Thermally Stable Rare Earth Dialkyl Complexes Supported by a Novel Bis(phosphinimine)pyrrole Ligand

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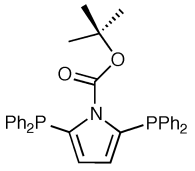
Supporting Information

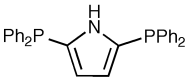
General Synthetic Procedures. All reactions were carried out under an argon atmosphere with the rigorous exclusion of oxygen and water using standard glovebox (MBraun) or high vacuum line techniques. The solvents tetrahydrofuran (THF), pentane and toluene were dried and purified using a solvent purification system (MBraun) and distilled under vacuum prior to use from sodium benzophenone ketyl (THF) or "titanocene" indicator (pentane and toluene). Deuterated solvents were dried over sodium benzophenone ketyl (benzene-d_6) or CaH_2 (chloroform-*d*), degassed *via* three freeze-pump-thaw cycles, distilled under vacuum, and stored over 4 Å molecular sieves in glass bombs under an argon atmosphere. Unless specified otherwise, solvents were introduced directly into reaction flasks by vacuum transfer with condensation at −78 °C. Samples for NMR spectroscopy were recorded on a 300 MHz Bruker Avance II (ultrashield) spectrometer (^{1}H 300.13 MHz, ^{13}C{^{1}H} 75.47 MHz, ^{31}P{^{1}H} 121.49 MHz) and referenced relative to either $SiMe_4$ through the residual solvent resonance(s) for ^{1}H and ^{13}C{^{1}H}; or to external 85% H_3PO_4 for ^{31}P{^{1}H}. All NMR spectra were recorded at ambient temperature (295 K) unless specified otherwise. Peak width at half-height is given for paramagnetically broadened resonances. Elemental analyses were performed using an Elementar Americas Vario MicroCube instrument. The reagents *para*-isopropylphenyl (Pipp) azide,[1] $Lu(CH_2SiMe_3)_3(THF)_2$,[2] $Er(CH_2SiMe_3)_3(THF)_2$,[2d] and $Sc(CH_2SiMe_3)_3(THF)_2$,[2b,3] were prepared according to literature procedures. The precursor *N*-(*tert*-butoxycarbonyl)-2,5-dibromopyrrole (**3**) was prepared by a slightly modified literature procedure: all synthetic conditions were maintained as previously reported,[4] with the exception that chloroform was used to extract the product in place of carbon tetrachloride. A comparable product yield was obtained following recrystallization from anhydrous ethanol at −35 °C. All other reagents were obtained from Aldrich Chemicals or Alfa Aesar and used as received.



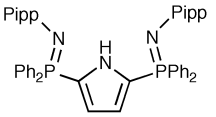
Synthesis of 2,5-Bis(diphenylphosphino)-*N*-(*tert*-butoxycarbonyl)pyrrole (4). A 2-neck round bottomed flask was charged with **3** (5.0 g, 15.4 mmol) and 200 mL of THF to give a pale yellow-beige coloured suspension. The flask was cooled to −78 °C and a hexane solution (1.6 M) of ^{n}BuLi (19.2 mL, 30.8 mmol) was added dropwise. The deep red solution was stirred at −78 °C for 1 h, after which chlorodiphenylphosphine (5.53 mL, 30.8 mmol) was added slowly by syringe. The mixture was allowed to slowly warm to ambient temperature with stirring over 18 h. The THF was removed under reduced pressure to afford a brown foamy residue. The residue was reconstituted in toluene and passed through a column of silica to remove insoluble impurities. After removal of the solvent under vacuum, a red oil remained. The oil was triturated with pentane to liberate the product as a white solid. The solid was collected by filtration and dried thoroughly under vacuum. Yield: 5.46 g (66.2%). ^{1}H NMR (benzene-d_6): δ 7.45 (m, 8H, phenyl *H*), 7.04 (ov m, 12H, phenyl *H*), 5.70 (s, 2H, pyrrole *H*), 1.07 (s, 9H, $OC(CH_3)_3$). ^{13}C{^{1}H} NMR (chloroform-*d*): δ 149.8 (s, *C*=O), 138.3 (d, $^1J_{CP}$ = 10.6 Hz, *ipso*-*C*),

