

SUPPLEMENTARY INFORMATION

Selective carbon-phosphorus bond cleavage: expanding the toolbox for accessing bulky divalent lanthanoid sandwich complexes

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1. Experimental

Materials and General Procedures

All manipulations were performed under nitrogen, using standard Schlenk techniques. Lanthanoid metals were from Santoku/Molycorp/Eutectix. Large chunks were filed in the drybox before use. Solvents (thf, toluene, C₆D₆) were pre-dried by distillation over sodium or sodium benzophenone ketyl before being stored under an atmosphere of nitrogen over 3 Å molecular sieves, and hexane and diethyl ether were purified by an SPS and stored over 5 Å molecular sieves. Chlorodiphenylphosphine was commercially available and used without further purification. Tetraphenylcyclopentadiene¹ and pentaphenylcyclopentadiene² were prepared by the literature methods. In all cases, unless specified, ca. 1 mg of I₂ (5 mol%) was used to activate the metal. Infrared spectra (4000–400 cm⁻¹) were obtained as Nujol mulls between NaCl plates with a Nicolet-Nexus FT-IR spectrometer. ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded on a Bruker 400 MHz spectrometer. ¹H and ¹³C NMR spectra were referenced against residual solvent peaks, and ¹⁹F and ³¹P NMR spectra were referenced externally against 85% H₃PO₄ (δ = 0) and CCl₃F (δ = 0) respectively. No interpretable NMR spectra could be collected for the highly paramagnetic europium complexes **3** and **6**. The chemical shifts are expressed in parts per million (ppm). MS were obtained with a Shimadzu LCMS-2020. Microanalyses were determined by the Elemental Analysis Service, Macquarie University, and all the samples were sealed in tubes under nitrogen before transport.

Crystal and refinement data

Single crystals covered with viscous hydrocarbon oil were mounted on a glass fibre. Data for **1**, **2** and **6-8** were obtained at -173 °C (100 K) on the MX1: Macromolecular Crystallography beamline at the Australian Synchrotron, Victoria, Australia. Data collection and integration on the MX1: Macromolecular Crystallography beamline was accomplished using Blu-Ice.³ The structures were solved using SHELXS7 and refined by full-matrix least-squares on all F₂ data using SHELX2014⁴ in conjunction with the X-Seed graphical user interface.⁵ Complex **3** was collected using a Bruker X8 Apex II diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71013$ Å). Data were initially processed with the SAINT program.⁶ All hydrogen atoms were placed in calculated positions using the riding model. CCDC 2150006-2150011 for compound **1**, **2**, **5'**, and **6 - 8** respectively, 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/data_request/cif.

Syntheses

Tetraphenylcyclopentadienyldiphenylphosphine (C₅Ph₄HPPH₂) (1)

A Schlenk flask equipped with a magnetic stirrer bar was charged with tetraphenylcyclopentadiene (0.50 g, 1.35 mmol) in anhydrous diethyl ether (5 mL). *n*-BuLi (2.5 M in hexanes) (0.76 mL, 1.9 mmol, 1.4 equivalents) was added slowly, and stirred overnight. To the resulting suspension was added PPh₂Cl (0.36 mL, 1.9 mmol, 1.4 equivalents) and stirred for four hours. The solvent was then removed under reduced pressure, and the residue taken up into toluene (5 mL) before isolating the supernatant solution by filter cannula. The solvent was again removed under reduced pressure, and the solid washed with hexane (2 x 5 mL) yielding an off-white powder (0.64 g, 1.15 mmol, 85%) Colourless crystals of **1** were grown from anhydrous diethyl ether. *Anal.* Calc. for C₄₁H₃₁P: C, 88.77; H, 5.63. Found: C, 88.84; H, 5.60%. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 7.48 (m, 4H, ArH), 7.29 (m, 4H, ArH), 7.04-6.88, (m, 20H, ArH), 6.87-6.81 (m, 2H, ArH), 5.36 (d, *J* = 0.41 Hz, 1H, CpH). ¹³C NMR (101 MHz, C₆D₆, 25 °C) δ 144.69 (s), 142.99 (s), 136.85 (s), 135.95 (s), 134.24 (d, *J* = 21.6 Hz), 133.53 (d, *J* = 22.0 Hz), 130.01 (s), 129.65 (s), 128.49 (s), 126.39 (d, *J* = 24.7 Hz). 57.02 (d, *J* = 32.8 Hz). ³¹P (162 MHz, C₆D₆, 25 °C): δ 13.36 (s). IR (Nujol, cm⁻¹): 2727 w, 1573 w, 1538 w, 1304 m, 1260 s, 1157 m, 1090 m, 1070 m, 1025 s, 919 w, 836 vs, 798s, 777 w, 756 m, 695 s.

Pentaphenylcyclopentadienyldiphenylphosphine (C₅Ph₅PPh₂) (2)

A Schlenk flask equipped with a magnetic stirrer bar was charged with pentaphenylcyclopentadiene (1.0 g, 2.24 mmol) and suspended in diethyl ether (10 mL). *n*-BuLi (2.0 M in hexanes) (1.35 mL, 2.70 mmol, 1.2 equivalents) was added slowly and the mixture was stirred overnight. To this suspension was added PPh₂Cl (0.5 mL, 2.70 mmol, 1.2 equivalents) and stirred overnight. The off-white suspension was allowed to settle, and the supernatant solution was removed by filter cannula. The solids were dried under reduced pressure, washed with anhydrous hexane (2 x 5 mL), and then taken up into anhydrous toluene (10 mL). The resulting suspension was heated until a deep purple solution had formed, and then the solution was separated from the remaining solid by filter cannula. The solvent was evaporated under reduced pressure, yielding a pale purple solid, which was washed with anhydrous hexanes (2 x 5 mL) yielding a pale yellow solid (1.30 g, 2.06 mmol, 92%). Colourless crystals of **2** were grown from the slow cooling of a hot toluene solution. *Anal.* Calc. for C₄₇H₃₅P: C, 89.50; H, 5.59. Found: C, 89.52; H, 5.716%. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 8.23 (br d, *J* = 5.81, 2H, ArH), 7.72 (tt, 4H, ArH), 7.22-7.16 (m, 6H, ArH), 6.99-6.80

(m, 17H, ArH), 6.73-6.70 (m, 6H, ArH). ^{13}C NMR (101 MHz, C_6D_6 , 25 °C) δ 150.36 (s), 145.92 (s), 140.40 (d, $J = 14.4$ Hz), 137.33 (d, $J = 16.9$ Hz), 135.90 (d, $J = 20.9$ Hz), 134.92 (d, $J = 20.9$ Hz), 131.64 (s), 131.27 (s), 130.36 (d, $J = 17.2$ Hz), 129.52 (s), 129.36 (d, $J = 2.4$ Hz), 127.99 (s), 127.28 (d, $J = 27.1$ Hz). ^{31}P NMR (162 MHz, C_6D_6 , 25 °C) δ 9.75 (s). IR (Nujol, cm^{-1}): 2332 w, 1946 m, 1884 m, 1811 m, 1757 w, 1595 s, 1571 s, 1459 s, 1377 m, 1340 w, 1276 w, 1260 w, 1178 m, 1162 w, 1152 w, 1095 m, 1027 s, 1009 w, 919 m, 849 m, 802 s, 778 w, 760 m, 691 m, 617 m, 587 m, 562 m.

[Eu(C₅Ph₄H)₂(dme)]·1.5dme (3)

Freshly filed europium metal (0.100 g, 0.658 mmol) was added to a Schlenk flask containing C₅Ph₄HPPPh₂ (**1**) (0.055 g, 0.10 mmol). Anhydrous thf (5 mL) and a crystal of iodine, to activate the metal, were added, and the suspension sonicated for 18 hours. The resulting suspension was left to settle, and the solution removed by filter cannula and evaporated to dryness under reduced pressure, yielding an orange solid. The solid was washed with anhydrous hexane (2 x 5 mL), yielding **3** as a bright orange powder (0.042 g, 93%). Bright orange crystals of **3** were grown from a dme solution at 4 °C, confirming the unit cell.⁷ *Anal.* Calc. for C₆₈H₆₇O₅Eu: C, 73.17; H, 6.05. Found: C, 72.65; H, 6.00%. IR (Nujol, cm^{-1}): 3057 w, 2355 w, 2311 w, 1962 w, 1594 s, 1578 m, 1534 m, 1506 w, 1495 w, 1305 m, 1260 vs, 1203 m, 1154 w, 1097 vs, 1078 m, 1069 s, 1046 vs, 1020 vs, 934 m, 916 m, 848 m, 799 vs, 757 s, 731 s, 700 s. Spectroscopic data were in agreement with those reported.⁷

[Sm(C₅Ph₄H)₂(thf)₂] (4)

Prepared as per the synthesis of **3** but using Sm metal filings (0.100 g, 0.667 mmol) in place of Eu metal, yielding a dark red solid (0.037 g, 84%). ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 20.53 (8H, s, ArH), 14.02 (8H, s, ArH), 11.15 (4H, s, ArH), 8.90 (8H, s), 7.55 (8H, s, ArH), 7.36 (4H, s, ArH), 4.90 (22H, m, thf CH₂), 0.81 (22H, m, thf CH₂), -6.55 (2H, s, CpH). IR (Nujol, cm^{-1}): 1595 m, 1508 m, 1306 w, 1261 w, 1166 w, 1072 w, 1026 w, 914 w, 790 w, 759 m, 737 m, 723 m, 696 s. Spectroscopic data were in agreement with those reported.⁷

[Yb(C₅Ph₄H)₂(thf)] (5)

Freshly filed ytterbium metal (0.100 g, 0.578 mmol) was added to a Schlenk flask containing C₅Ph₄HPPPh₂ (**1**) (0.055 g, 0.10 mmol). Anhydrous thf (5 mL) and a crystal of iodine, to activate the metal, were added, and the suspension sonicated for 18 hours. The resulting suspension was left to settle, and the solution removed by filter cannula and evaporated to a paste, but not

to dryness. Anhydrous toluene (5 mL) was added and the solid precipitated at 4 °C. The supernatant solution was then removed. Owing to the susceptibility of **5** to decomposition when desolvated, the solid was not dried under reduced pressure, and thus an accurate yield could not be recorded. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 7.52 (4H, d, *J* = 7.5 Hz, ArH), 7.36 (2H, s, ArH), 7.30 (4H, d *J* = 7.7 Hz, ArH), 7.06 (24H, d, *J* = 7.1 Hz, ArH), 6.96 (6H, s, ArH), 6.72 (2H, s, CpH). IR (Nujol, cm⁻¹): 1596 m, 1509 w, 1307 w, 1260 w, 1132 m, 1071 m, 1025 m, 916 w, 790 w, 760 s, 723 s, 696 s. Spectroscopic data were in agreement with those reported, with slight chemical shift deviations due to influence of excess solvent.⁸

[Yb(C₅Ph₄H)I(thf)₂]₂·2 C₆D₆ (5'**)**

As per synthesis of **5** but using ca. 5 mg of I₂ (25 mol%), a small crop of crystals of **5'** were isolated from the mixture. Owing to the limited yield, only an X-ray crystal structure was obtained (Figure S22).

