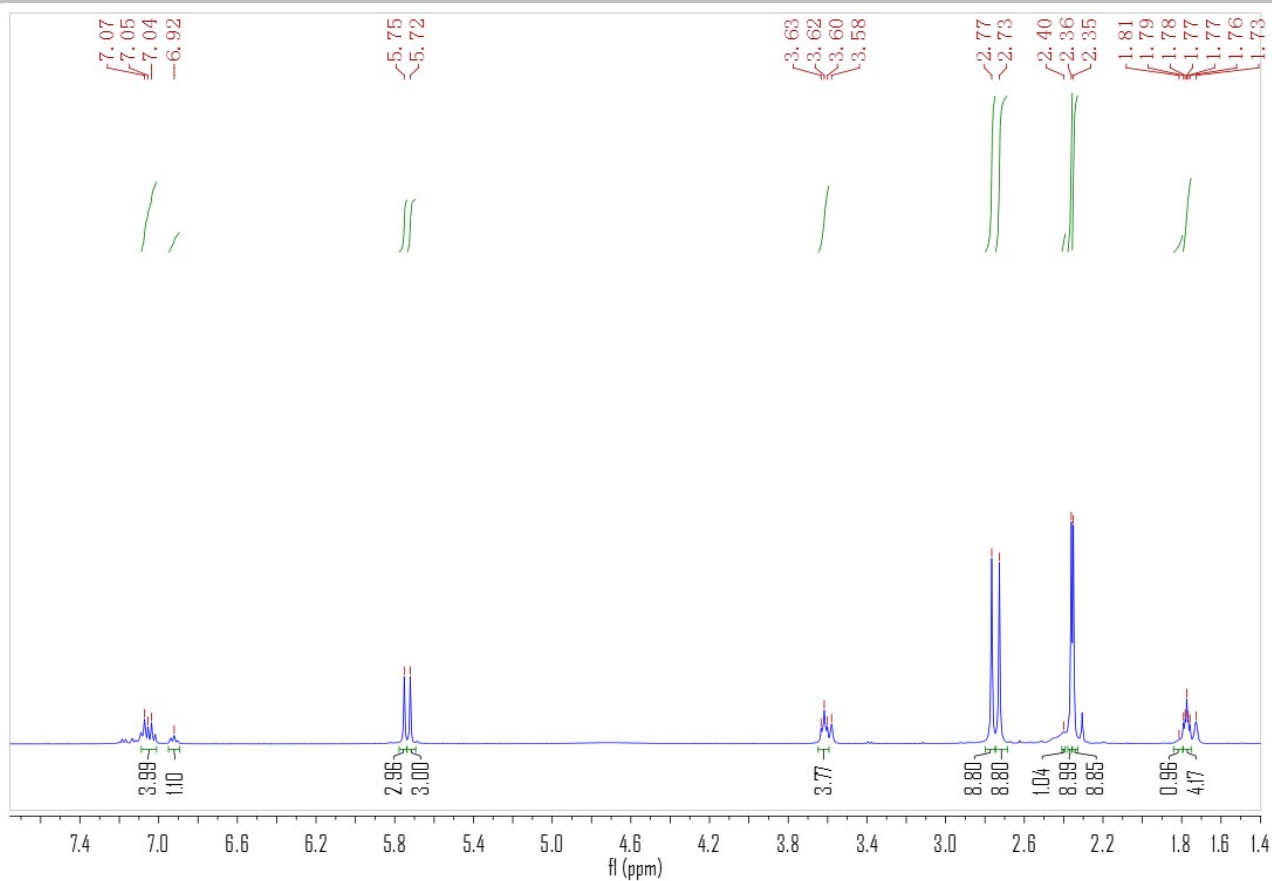


Figure S8. ^1H NMR spectrum of complex 2^{Lu} in $\text{THF-}d_8$ at room temperature.

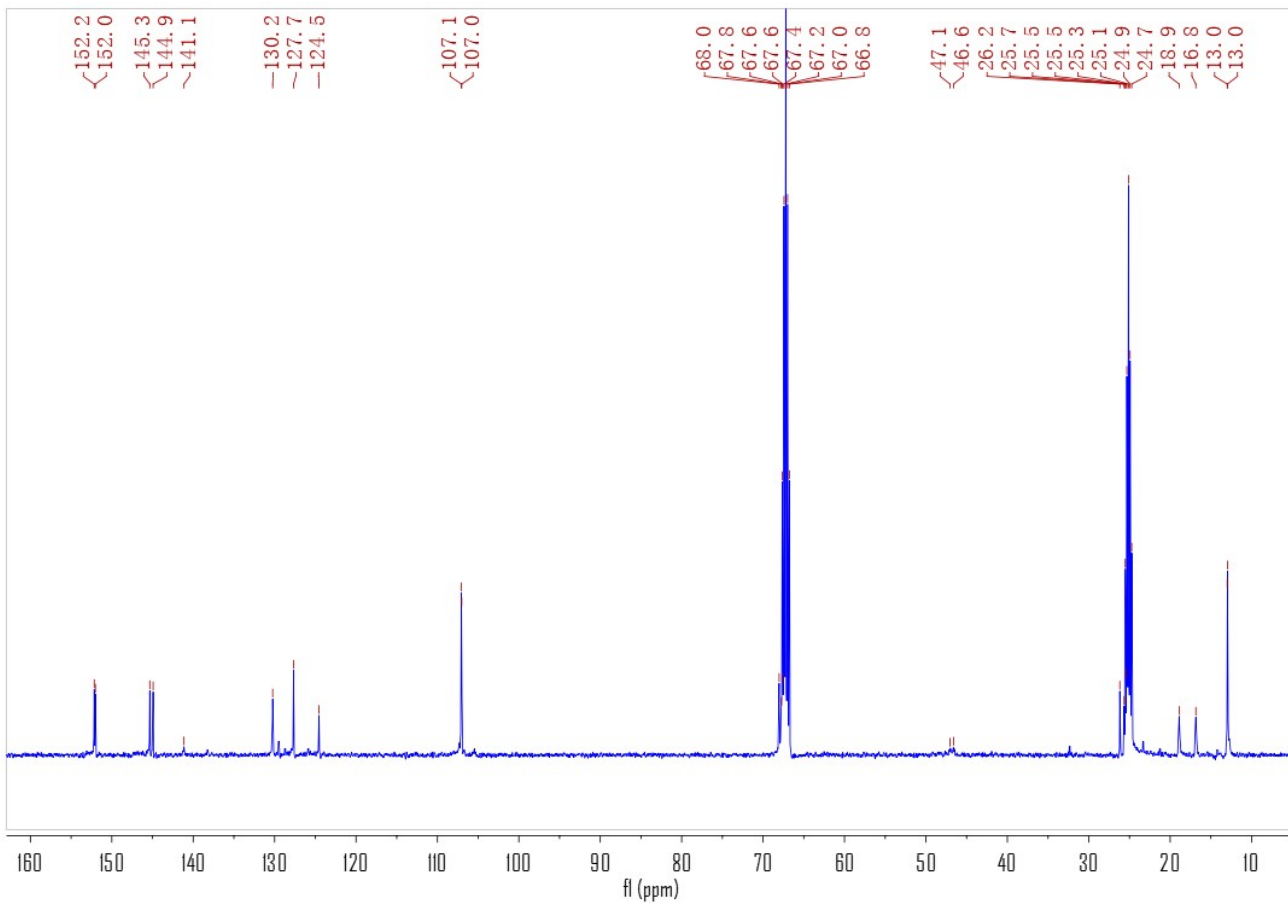


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex 2^{Lu} in $\text{THF-}d_8$ at room temperature.