136.2 (d, $^{1}J_{CP}$ = 17.5 Hz, *ipso*-*C*), 133.7 (d, J_{CP} = 20.8 Hz, phenyl *C*H), 128.6 (d, J_{CP} = 24.8 Hz, phenyl *C*H), 128.4 (s, phenyl *C*H), 122.7 (s, pyrrole *C*H), 86.4 (s, O*C*(CH$_3$)$_3$), 27.6 (s, OC(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (benzene-d_6): δ −14.5. Anal. Calcd. (%) for $C_{33}H_{31}NO_2P_2$: C, 74.01; H, 5.83; N, 2.62. Found: C, 74.02; H, 5.81; N, 2.62.

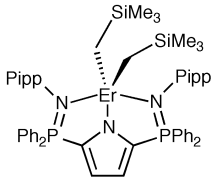
Synthesis of 2,5-Bis(diphenylphosphino)pyrrole (5). Toluene (50 mL) was added to a 500 mL bomb charged with **4** (3.34 g, 6.24 mmol) and the solution was heated to 155 ºC for 18 h. The solution was transferred by cannula to a round bottomed flask, and the solvent was then removed under vacuum leaving a yellow solid. The residue was reconstituted in a minimal amount of toluene and left at −35 ºC to crystallize. White crystals of the product were collected by filtration, washed with cold pentane and dried thoroughly under reduced pressure. Yield: 2.51 g (92.4%). ^{1}H NMR (benzene-d_6): δ 7.91 (br s, 1H, N*H*), 7.28 (m, 8H, phenyl *H*), 6.98 (m, 12H, phenyl *H*), 6.61 (dd, $^{3}J_{HP}$ = 4.1 Hz, $^{4}J_{HP}$ = 2.0 Hz, 2H, pyrrole *H*). ^{13}C{^{1}H} NMR (benzene-d_6): δ 137.9 (d, $^{1}J_{CP}$ = 9.4 Hz, phenyl *ipso*-*C*) 133.3 (d, $^{2}J_{CP}$ = 19.2 Hz, phenyl *C*H), 130.1 (dd, $^{1}J_{CP}$ = 14.8 Hz, $^{3}J_{CP}$ = 1.3 Hz, pyrrole *ipso*-*C*), 128.9 (s, phenyl *C*H), 128.8 (s, phenyl *C*H), 120.8 (dd, $^{2}J_{CP}$ = 20.9 Hz, $^{3}J_{CP}$ = 6.0 Hz, pyrrole *C*H). ^{31}P{^{1}H} NMR (benzene-d_6): δ −25.0. Anal. Calcd. (%) for $C_{28}H_{23}NP_2$: C, 77.23; H, 5.32; N, 3.22. Found: C, 77.09; H, 5.36; N, 3.49.



Synthesis of HL (6). Toluene (40 mL) was added to a 100 mL round bottomed flask charged with **5** (1.50 g, 3.44 mmol) to give a pale yellow solution. An aliquot of *para*-isopropylphenyl azide (1.11 g, 6.89 mmol) was added to the flask *via* syringe at ambient temperature. Upon addition of the azide, the solution immediately began to bubble with the evolution of nitrogen gas. The reaction mixture was stirred for 1 h, after which all volatiles were removed *in vacuo* to liberate an off-white solid. Yield: 2.38 g (98.6%). ^{1}H NMR (benzene-d_6): δ 10.47 (br s, 1H, N*H*), 7.74 (m, 8H, phenyl *H*), 7.13 (ov d, 4H, Pipp *H*), 7.06 − 6.88 (ov m, 16H, phenyl *H* + Pipp *H*), 6.52 (m, 2H pyrrole *H*), 2.77 (sp, $^{3}J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.20 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 148.9 (s, Pipp *ipso*-*C*), 138.1 (s, Pipp *ipso*-*C*), 132.0 (d, J_{CP} = 110.9 Hz, aromatic *ipso*-*C*), 132.6 (d, J_{CP} = 10.5 Hz, aromatic *C*H), 131.8 (d, J_{CP} = 2.2 Hz, aromatic *C*H), 128.8 (d, J_{CP} = 12.5 Hz, aromatic *C*H), 127.3 (s, aromatic *C*H), 126.8 (d, J_{CP} = 6.2 Hz, aromatic *ipso*-*C*), 123.6 (d, J_{CP} = 18.5 Hz, aromatic *C*H), 119.4 (dd, $^{2}J_{CP}$ = 13.3 Hz, $^{3}J_{CP}$ = 13.2 Hz, pyrrole C*H*), 33.8 (s, *C*H(CH$_3$)$_2$), 24.7 (s, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (benzene-d_6): δ −8.1. Anal. Calcd. (%) for $C_{46}H_{45}N_3P_2$: C, 78.72; H, 6.46; N, 5.99. Found: C, 78.68; H, 6.37; N, 5.76.