[Sm(C₅Ph₅)₂]₂·PhMe (6**)**

Freshly filed samarium (0.100 g, 0.667 mmol) was added to a Schlenk flask containing C₅Ph₅PPh₂ (**2**) (0.063 g, 0.10 mmol). To this Schlenk flask, 5 mL of anhydrous thf, and a crystal of iodine, to activate the metal were added, and the suspension sonicated for 18 hours. The resulting suspension was left to settle before isolating the supernatant liquid by a filtration cannula. The resulting filtrate was evaporated to dryness under reduced pressure, yielding a dark brown solid, and then taken up into anhydrous toluene (5 mL) to form **6** as an insoluble dark brown solid. The supernatant solution was concentrated to 2 mL, before removing by filter cannula, and drying the solid under reduced pressure. Dark red crystals of **6** were grown from a hot toluene solution (0.035g, 67%). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 11.46 (br s, 20H, ArH), 9.78 br s, 10H, ArH). IR (Nujol, cm⁻¹): 1594 m, 1501 m, 1309 w, 1261 w, 1154 w, 1076 m, 1026 m, 915 w, 840 w, 802 m, 778 m, 738 m, 700 s. Spectroscopic data were in agreement with those reported.⁷

[Eu(C₅Ph₅)₂]₂·PhMe (7**)**

Method 1: Prepared as per the synthesis of **6** but using europium metal filings (0.100 g, 0.658 mmol) in place of samarium, and C₅Ph₅PPh₂ (**2**) (0.063 g, 0.10 mmol). Bright orange crystals of **7** were grown from a hot toluene solution (0.045 g, 85%). IR (Nujol, cm⁻¹): 1594 m, 1574 w, 1501 m, 1261 m, 1179 w, 1154 w, 1143 w, 1076 m, 1025 m, 914 m, 012 m, 778 m, 736 m, 702 s, 679 w. Spectroscopic data were in agreement with those reported.⁷

Method 2: As per *Method 1*, however without addition of I₂. The reaction mixture was sonicated for 96 hours before complete consumption of **2** was observed by ³¹P NMR spectroscopy. Yielded **7** as a bright orange solid (0.042 g, 79%).

[Yb(C₅Ph₅)₂]·**2.5 C₆D₆ (**8**)**

Method 1: Freshly filed ytterbium metal (0.100 g, 0.578 mmol) was added to a Schlenk flask containing C₅Ph₅PPh₂ (**2**) (0.030 g, 0.048 mmol). To this Schlenk flask, 5mL of anhydrous thf, and a crystal of iodine, to activate the metal were added, and the suspension sonicated for 18 hours. The resulting suspension was left to settle before separating the supernatant liquid by a filtration cannula. The resulting filtrate was evaporated to dryness under reduced pressure, yielding a dark brown solid, which was then taken up into anhydrous toluene (5 mL) to form the desired sandwich as an insoluble dark green solid. The solvent was then removed under reduced pressure, and the solid washed with anhydrous hexane (2 x 5 mL) (0.018g, 71%). Dark green crystals of **8** were grown from a hot C₆D₆ solution. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 6.99 (m, 20H, ArH), 6.90 (m, 10H, ArH), 6.80 (m, 20H, ArH). IR (Nujol, cm⁻¹): 1594 m, 1574 w, 1501 m, 1307 w, 1155 w, 1075 m, 1026 m, 1013 m, 917 m, 862 m, 801 m, 776 m, 737 m, 722 m, 701 s, 678 w. Spectroscopic data were in agreement with those reported.⁹

Method 2: As per *Method 1*, however without addition of I₂. The reaction mixture was sonicated for 96 hours before complete consumption of **2** was observed by ³¹P NMR spectroscopy. Yielded **8** as a dark brown solid (0.016 g, 65%).

2. NMR Spectra

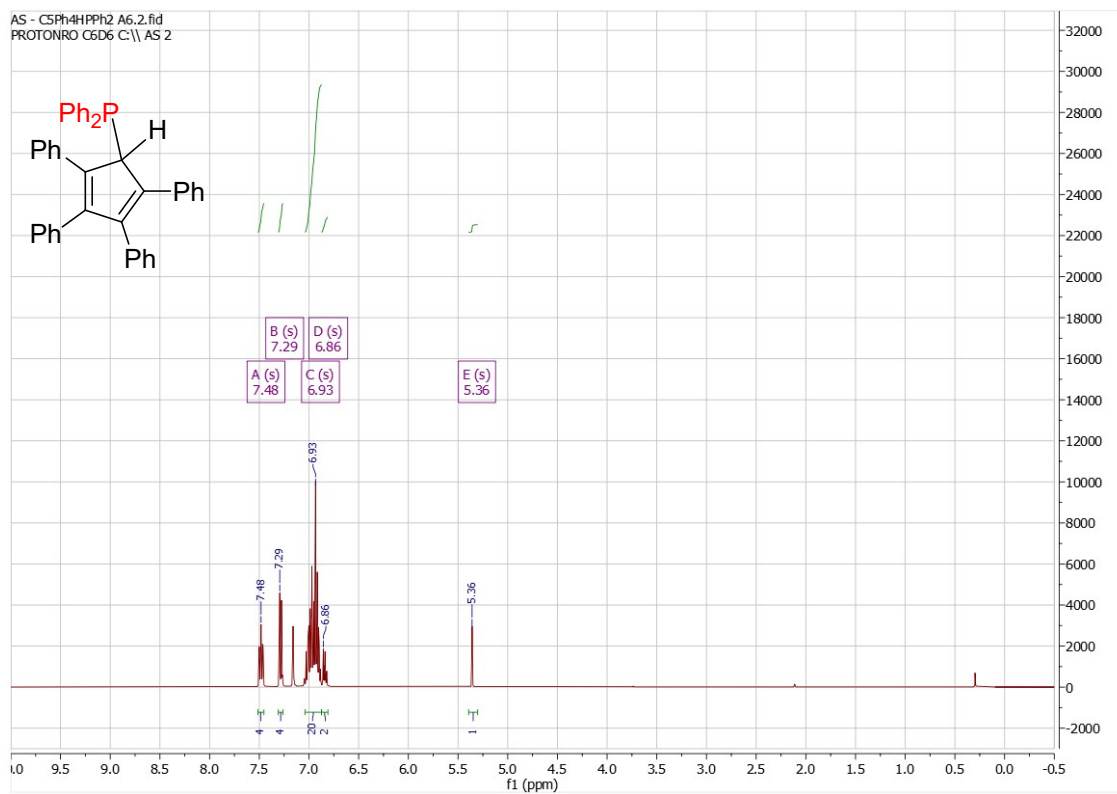


Figure S1 - 1H NMR spectrum of $C_5Ph_4HPPH_2$ (1) in C_6D_6

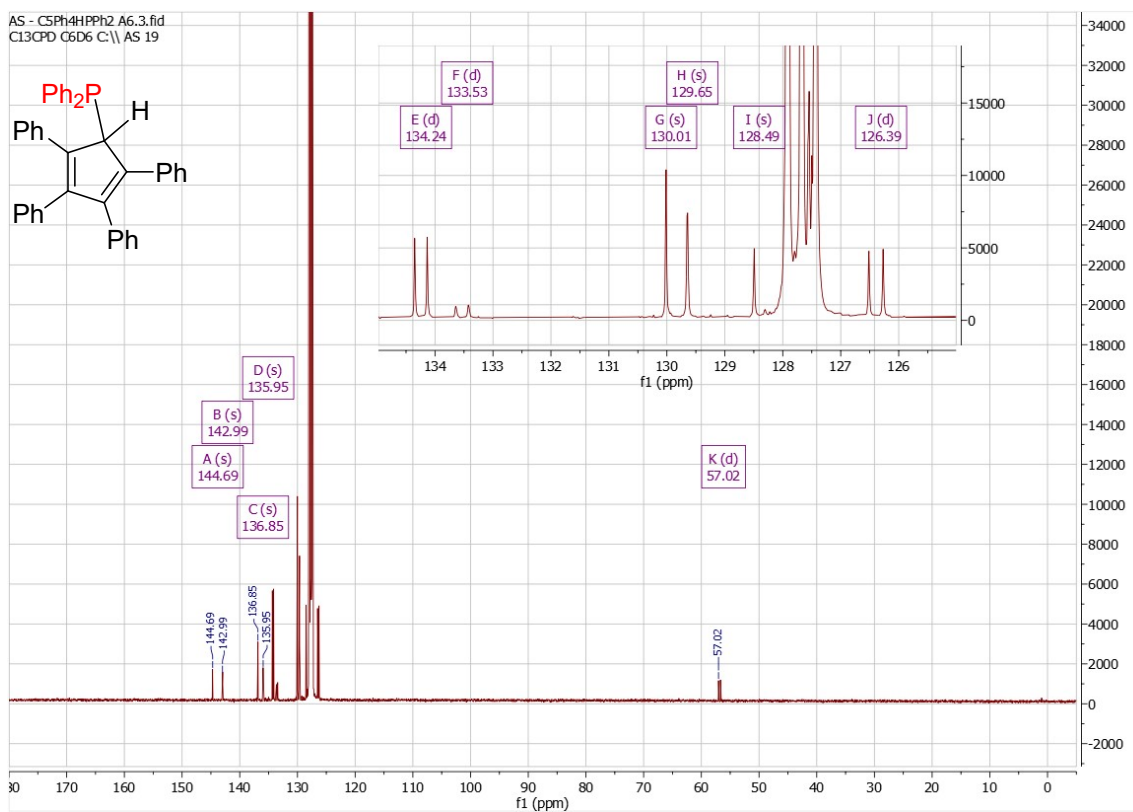


Figure S2 – ^{13}C NMR spectrum of $\text{C}_5\text{Ph}_4\text{HPPH}_2$ (**1**) in C_6D_6