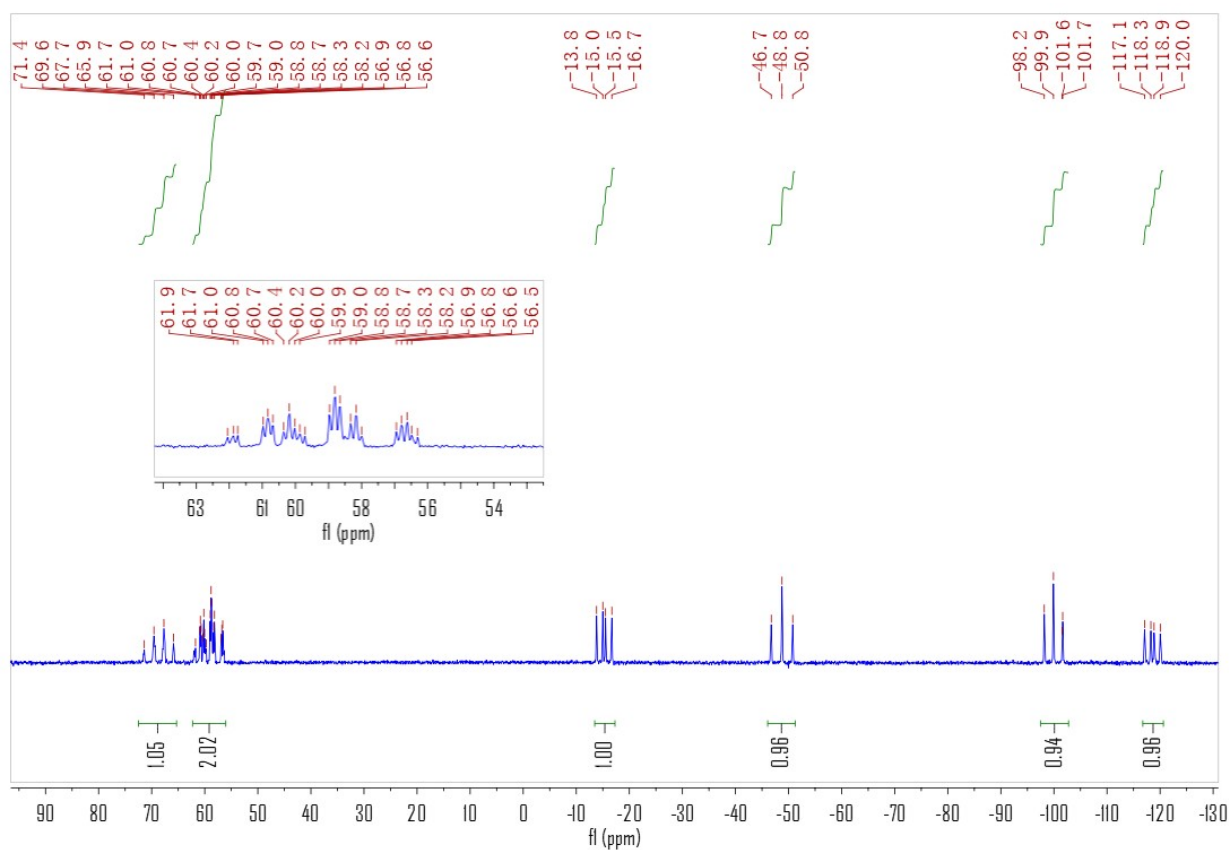


Figure S10. ^{31}P NMR spectrum of complex 2^{Lu} in $\text{THF-}d_9$ at room temperature.