Synthesis of LEr(CH$_2$SiMe$_3$)$_2$ (7a). In a glovebox, toluene (1 mL) was added to a 25 mL Erlenmeyer flask charged with **6** (0.261 g, 0.372 mmol) and Er(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.213 g, 0.372 mmol) to give a cloudy orange-pink solution. The reaction mixture was stirred at ambient temperature for 30 min and rapidly clarified as the reaction progressed. The solution was filtered through a bed of Celite and the Celite was washed with a further 1 mL of toluene. The clear orange-pink filtrate was concentrated to 0.5 mL under vacuum and then left at −35 ºC to crystallize. Pale pink crystals of **7a** were collected by filtration, washed with cold pentane, and dried under reduced pressure. Yield: 0.314 g (81.0%). ^{1}H NMR (benzene-d_6): δ 86.32 (Δν$_{1/2}$ = 571 Hz), 29.75 (Δν$_{1/2}$ = 55 Hz), 17.31 (Δν$_{1/2}$ = 123 Hz), 14.64 (Δν$_{1/2}$ = 31 Hz), 9.95 (Δν$_{1/2}$ = 20 Hz), 8.57 (Δν$_{1/2}$ = 22 Hz), 8.15 (Δν$_{1/2}$ = 24 Hz), 7.55 (Δν$_{1/2}$ = 66 Hz), −23.06 (Δν$_{1/2}$ = 108 Hz), −184.58 (Δν$_{1/2}$ = 2000 Hz). ^{31}P{^{1}H} NMR (benzene-d_6): δ −0.29. Anal. Calcd. (%) for $C_{54}H_{66}ErN_3P_2Si_2$: C, 62.21; H, 6.38; N, 4.03. Found: C, 62.42; H, 6.23; N, 4.17.



Synthesis of LLu(CH$_2$SiMe$_3$)$_2$ (7b). In a glovebox, toluene (2 mL) was added to a 25 mL Erlenmeyer flask charged with **6** (0.604 g, 0.861 mmol) and Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.502 g, 0.864 mmol) to give a cloudy colourless solution. The reaction mixture was stirred at ambient temperature for 30 min and rapidly clarified as the reaction progressed to generate a clear pale yellow appearance. The solution was filtered through a bed of Celite and the Celite was washed with a further 1 mL of toluene. The clear yellow filtrate was concentrated to 1 mL under vacuum and then left at −35 ºC to crystallize. Colourless crystals of **7b** were collected by filtration, washed with cold pentane, and dried under reduced pressure. Yield: 0.745 g (82.4%). ^{1}H NMR (benzene-d_6): δ 7.71 (ddd, $^3J_{HP}$ = 12.3 Hz, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.5 Hz, 8H, *o*-phenyl *H*) 7.36 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HP}$ = 2.1 Hz, 4H, *o*-Pipp *H*), 7.05 (d, $^3J_{HH}$ = 8.3 Hz, 4H, *m*-Pipp *H*), 7.03–6.90 (ov m, 12H, *m*-phenyl + *p*-phenyl *H*), 6.62 (dd, $^3J_{HP}$ = 2.3 Hz, $^4J_{HP}$ = 1.2 Hz, 2H, pyrrole *H*), 2.66 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 0.18 (s, 18H, Si(C*H*$_3$)$_3$), −0.20 (s, 4H, C*H*$_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 144.0 (m, aromatic *ipso*-*C*), 142.6 (d, J_{CP} = 5.7 Hz, aromatic *ipso*-*C*), 133.3 (d, J_{CP} = 10.3 Hz, aromatic *C*H), 132.4 (s, aromatic *C*H), 131.4 (s, aromatic *ipso*-*C*), 130.2 (s, aromatic *ipso*-*C*), 128.7 (d, J_{CP} = 12.3 Hz, aromatic *C*H), 128.6 (d, J_{CP} = 7.7 Hz, aromatic *C*H), 127.5 (d, J_{CP} = 1.0 Hz, aromatic *C*H), 119.3 (dd, $^2J_{CP}$ = 28.0 Hz, $^3J_{CP}$ = 10.7 Hz, pyrrole *C*H), 41.3 (s, *C*H$_2$), 33.8, (s, *C*H(CH$_3$)$_2$), 24.2 (s, CH(*C*H$_3$)$_2$), 4.9 (s, Si(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (benzene-d_6): δ 25.0. Anal. Calcd. (%) for C$_{54}$H$_{66}$LuN$_3$P$_2$Si$_2$: C, 61.76; H, 6.33; N, 4.00. Found: C, 61.56; H, 5.98; N, 4.08.