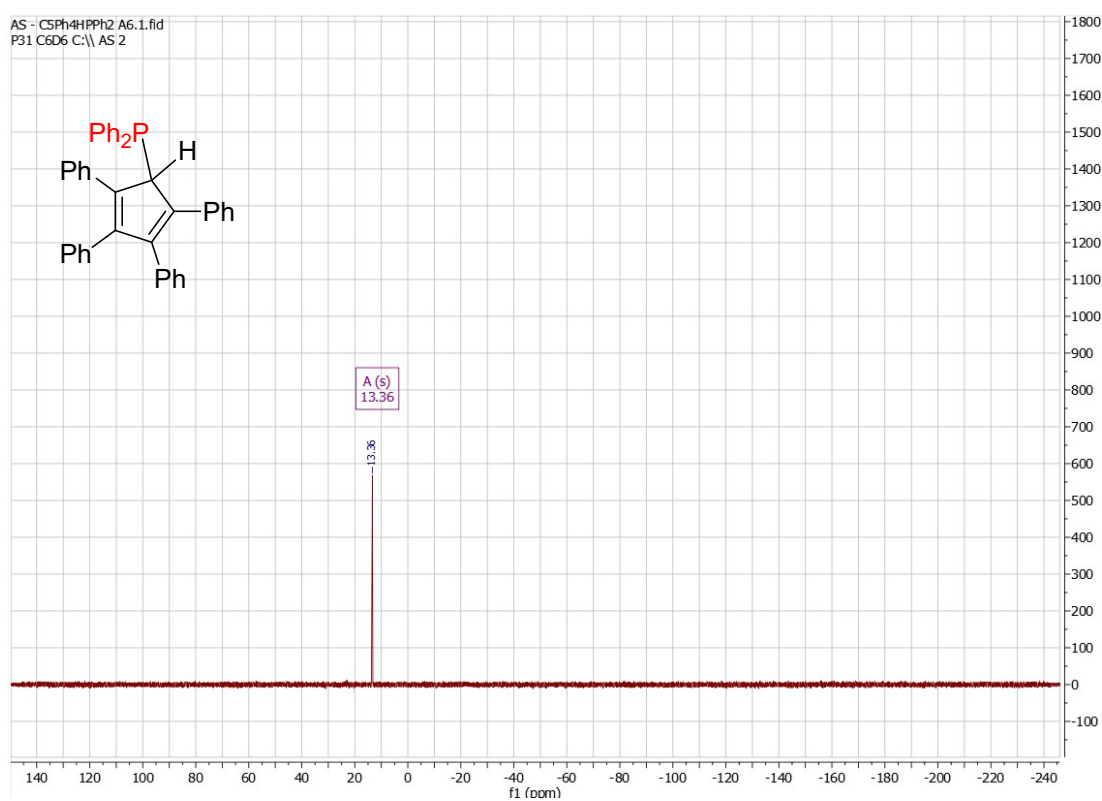


Figure S3 – ^{31}P NMR spectrum of $\text{C}_5\text{Ph}_4\text{HPPH}_2$ (**1**) in C_6D_6

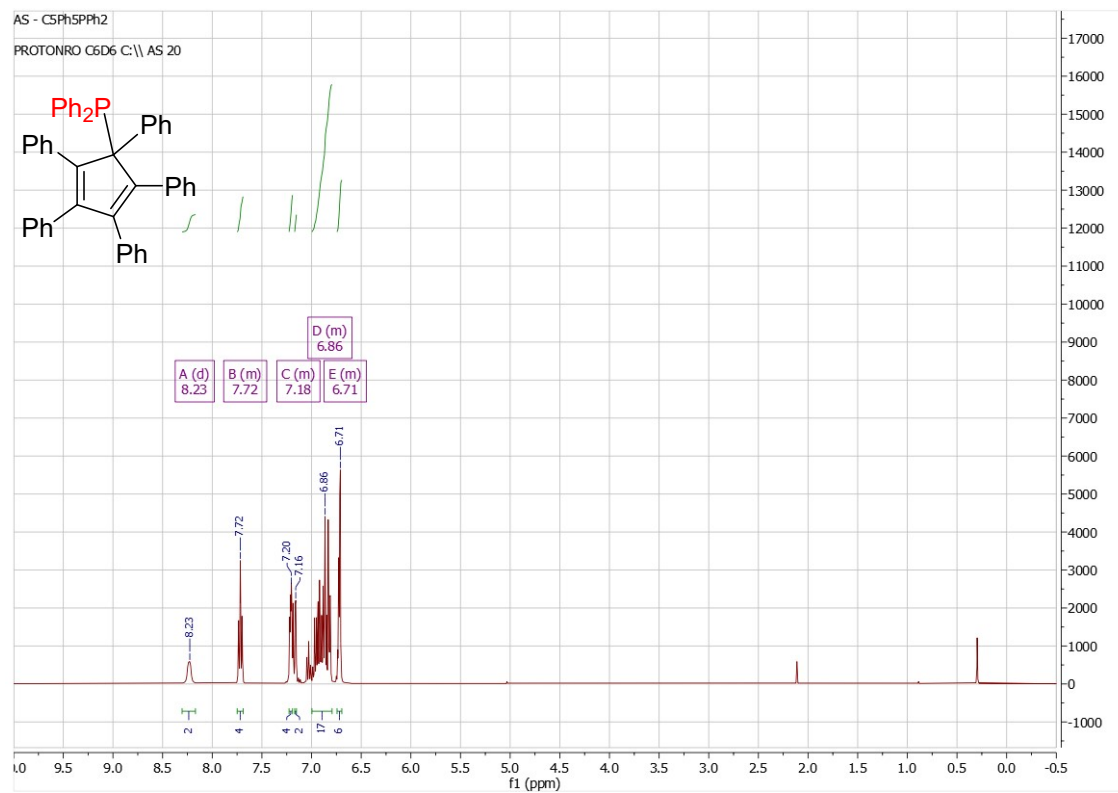


Figure S4 – ^1H NMR spectrum of $\text{C}_5\text{Ph}_5\text{PPh}_2$ (**2**) in C_6D_6

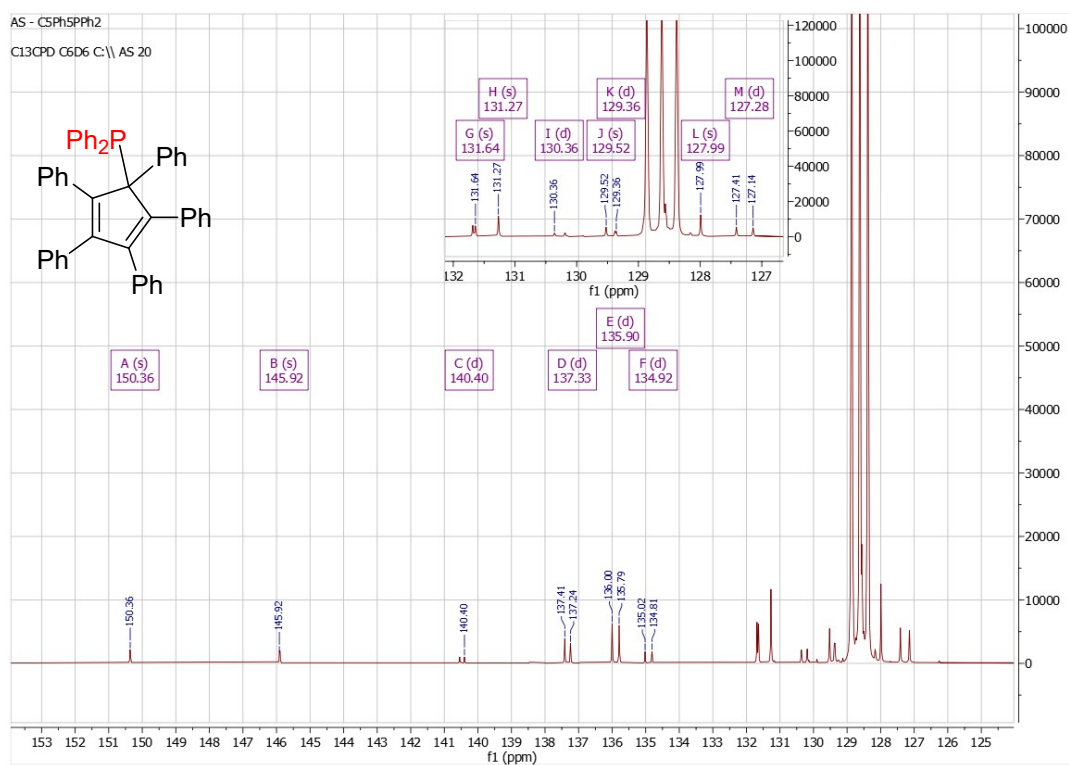


Figure S5 – ^{13}C NMR spectrum of $\text{C}_5\text{Ph}_5\text{PPh}_2$ (**2**) in C_6D_6