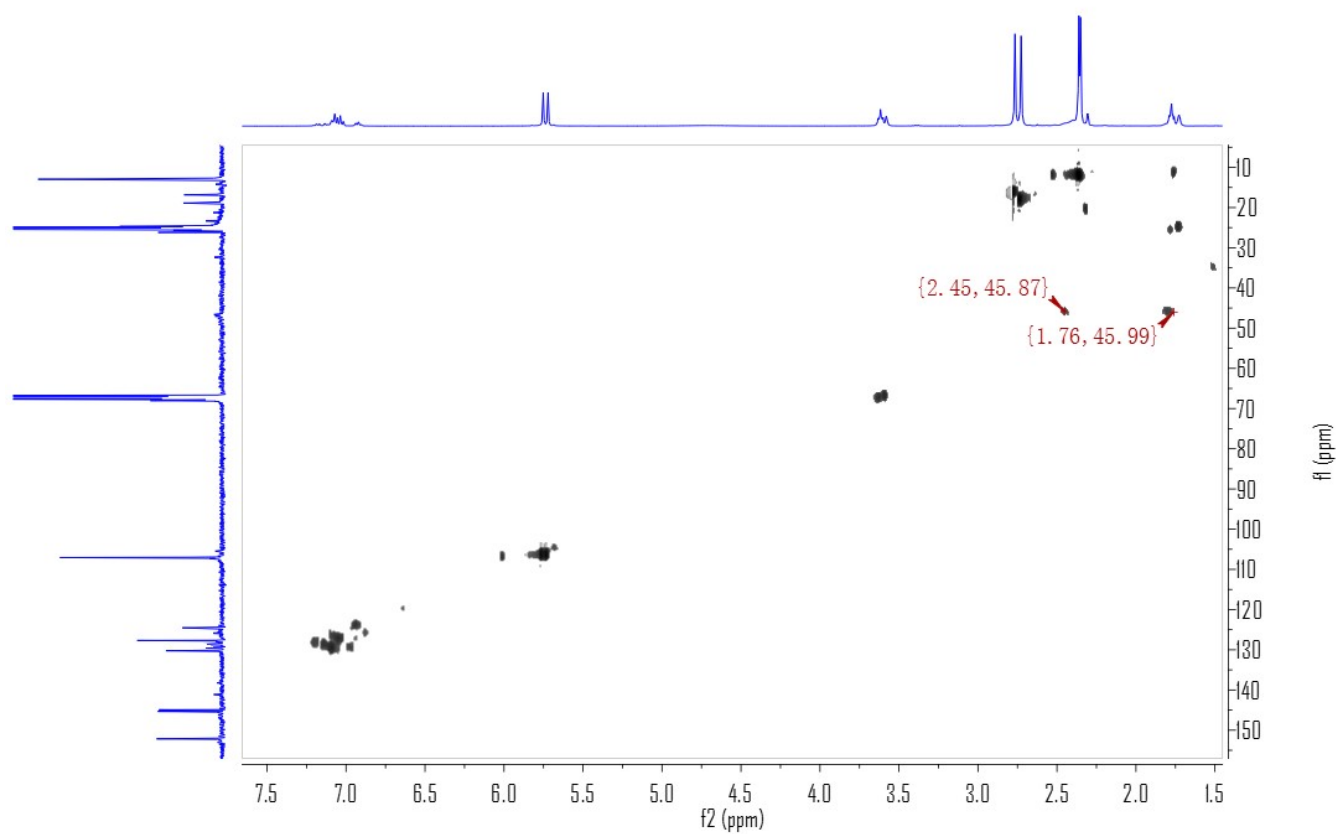


Figure S11. HSQC spectrum of complex 2^{Lu} in $\text{THF-}d_9$ at room temperature.

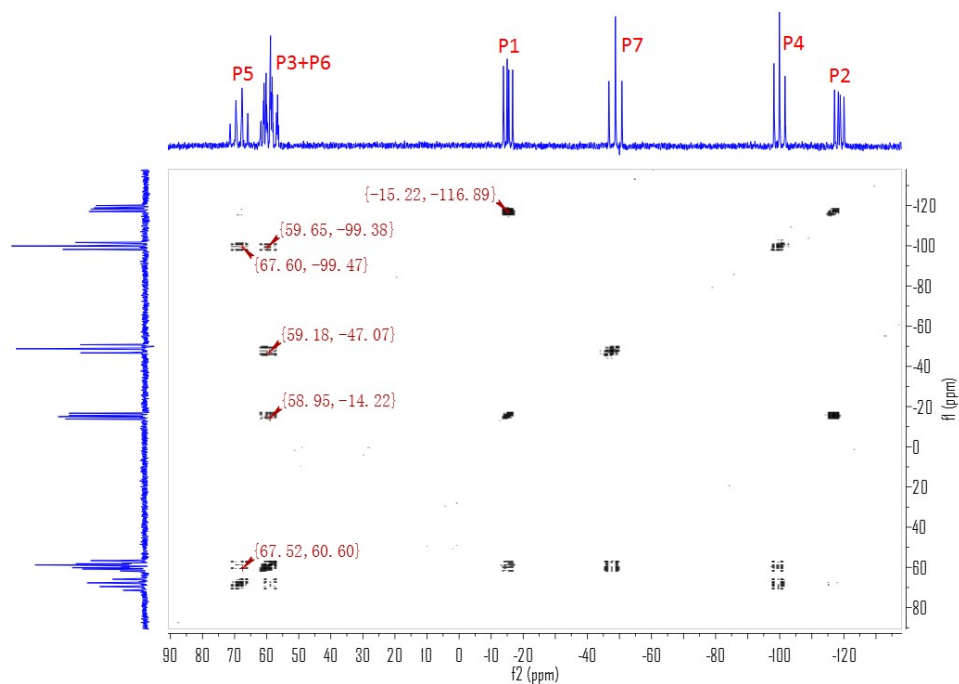


Figure S12. $^{31}\text{P}\{^1\text{H}\}$ COSY spectrum of complex 2^{Lu} in $\text{THF-}d_8$ at room temperature.

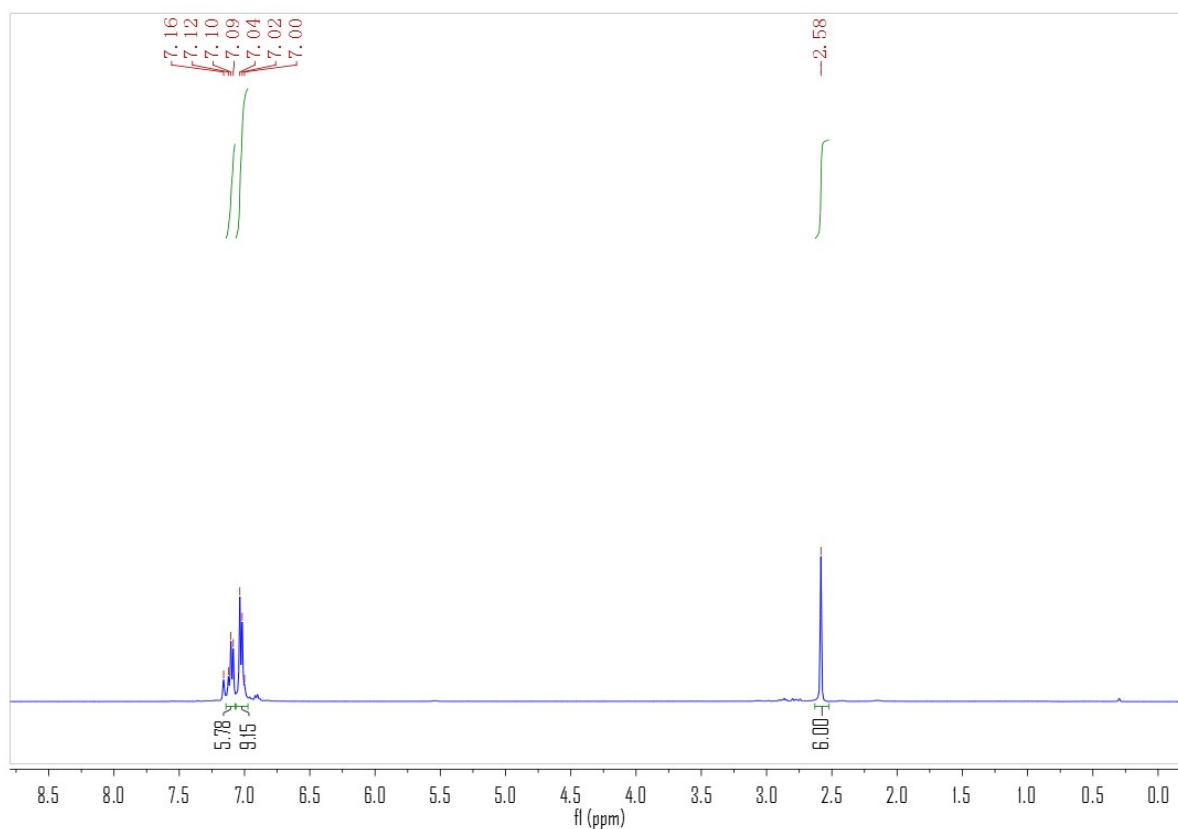


Figure S13. ^1H NMR spectrum of compound **I** in C_6D_6 at room temperature.