Synthesis of LSc(CH$_2$SiMe$_3$)$_2$ (7c). In a glovebox, toluene (2 mL) was added to a flask charged with **6** (0.377 g, 0.537 mmol) and Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.242 g, 0.537 mmol). The solution was stirred at ambient temperature for 30 min and rapidly clarified as the reaction progressed to generate a clear yellow appearance. The solution was filtered through a bed of Celite and the Celite was washed with a further 1 mL of toluene. All volatiles were removed from the filtrate under reduced pressure to afford a yellow residue. The product was reconstituted in toluene (0.5 mL) and layered with pentane (0.5 mL) at ambient temperature to recrystallize. After 1 h, the vessel was cooled to −35 ºC for 17 h to promote further crystal growth. Yellow crystals of **7c** were collected by filtration, washed with cold pentane, and dried under reduced pressure. Yield: 0.400 g (80.9%). ^{1}H NMR (benzene-d_6): δ 7.73 (ddd, $^3J_{HP}$ = 12.3 Hz, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.5 Hz, 8H, *o*-phenyl *H*) 7.41 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HP}$ = 2.2 Hz, 4H, *o*-Pipp *H*), 7.06 (d, $^3J_{HH}$ = 8.0 Hz, 4H, *m*-Pipp *H*), 7.03-6.90 (ov m, 12H, *m*-phenyl + *p*-phenyl *H*), 6.61 (dd, $^3J_{HP}$ = 2.2 Hz, $^4J_{HP}$ = 1.2 Hz, 2H, pyrrole *H*), 2.68 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 0.55 (s, 4H, C*H*$_2$), 0.11 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 144.0 (m, aromatic *ipso*-*C*), 143.7 (d, J_{CP} = 6.1 Hz, aromatic *ipso*-*C*), 133.4 (d, J_{CP} = 10.6 Hz, aromatic *C*H), 132.3 (d, J_{CP} = 1.1 Hz, aromatic *C*H), 131.2 (s, aromatic *ipso*-*C*), 130.0 (s, aromatic *ipso*-*C*), 129.6 (d, J_{CP} = 7.5 Hz, aromatic *C*H), 128.7 (d, J_{CP} = 12.4 Hz, aromatic *C*H), 127.3 (dd, J_{CP} = 1.2 Hz, J_{CP} = 1.1 Hz, aromatic *C*H), 118.6 (dd, J_{CP} = 26.7 Hz, J_{CP} = 10.8 Hz, pyrrole *C*H), 40.5 (br s, *C*H$_2$), 33.9, (s, *C*H(CH$_3$)$_2$), 24.2 (s, CH(*C*H$_3$)$_2$), 4.4 (s, Si(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (benzene-d_6): δ 23.8. Anal. Calcd. (%) for C$_{54}$H$_{66}$N$_3$P$_2$ScSi$_2$: C, 70.48; H, 7.23; N, 4.57. Found: C, 70.45; H, 7.18; N, 4.68.