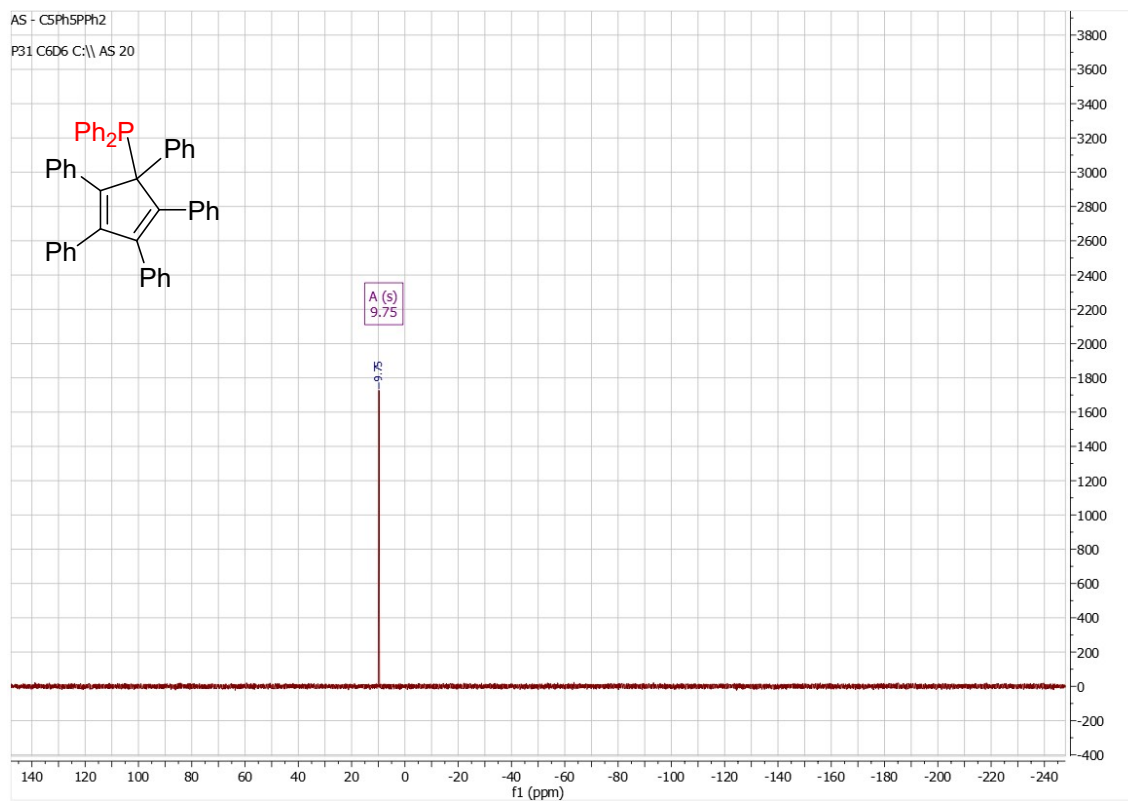


Figure S6 – ^{31}P NMR spectrum of $\text{C}_5\text{Ph}_5\text{PPh}_2$ (**2**) in C_6D_6

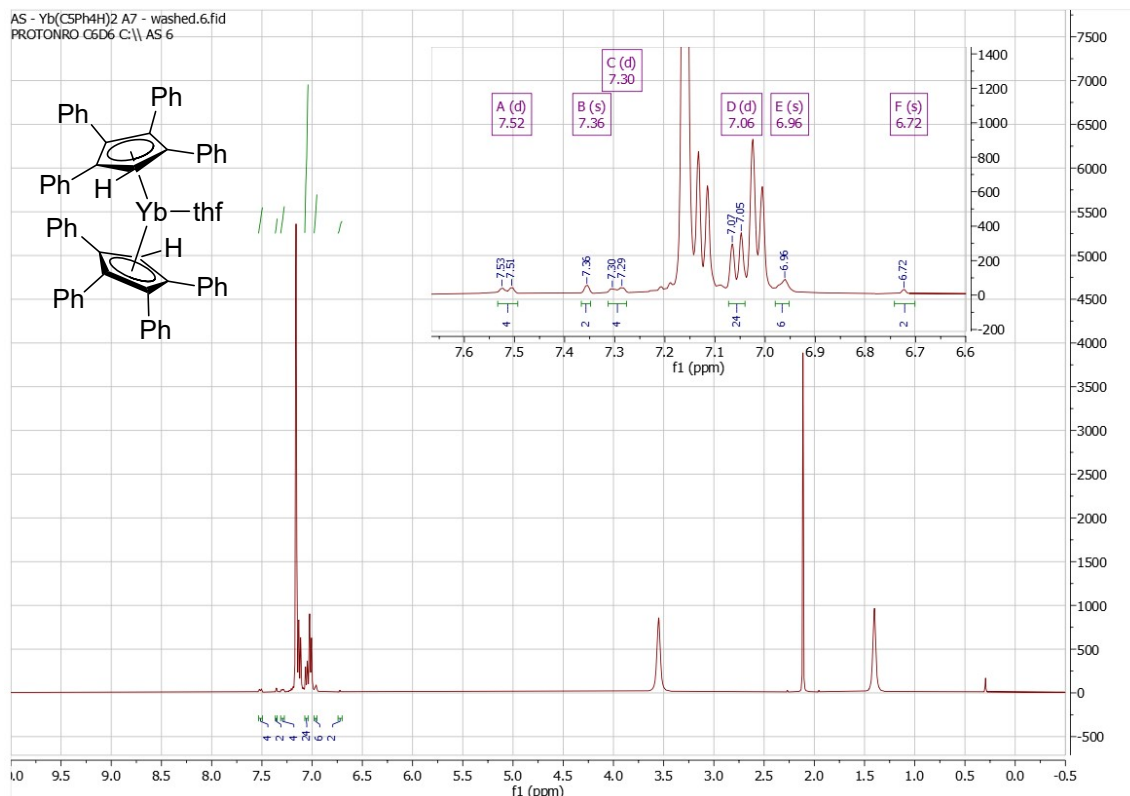


Figure S7 – ^1H NMR spectrum of $[\text{Yb}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})]$ (**5**) in C_6D_6 with expansion of aromatic region. Excess thf and toluene are present due to **5**'s sensitivity to desolvation.

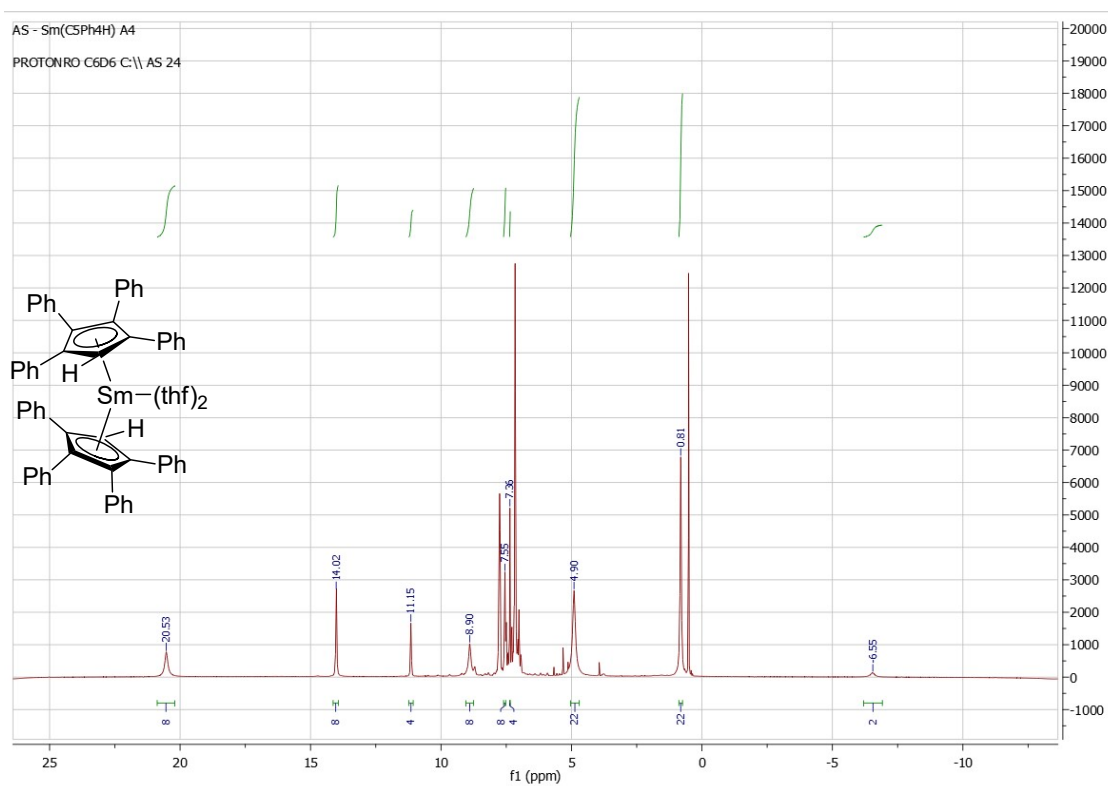


Figure S8 – ^1H NMR of crude $[\text{Sm}(\text{C}_5\text{Ph}_4\text{H})_2(\text{thf})_2]$ (**6**) in C_6D_6 containing a small excess of thf and grease.