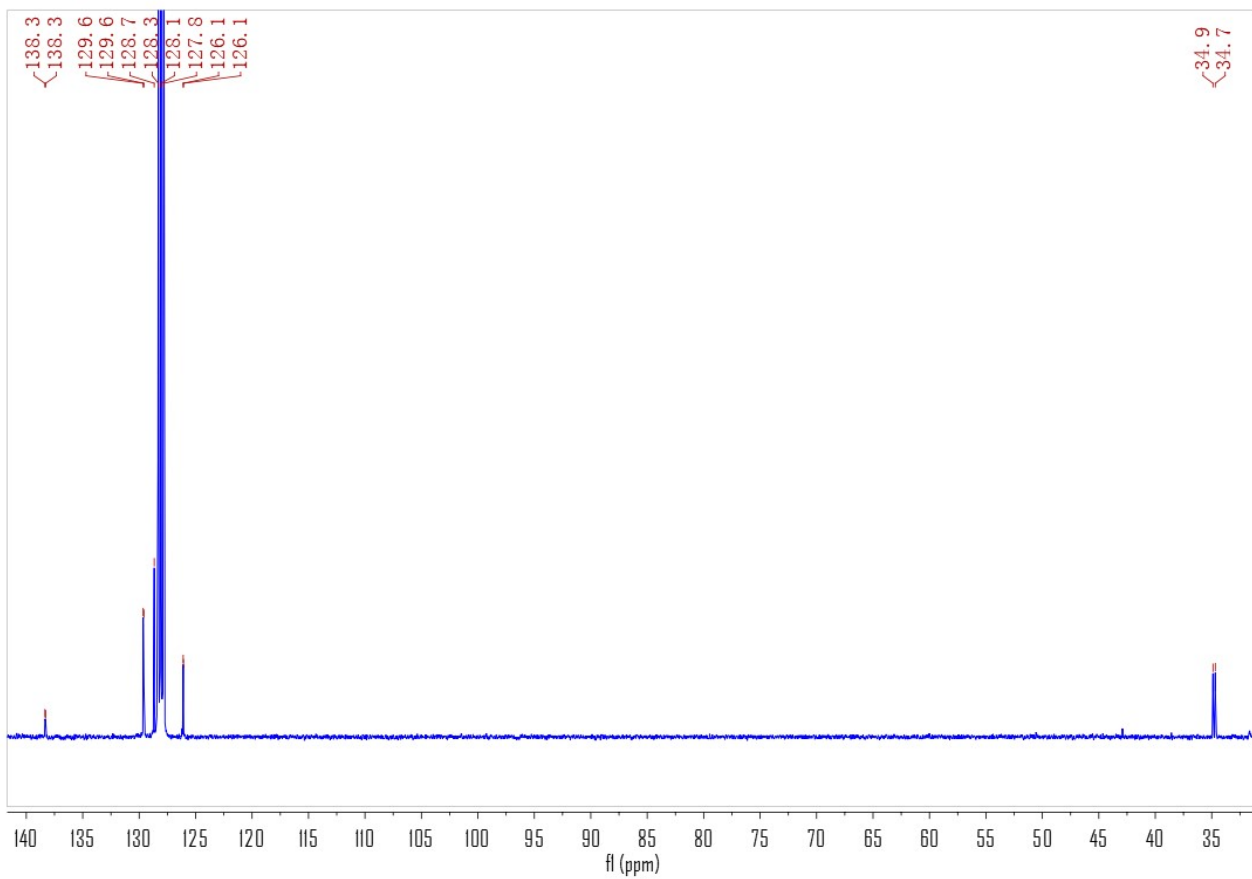


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound I in C_6D_6 at room temperature.

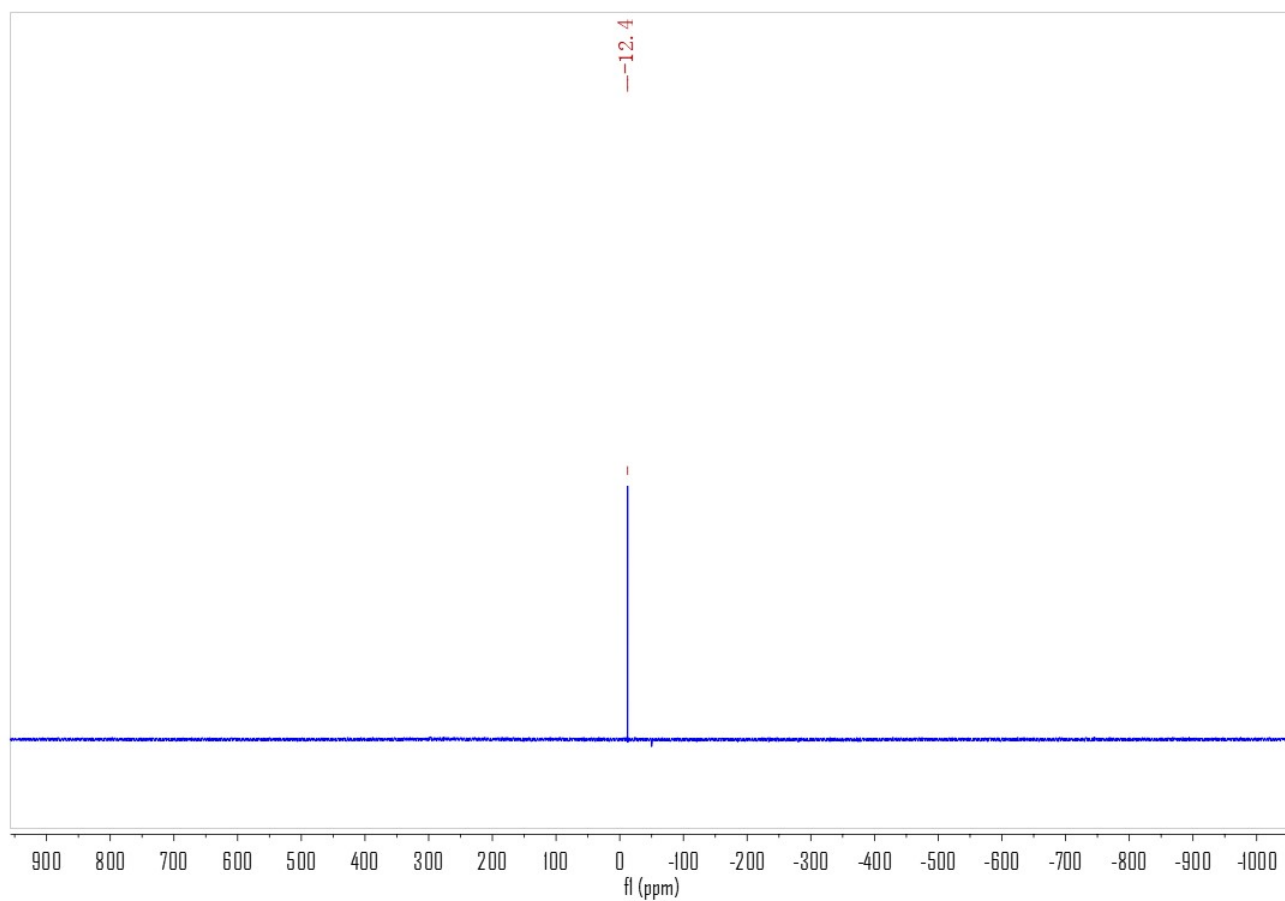
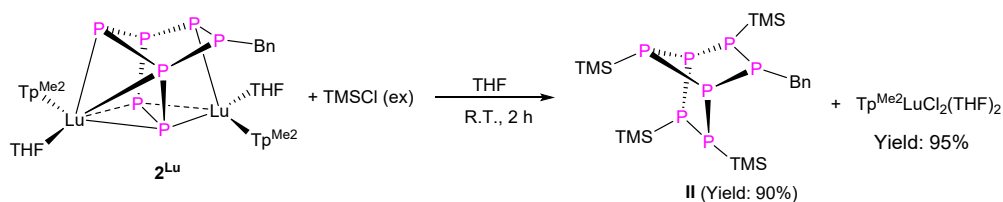