(162 MHz, d_8 thf, 25 °C) δ -2.49 (br s) (reported at -2.49 ppm in thf- d_8)¹⁰. Upon addition of C_6D_6 to the NMR tube containing **9**, Yb-P satellites became well resolved, and a subsequent shift to 4.75 ppm observed (Figure S11).

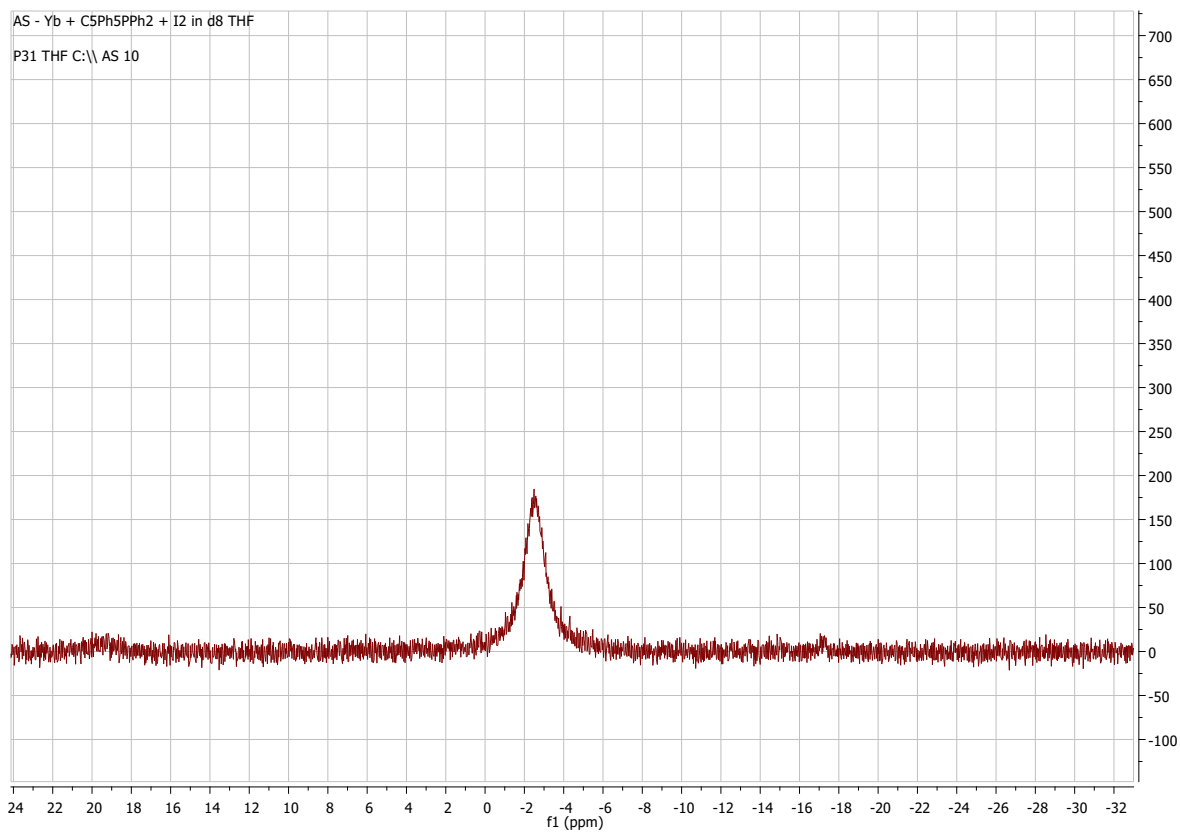


Figure S11 – ^{31}P NMR spectrum of $Yb(PPh_2)_2$ (**9**) in thf- d_8

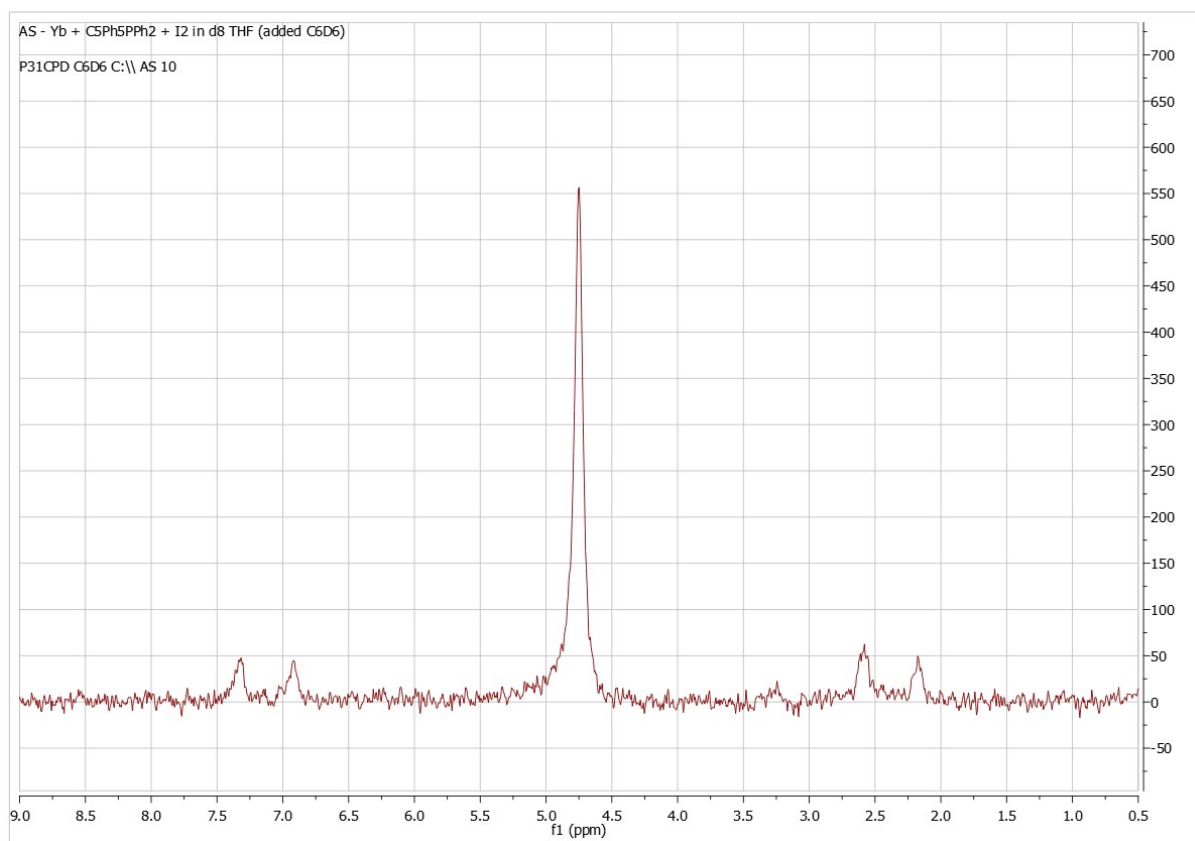


Figure S12 – ^{31}P NMR spectrum of $\text{Yb}(\text{PPh}_2)_2$ (**9**) in C_6D_6

Addition of $\text{C}_6\text{F}_5\text{H}$ to $[\text{Ln}(\text{PPh}_2)_2(\text{thf})_x]$ to form $\text{PPh}_2(\text{C}_6\text{F}_4\text{H})$ (10**)**

To the crude reaction mixture (from treatment of Ln with **2**) containing $[\text{Yb}(\text{PPh}_2)_2(\text{thf})_4]$ (or $[\text{Eu}(\text{PPh}_2)_2(\text{thf})_x]$) was added $\text{C}_6\text{F}_5\text{H}$ (1 mL, excess). A precipitate of LnF_2 immediately formed. The resulting solution was isolated by a filter cannula, and the solvent and excess $\text{C}_6\text{F}_5\text{H}$ removed under reduced pressure. The solid was analysed by ^1H , ^{19}F and ^{31}P NMR. ^1H NMR (400 MHz, C_6D_6 , 25 °C) δ 7.41 (m, 5H, ArH), 7.02 (m, 5H, ArH), 6.20 (tt, 1H, $\text{C}_6\text{F}_4\text{H}$). ^{19}F NMR (377 MHz, C_6D_6 , 25 °C) δ -128.46 (m, 2F), -137.81 (m, 2F). ^{31}P NMR (162 MHz, C_6D_6 , 25 °C) δ -23.74 (tt).

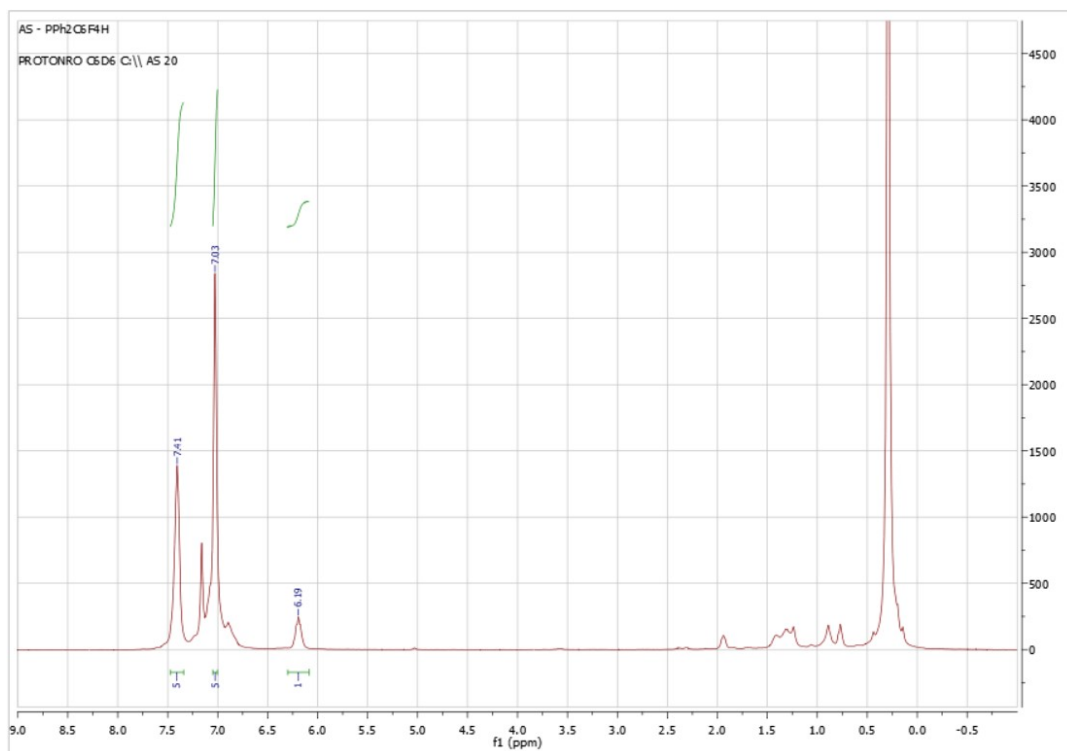


Figure S13 – ^1H NMR spectrum of $\text{PPh}_2(\text{C}_6\text{F}_4\text{H})$ (**10**) in C_6D_6

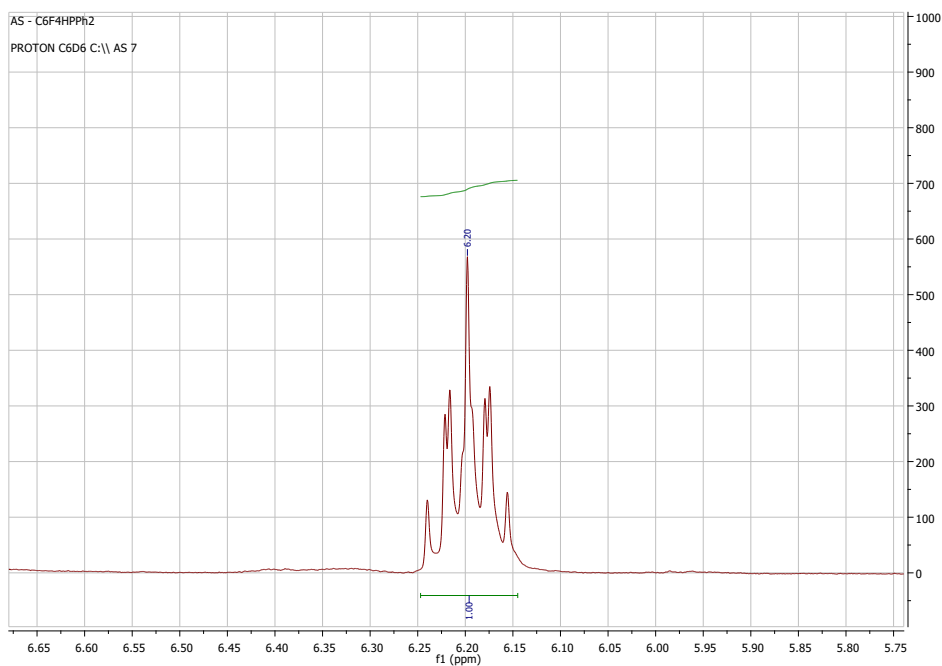


Figure S14 – Expansion of ^1H NMR spectrum of $\text{PPh}_2(\text{C}_6\text{F}_4\text{H})$ (**10**) in C_6D_6 showing characteristic proton peak of a monosubstituted 1,2,4,5 tetrafluorobenzene (tt)

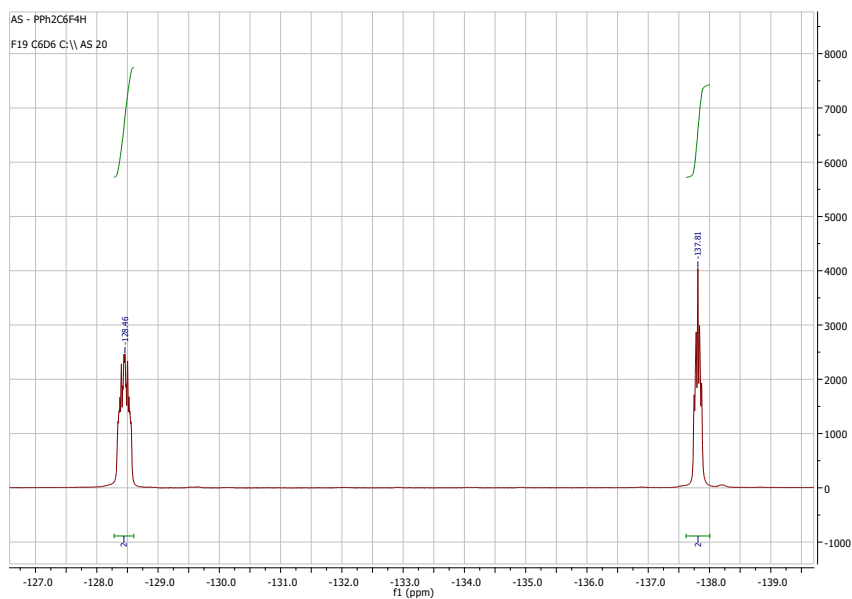


Figure S15 – ^{19}F NMR spectrum of $\text{PPh}_2(\text{C}_6\text{F}_4\text{H})$ (**10**) in C_6D_6

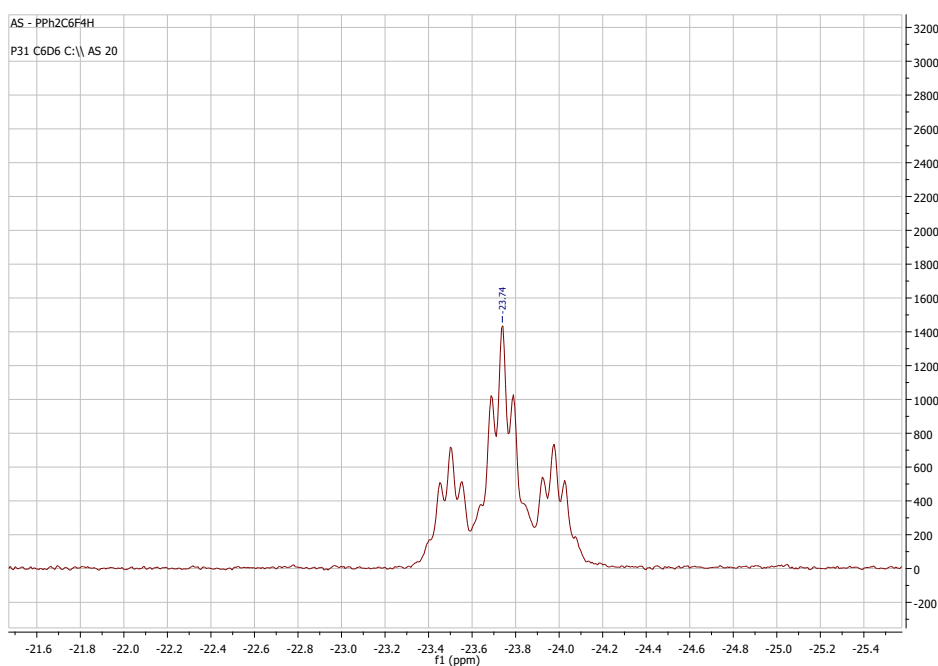


Figure S16 – ^{31}P NMR Spectrum of $\text{PPh}_2(\text{C}_6\text{F}_4\text{H})$ in C_6D_6 showing ^{31}P - ^{19}F coupling (*tt*)

Oxidation of $\text{PPh}_2(\text{C}_6\text{F}_4\text{H})$ to $\text{O}=\text{PPh}_2(\text{C}_6\text{F}_4\text{H})$ (**10'**)

The dried solid from the previous reaction was taken up into hexane (to remove it from $\text{Ln}(\text{C}_5\text{Ph}_5)_2$) and transferred into a Schlenk with excess MCPBA. The resulting solution was stirred overnight, and the crude reaction mixture analysed by ^{19}F and ^{31}P NMR. ^{19}F NMR (377 MHz, C_6D_6 , 25 °C) δ -128.74 (m, 2F), -136.19 (m, 2F). ^{31}P NMR (162 MHz, C_6D_6 , 25 °C) δ 22.08 (*tt*). MS (APCI) m/z Calc. for $\text{C}_{18}\text{H}_{11}\text{OF}_4\text{P}$ (350.2 + 1). Found 351 ($\text{M}^+ + 1$).