Figure S15. ^{31}P NMR spectrum of compound I in C_6D_6 at room temperature.

2.6 Synthesis and characterization of P₇BnTMS (II).



The 5 mL toluene solution of Me₃SiCl (217.0 mg, 2.0 mmol) was added slowly to a 10 mL toluene solution of 2^{Lu} (698.2 mg, 0.5 mmol). After stirring for 2 h, the toluene solution was evaporated to dryness under vacuum and hexane (10 mL×3) was added to the residue. After stirring for 30 min, the mixture was filtered and the filtrate was concentrated to dry to afford compound II as light yellow oil. Yield: 270.3 mg (90%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) 0.33-0.35 (m, 18H, TMS), 0.47-0.51 (m, 18H, TMS), 2.58-2.64 (m, 1H, CH₂Ph), 3.29-3.32 (m, 1H, CH₂Ph), 6.99-7.03 (m, 1H, CH₂Ph), 7.09-7.13 (m, 2H, CH₂Ph), 7.20-7.22 (m, 2H, CH₂Ph); ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) 0.0 (TMS), 3.7 (TMS), 37.9 (d, ¹J_{PC}= 30Hz, CH₂Ph), 126.5 (CH₂Ph), 128.9 (CH₂Ph), 129.6 (d, ²J_{PC}= 30Hz, CH₂Ph), 139.1 ((CH₂Ph)); ³¹P NMR (160 MHz, C₆D₆, 25 °C): δ (ppm) -107.0 (dd, 1P, ¹J_{PP}= 296.69 Hz, 199.72 Hz), -58.6 (m, 1P), -31.6 (td, 1P, ¹J_{PP}= 300.67 Hz, 111.32 Hz), -4.2 (m, 1P), 13.2 (m, 2P), 30.3 (q, 1P, ¹J_{PP}= 312.4 Hz). Elemental Analysis Calcd for C₁₉H₄₃P₇Si₄ (600.70): C, 37.99; H, 7.22. Found: C, 38.06; H, 7.26. The filter cake was dried to give a colorless powder Tp^{Me}₂LuCl₂(THF) (788.5 mg, 95%).

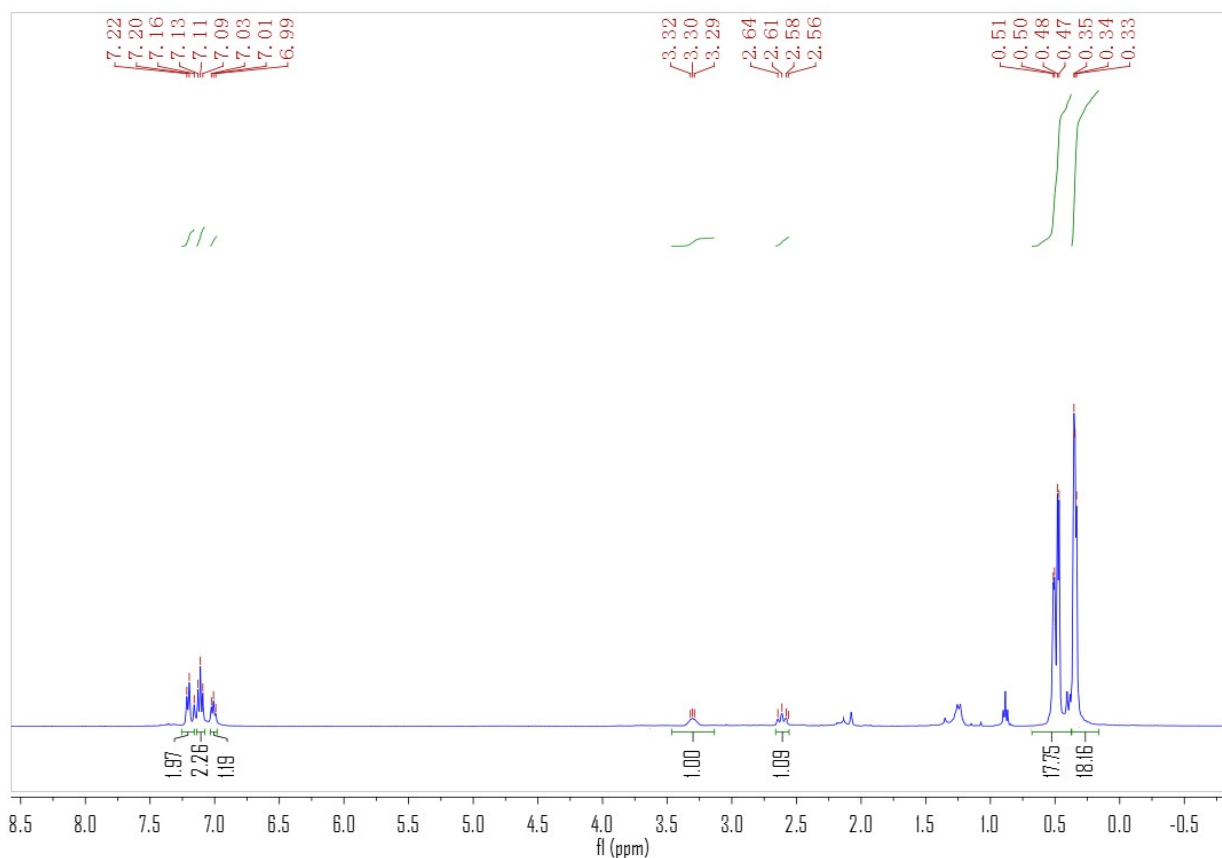


Figure S16. ¹H NMR spectrum of compound II in C₆D₆ at room temperature.