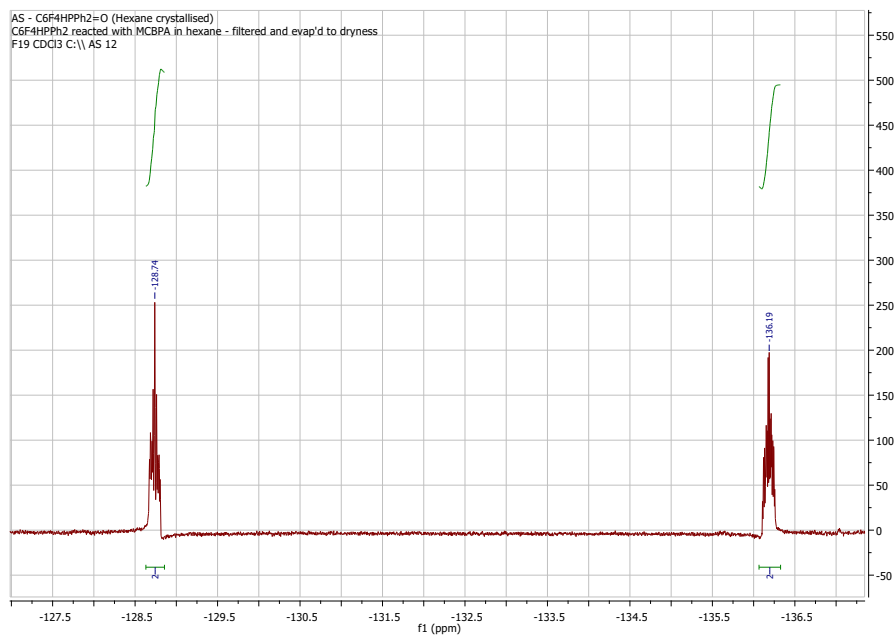


Figure S17 – ^{19}F NMR Spectrum of $\text{O}=\text{PPh}_2(\text{C}_6\text{F}_4\text{H})$ (**10'**) in C_6D_6

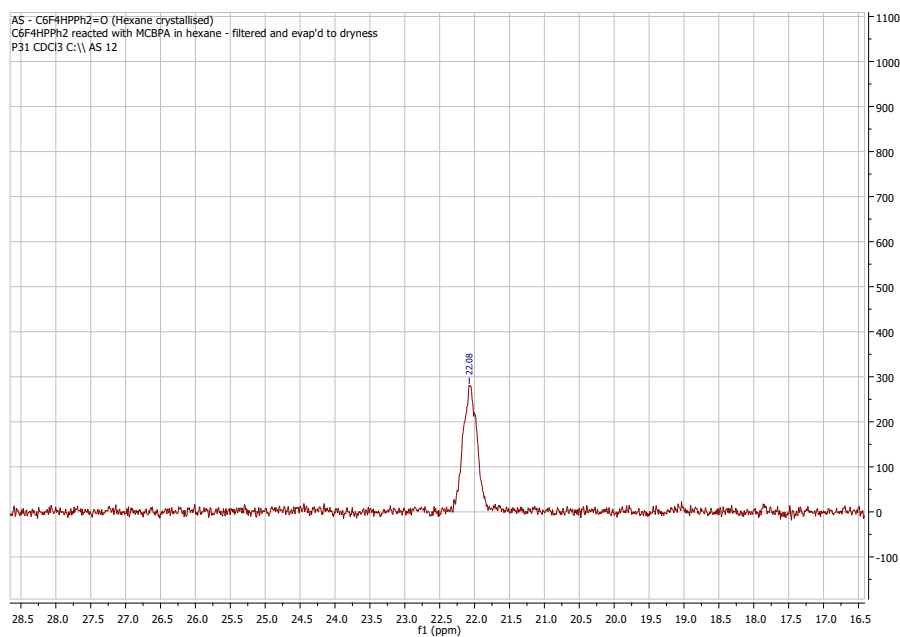


Figure S18 – ^{31}P NMR Spectrum of $\text{O}=\text{PPh}_2(\text{C}_6\text{F}_4\text{H})$ (**10'**) in C_6D_6 . Upon oxidation, a significant shift from -23.74 ppm to 22.08 ppm occurred.

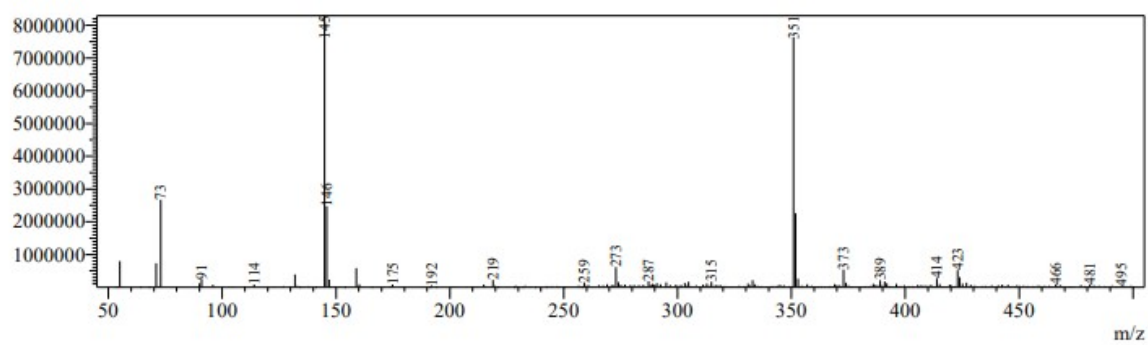


Figure S19 – Mass spectrum of $\text{O=PPh}_2(\text{C}_6\text{F}_4\text{H})$ (**10'**) showing M+1 peak of **10'** at 351 m/z

4. X-ray crystallography

Table S1. Crystal data and structural refinement for compounds 1 , 2 , 5' , and 6-8			
	1	2	5'
	C ₅ Ph ₄ HPPPh ₂	C ₅ Ph ₅ PPPh ₂	[Yb(C ₅ Ph ₄ H)I(thf) ₂] ₂ ·2 C ₆ D ₆
Empirical formula	C ₄₁ H ₃₁ P	C ₄₇ H ₃₅ P	C ₉₈ H ₉₈ I ₂ O ₄ Yb ₂
Formula weight	554.63	630.72	1939.64
Space group	P-1	P-1	P-1
a/Å	6.0760(12)	9.1150(18)	11.9588(2)
b/Å	12.198(2)	10.483(2)	12.29030(10)
c/Å	19.747(4)	19.585(4)	14.33660(10)
α/°	92.67(3)	96.14(3)	88.2270(10)
β/°	92.54(3)	90.06(3)	80.3900(10)
γ/°	90.16(3)	115.02(3)	82.4170(10)
Volume/Å ³	1460.5(5)	1683.8(7)	2059.33(4)
Z	2	2	1
ρ _{calc} /cm ³	1.261	1.244	1.564
μ/mm ⁻¹	0.123	0.115	10.367
Reflections collected	18649	49067	41407
Independent reflections	4789 [R _{int} = 0.1401, R _{sigma} = 0.1142]	6286 [R _{int} = 0.0473, R _{sigma} = 0.0208]	7811 [R _{int} = 0.0722, R _{sigma} = 0.0447]
Goodness-of-fit on F ²	1.056	1.039	1.073
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0699, wR ₂ = 0.1803	R ₁ = 0.0443, wR ₂ = 0.1206	R ₁ = 0.0340, wR ₂ = 0.0855
Final R indexes [all data]	R ₁ = 0.0898, wR ₂ = 0.1903	R ₁ = 0.0457, wR ₂ = 0.1224	R ₁ = 0.0360, wR ₂ = 0.0868

	6	7	8
	[Sm(C ₅ Ph ₅) ₂]·PhMe	[Eu(C ₅ Ph ₅) ₂]·PhMe	[Yb(C ₅ Ph ₅) ₂]·2.5C ₆ D ₆
Empirical formula	C ₈₄ H ₆₆ Sm	C ₈₄ H ₆₆ Eu	C ₉₇ H ₇₇ Yb
Formula weight	1225.71	1227.32	1415.62
Space group	P2 ₁ /c	P2 ₁ /c	P-1
a/Å	10.481(2)	10.480(2)	12.870(3)
b/Å	17.845(4)	17.830(4)	13.490(3)
c/Å	16.322(3)	16.380(3)	21.010(4)
α/°	90	90	83.15(3)
β/°	95.03(3)	94.90(3)	87.83(3)
γ/°	90	90	79.75(3)
Volume/Å ³	3041.0(11)	3049.6(11)	3563.4(13)
Z	2	2	2
ρ _{calc} /cm ³	1.339	1.337	1.319
μ/mm ⁻¹	1.013	1.076	1.362
Reflections collected	31042	55676	61483
Independent reflections	5119 [R _{int} = 0.2739, R _{sigma} = 0.1712]	6700 [R _{int} = 0.0387, R _{sigma} = 0.0208]	12701 [R _{int} = 0.0264, R _{sigma} = 0.0205]
Goodness-of-fit on F ²	0.979	1.066	1.053
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.1207, wR ₂ = 0.2836	R ₁ = 0.0538, wR ₂ = 0.1387	R ₁ = 0.0361, wR ₂ = 0.0934
Final R indexes [all data]	R ₁ = 0.1563, wR ₂ = 0.3250	R ₁ = 0.0645, wR ₂ = 0.1493	R ₁ = 0.0420, wR ₂ = 0.0972

5. ORTEP plots

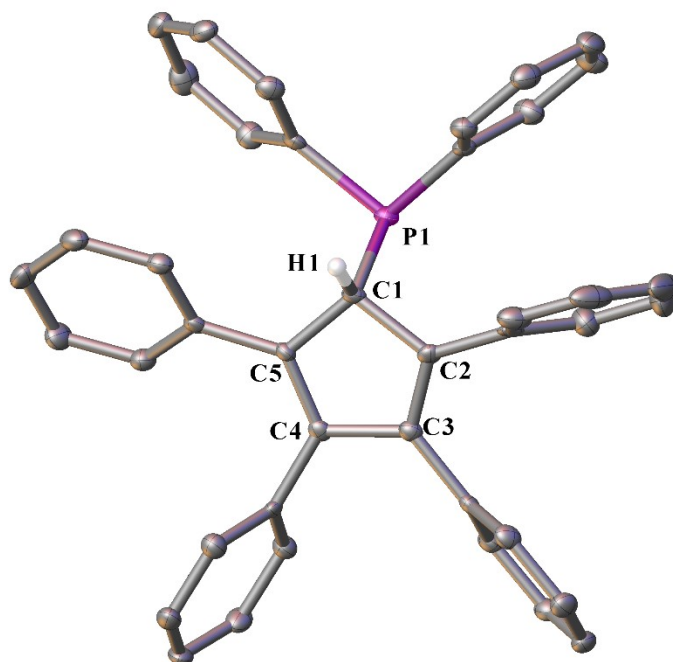


Figure S20 – ORTEP plot of $C_5Ph_4HPPH_2$ (1). Thermal ellipsoids are drawn at the 50% probability level. Phenyl hydrogen atoms are omitted for clarity.

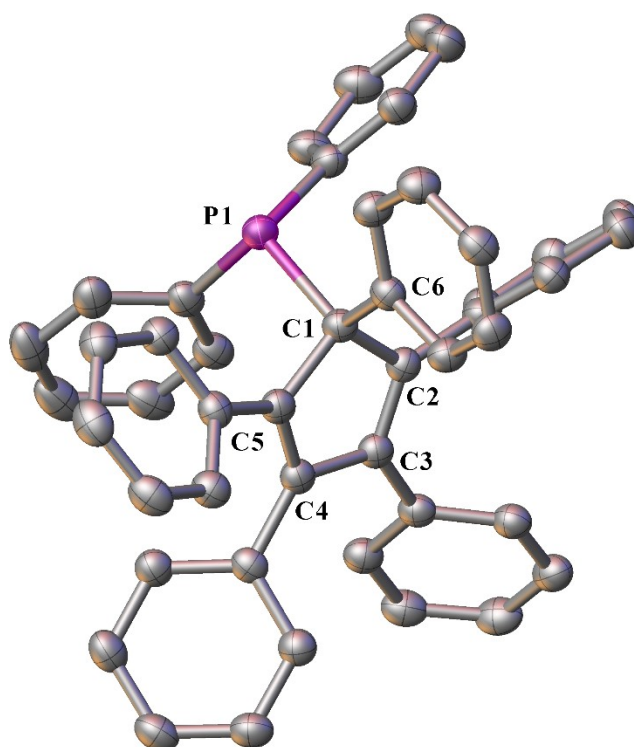


Figure S21 – ORTEP plot of $C_5Ph_5PPH_2$ (2). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

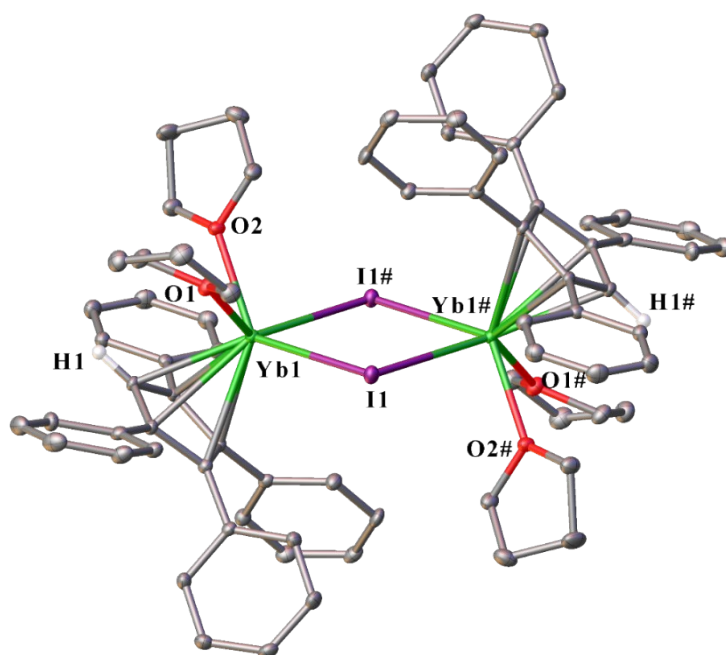


Figure S22 – ORTEP plot of **5'**. Thermal ellipsoids are drawn at the 50% probability level. Phenyl hydrogen atoms are omitted for clarity. # Generated by symmetry (symmetry operation used 1-X, 1-Y, 2-Z). Selected bond lengths (Å): Yb(1) – I(1) 3.1257(3), Yb(1)-I(1)# 3.1925(3), Yb(1)-C(centroid) 2.4748(14) Yb(1)-O(1) 2.450(2), Yb(1)-O(2) 2.403(2).

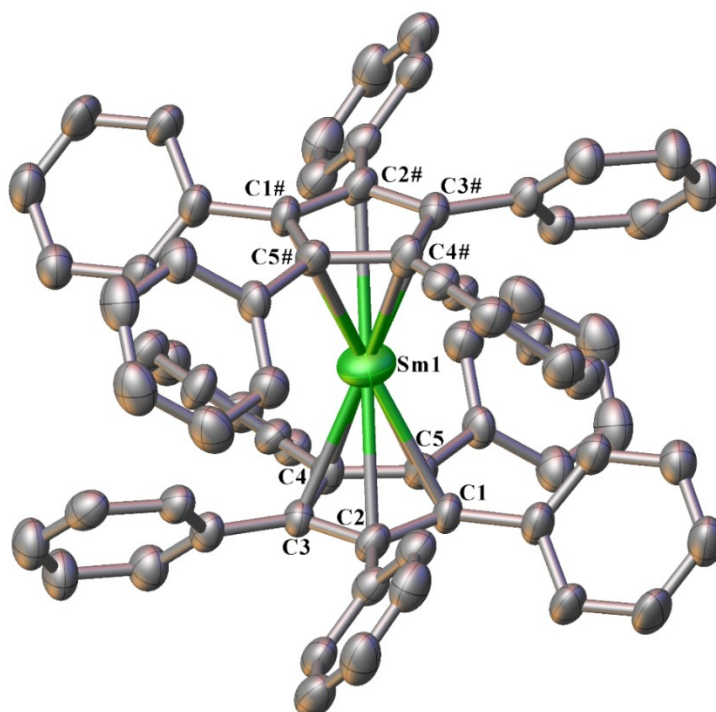


Figure S23 – ORTEP plot of **6** showing connectivity. Thermal ellipsoids are drawn at the 50% probability level. Phenyl hydrogen atoms and lattice toluene are omitted for clarity. # Generated by symmetry (symmetry operation used -X, 1-Y, 1-Z).

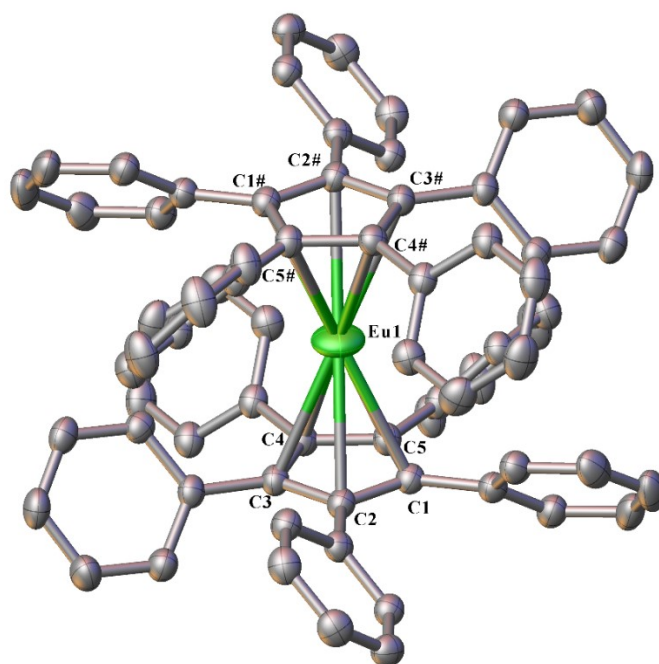


Figure S24 – ORTEP plot of **7**. Thermal ellipsoids are drawn at the 50% probability level. Phenyl hydrogen atoms and lattice toluene are omitted for clarity. # Generated by symmetry (symmetry operation used 2-X, 1-Y, 1-Z).

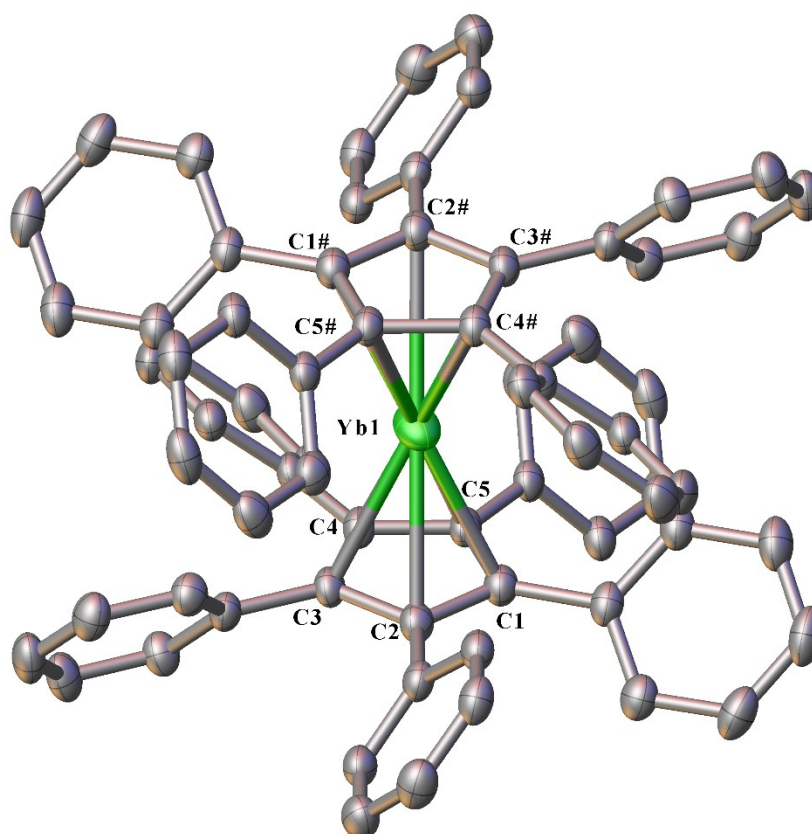


Figure S25 – ORTEP plot of **8**. Thermal ellipsoids are drawn at the 50% probability level. Phenyl hydrogen atoms and lattice C_6D_6 are omitted for clarity. # Generated by symmetry (symmetry operation used -X, 1-Y, 1-Z).

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