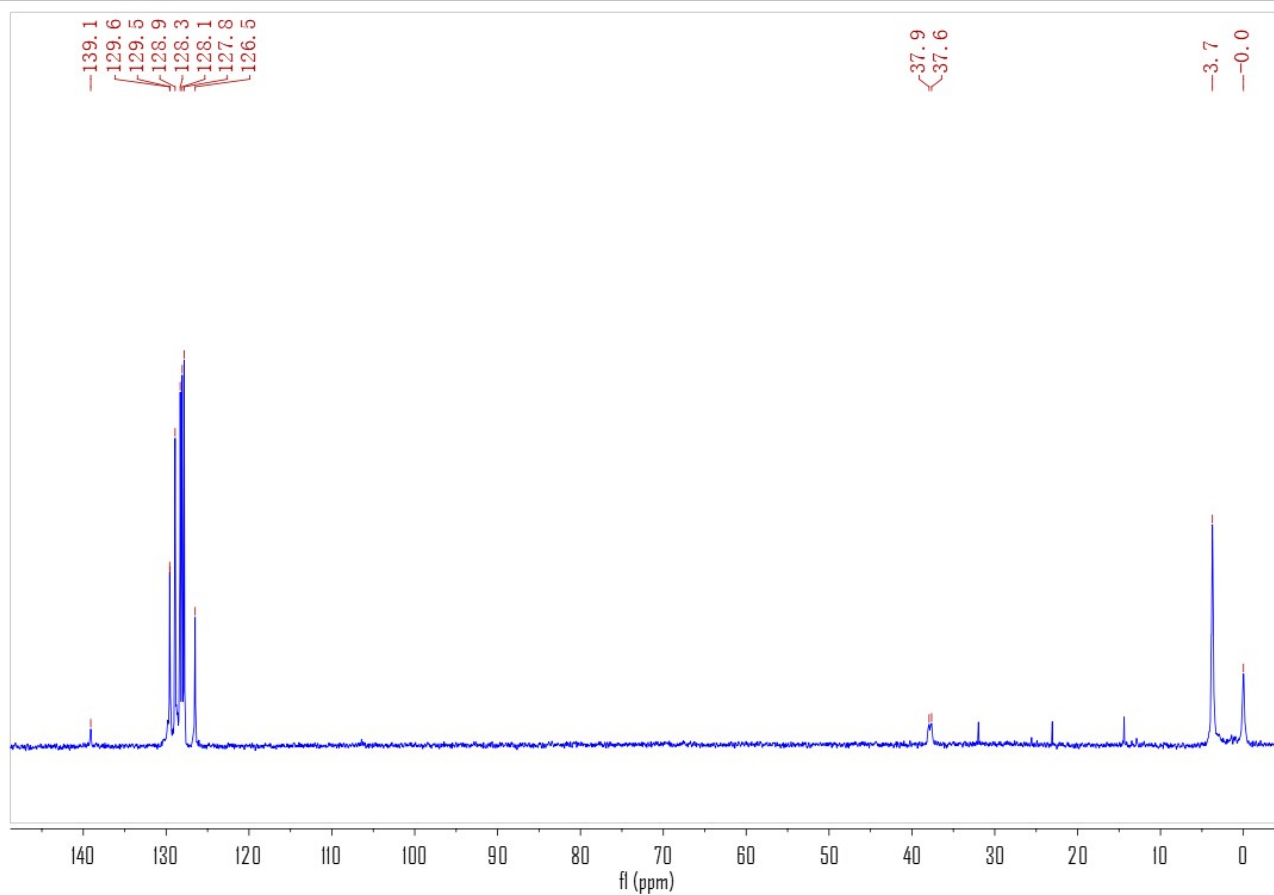


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **II** in C_6D_6 at room temperature.

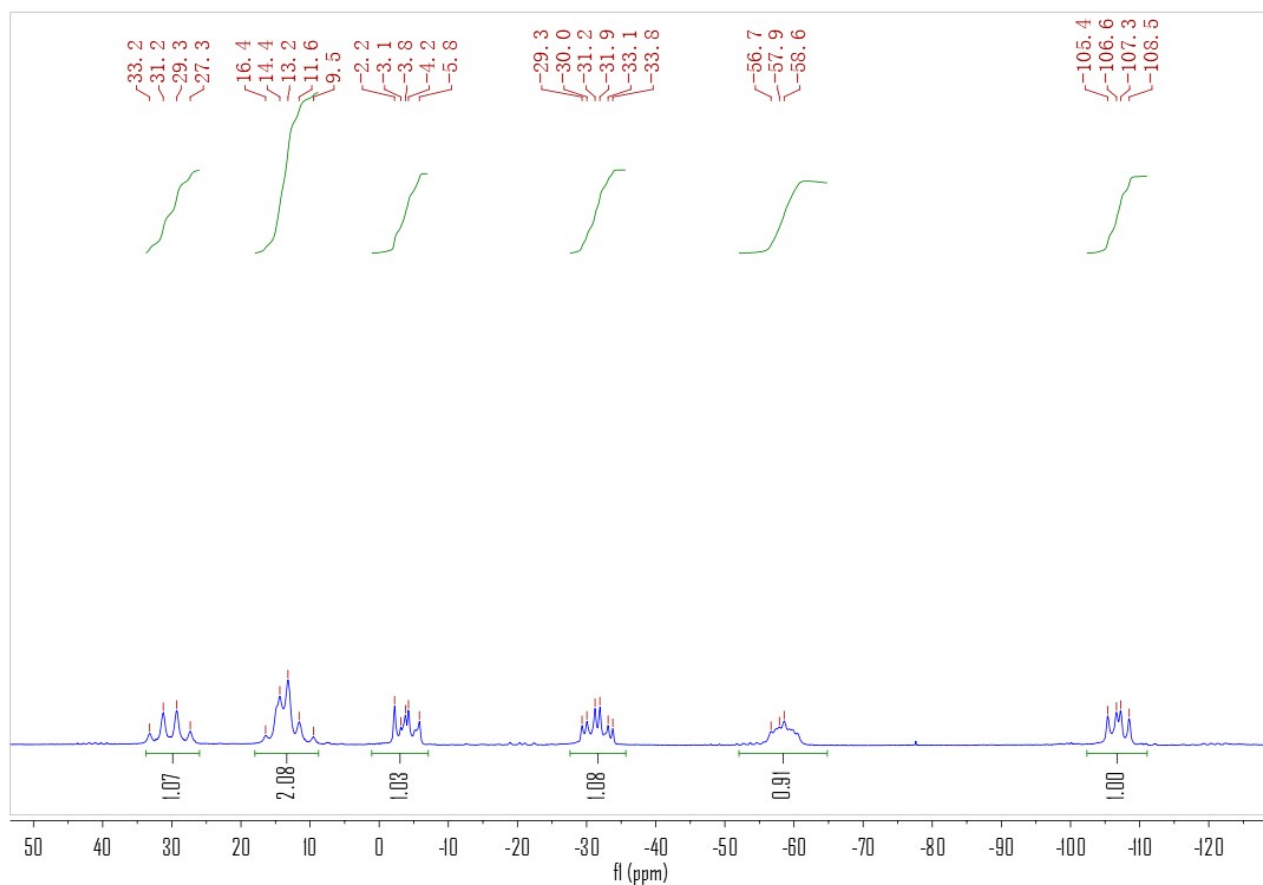


Figure S18. ^{31}P NMR spectrum of compound **II** in C_6D_6 at room temperature.

Stepwise reactions of $\text{Tp}^{\text{Me}_2}\text{LuCl}_2(\text{THF})_2$ with KBN , P_4 , and Me_3SiCl : The 2 mL THF solution of KBN (208.2 mg, 1.60 mmol) was added slowly to a 3 mL THF solution of the recovered $\text{Tp}^{\text{Me}_2}\text{LuCl}_2(\text{THF})_2$ (492.1 mg, 0.80 mmol) at ambient temperature. After stirring for 24 h, the THF solvent was removed under vacuum and the residue was redissolved with toluene (10 mL). After removing KCl by filter, P_4 (49.7 mg, 0.40 mmol) was added in the toluene solution at room temperature, and the reaction mixture was taken out from the glovebox and stirred at 40 °C. Keeping stirring for 2 days at this temperature, all the volatiles were removed under vacuum. The residue was extracted by *n*-hexane two times (10 mL \times 4) and dried under vacuum to give orange powder **2^{Lu}** (525.1 mg, 94%). Concentration of the *n*-hexane extraction afforded colorless crystals of PBn_3 (**I**) (105.9 mg, 87%). The orange powder was redissolved in a 10 mL toluene, and Me_3SiCl (173.6 mg, 1.6 mmol) was added at ambient temperature. After stirring for 2 h, the light yellow solution was evaporated to dryness under vacuum and hexane (10 mL \times 5) was added to the residue. After stirring for 30 min, the mixture was filtered and the filter cake was dried to give a colorless powder $\text{Tp}^{\text{Me}_2}\text{LuCl}_2(\text{THF})_2$ (456.2 mg, 81%). The filtrate was concentrated to dry to afford compound **II** (206.6 mg, 86%) as light yellow oil.

3. X-ray Crystallographic Analyses of Complexes **2**, **3** and **I**

Single crystals suitable for X-ray analysis were grown as shown in experimental section. Suitable crystals were wrapped in mineral oil and then were frozen at 173K or 223K. Data collections were performed on a Bruker SMART APEX (at 293K) or Bruker SMART APEX (II) (at 173K, or 293K) diffractometer with CCD area detector using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The determination of crystal class and unit cell was carried out by SMART program package. The raw frame data were processed using SAINT^[4] and SADABS^[5] to yield the reflection data file. All structures were solved by using SHELXTL program^[6] and refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at the calculated positions and included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Details of SQUEEZE are given in cif files. Calculations were carried out using the *SHELXL-2008* or *SHELXL-2014* program. CCDC 2016383 (for **2^Y**), 2016387 (for **2^{Lu(a)}**), 2016380 (for **2^{Lu(b)}**), 2016381 (for **3^Y**), and 2016382 (for **I**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336033; or deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and collection parameters of complexes **2^Y** and **3^Y**

Identification code	2^Y	3^Y
Formula	$\text{C}_{45}\text{H}_{67}\text{B}_2\text{N}_{12}\text{O}_2\text{P}_7\text{Y}_2$	$\text{C}_{66}\text{H}_{82}\text{B}_2\text{N}_{12}\text{P}_6\text{O}_2\text{Y}_2$
Formula weight	1224.33	1460.7
Temperature (K)	103(2)	296(2)
Wavelength (\AA)	1.5418	0.71073
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (\AA)	11.487(4)	11.0538(18)
<i>b</i> (\AA)	16.730(6)	14.006(2)
<i>c</i> (\AA)	17.252(6)	14.040(2)
α (deg)	96.369(1)	95.369(3)
β (deg)	102.702(1)	90.527(3)
γ (deg)	102.918(1)	100.145(3)
<i>V</i> (\AA^3)	3121.77(2)	2129.5(6)
<i>Z</i>	2	1
<i>D</i> _c (g/m^3)	1.302	1.139
μ (mm^{-1})	4.524	1.511
<i>F</i> (000)	1260	756
Crystal size (mm)	0.18 x 0.04 x 0.03	0.40 x 0.24 x 0.18
θ range ($^\circ$)	2.661 to 67.995	1.46 to 25.05
<i>h</i> , <i>k</i> , <i>l</i> range	-13 \leq h \leq 13 -19 \leq k \leq 20	-9 \leq h \leq 13 -16 \leq k \leq 16

	-20<= θ <=20	-16<= θ <=16
Reflections collected / unique	63360 / 11254	12531 / 7429
	[R(int) = 0.0551]	[R(int) = 0.0486]
Completeness to θ	98.9 % ($\theta = 25.10$)	98.4% ($\theta = 25.10$)
Max. and min. transmission	0.7531 and 0.5284	0.7726 and 0.5831
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	11254 / 87 / 700	7429 / 56 / 412
Goodness-of-fit on F^2	1.046	1.054
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0909$	$R_1 = 0.0850$
	$wR_2 = 0.3237$	$wR_2 = 0.2314$
R indices (all data)	$R_1 = 0.0974$	$R_1 = 0.1262$
	$wR_2 = 0.3429$	$wR_2 = 0.2588$
Largest diff. peak and hole ($e\cdot\text{\AA}^{-3}$)	3.375 and -1.307	2.104 and -0.749

Table S2. Crystal data and collection parameters of complexes **2^{Lu} (a)**, **2^{Lu} (b)** and **4**

Identification code	2^{Lu} (a)	2^{Lu} (b)	4
Formula	C ₄₅ H ₆₇ B ₂ N ₁₂ P ₇ O ₂ Y	C ₄₅ H ₆₇ B ₂ N ₁₂ P ₇ O ₂ Lu ₂	C ₂₁ H ₂₁ P
Formula weight	1396.45	1396.46	304.35
Temperature (K)	173(2)	173(2)	203(2)
Wavelength (Å)	1.5418	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	11.509(4)	12.604(12)	10.988(5)
<i>b</i> (Å)	16.682(8)	15.254(15)	9.693(4)
<i>c</i> (Å)	17.387(7)	17.214(17)	16.198(7)
α (deg)	96.505(2)	80.983(2)	90
β (deg)	102.830(2)	84.810(2)	91.234(7)
γ (deg)	102.311(2)	81.211(2)	90
<i>V</i> (Å ³)	3134.6(2)	3222.8(5)	1724.9(14)
<i>Z</i>	2	2	4
D _c (g/m ³)	1.480	1.440	1.172
μ (mm ⁻¹)	7.913	3.261	0.154
<i>F</i> (000)	1388	1390	648
Crystal size (mm)	0.18 x 0.04 x 0.03	0.18 x 0.16 x 0.14	0.90 x 0.20 x 0.18
θ range (°)	2.644 to 68.568	1.200 to 25.098	2.218 to 25.047
<i>h, k, l</i> range	-13<= <i>h</i> <=13 -20<= <i>k</i> <=20 -20<= <i>l</i> <=20	-15<= <i>h</i> <=15 -17<= <i>k</i> <=18 -20<= <i>l</i> <=20	-13<= <i>h</i> <=12 -11<= <i>k</i> <=11 -19<= <i>l</i> <=13
Reflections collected / unique	20646 / 11393 [<i>R</i> (int) = 0.0532]	19642 / 11307 [<i>R</i> (int) = 0.0302]	9674 / 3034 [<i>R</i> (int) = 0.0512]
Completeness to θ	99.0 % (θ = 25.10)	98.4 % (θ = 25.10)	99.2 % (θ = 25.10)
Max. and min. transmission	0.7531 and 0.5062	0.658 and 0.591	0.7456 and 0.5821
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	11393 / 53 / 700	11307 / 18 / 643	3034 / 0 / 199
Goodness-of-fit on <i>F</i> ²	1.032	1.050	1.03
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0792 <i>wR</i> ₂ = 0.2198	<i>R</i> ₁ = 0.0516 <i>wR</i> ₂ = 0.1781	<i>R</i> ₁ = 0.0472 <i>wR</i> ₂ = 0.1364
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1135 <i>wR</i> ₂ = 0.2552	<i>R</i> ₁ = 0.0825 <i>wR</i> ₂ = 0.2511	<i>R</i> ₁ = 0.0742 <i>wR</i> ₂ = 0.1584
Largest diff. peak and hole (e·Å ⁻³)	2.675 and -0.99	3.632 and -2.422	0.385 and -0.288

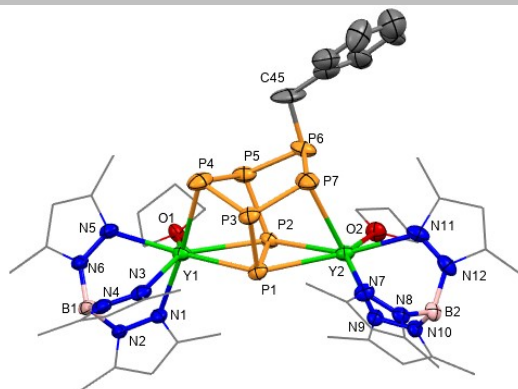


Figure S19. Molecular structure of 2^Y with ellipsoids set at 30% probability. All hydrogen atoms and Tp^{Me2} groups are omitted for clarity.

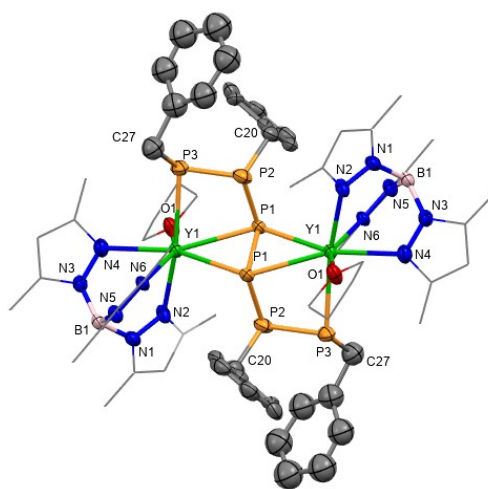


Figure S20. Molecular structure of 3^Y with ellipsoids set at 30% probability. All hydrogen atoms and Tp^{Me2} groups are omitted for clarity.

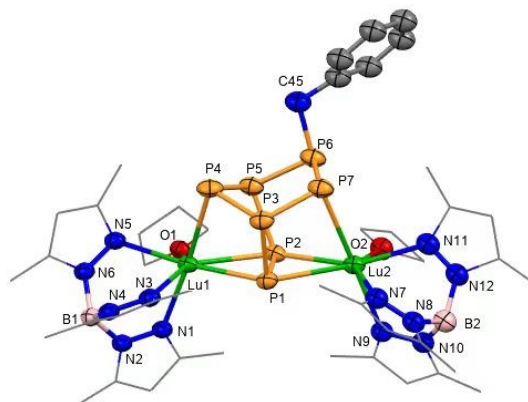


Figure S21. Molecular structure of 2^{Lu(a)} with ellipsoids set at 30% probability. All hydrogen atoms and Tp^{Me2} groups are omitted for clarity.

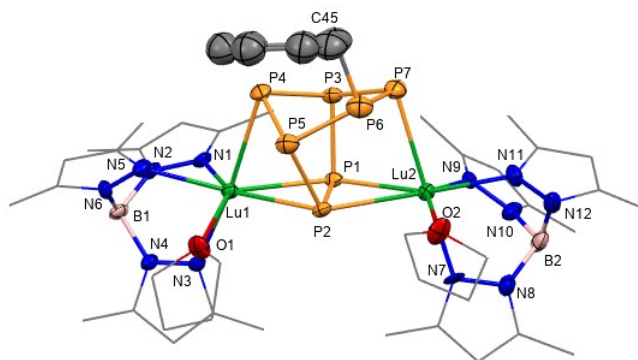


Figure S22. Molecular structure of $2^{Lu}(b)$ with ellipsoids set at 30% probability. All hydrogen atoms and Tp^{Me_2} groups are omitted for clarity.

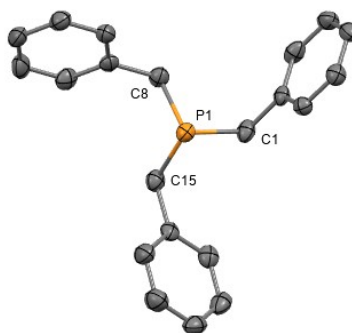


Figure S23. Molecular structure of **I** with ellipsoids set at 30% probability. Selected bond lengths (Å) and bond angles (°) of **I**: P(1)-C(8) 1.859(3), P(1)-C(1) 1.864(3), P(1)-C(15) 1.864(3); C(8)-P(1)-C(1) 97.56(13), C(8)-P(1)-C(15) 99.73(13), C(1)-P(1)-C(15) 98.60(13).

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