General Crystallographic Details for 6, 7a and 7b. Recrystallization of compound **6** from a concentrated toluene solution at 295 K, **7a** from a concentrated mixture of toluene and THF at 238 K and **7b** from a concentrated mixture of toluene and THF at 295 K afforded single crystals suitable for X-ray diffraction. Crystals were coated in dry Paratone oil under an argon atmosphere and mounted onto a glass fibre. Data were collected at 173 K using a Bruker SMART APEX II diffractometer (Mo Kα radiation, λ = 0.71073 Å) outfitted with a CCD area-detector and a KRYO-FLEX liquid nitrogen vapour cooling device. A data collection strategy using ω-2θ scans at 0.5° steps yielded full

hemispherical data with excellent intensity statistics. Unit cell parameters were determined and refined on all observed reflections using APEX2 software.[5] Data reduction and correction for Lorentz polarization were performed using SAINT-Plus software.[6] Absorption corrections were applied using SADABS.[7] The structures were solved by direct (**6**) or Patterson (**7a** and **7b**) methods and refined by the least squares method on F^2 using the SHELXTL software suite.[8] Disordered atoms (*vide infra*) were modeled as isotropic mixtures. All other non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and isotropically refined as riding models to their parent atoms. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table S1.

Specific Crystallographic Refinement Details for 6. A high-quality data set was collected (R_{int} = 0.0344), however, many of the organic substituents were disordered. The 4-isopropylphenyl group bound to N3 and both phenyl rings attached to P1 were disordered over two positions. These moieties were modeled as isotropic mixtures at either 50:50 or 60:40 occupancy, and geometric restraints were applied in order to obtain reasonable bond distances. A molecule of toluene was present in the unit cell, however, it was poorly defined and no suitable model for its refinement was determined. The SQUEEZE subroutine of the PLATON program was used to remove the electron density associated with this molecule from the reflection data.[9] Reduced residuals were observed in the final SQUEEZED structure confirming that the uncertainty in the model was a result of the disordered solvent.

A thermal ellipsoid plot (50% probability) of **6** is depicted in Figure S1. In the solid-state, **6** assembles into centrosymmetric hydrogen-bonded pairs, with the pyrrole N–H on each molecule associating with an imine nitrogen (N3) on the other (d(N···N) = 2.851(3) Å). A packing diagram depicting this interaction is illustrated in Figure S2.

Specific Crystallographic Refinement Details for 7a. In the refinement of **7a**, various substituents (one phenyl ring: C23, 38% / C23b, 62%; one 4-isopropylphenyl ring: C38, 51% / C38b, 49%; and one trimethylsilyl group: Si1, 61% / Si1b, 39%) were disordered over two positions and were modeled as isotropic mixtures. A thermal ellipsoid plot (50% probability) of **7a** is depicted in Figure S3.

Specific Crystallographic Refinement Details for 7b. In the refinement of **7b**, various substituents (one phenyl ring: C5, 62% / C5b, 38%; one 4-isopropylphenyl ring: C29, 49% / C29b, 51%; and one trimethylsilyl group: Si2, 57% / Si2b, 43%) were disordered over two positions and were modeled as isotropic mixtures. A thermal ellipsoid plot (50% probability) of **7b** is depicted in Figure S4.

Table S1. Summary of crystallography data collection and structure refinement for compounds 6, 7a and 7b

	6[a]	**7a**	**7b**
Formula	$C_{46}H_{45}N_3P_2$	$C_{54}H_{66}ErN_3P_2Si_2$	$C_{54}H_{66}LuN_3P_2Si_2$
FW /g·mol^{-1}	701.79	1042.48	1050.19
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*−1	*P*−1	*P*−1
a /Å	12.9263(2)	9.729(5)	9.7163(6)
b /Å	14.5326(2)	12.188(6)	12.1266(7)
c /Å	14.8331(3)	24.287(11)	24.2569(14)
α /°	112.5870(10)	84.796(5)	84.9530(10)
β /°	103.5210(10)	78.920(5)	78.9220(10)
γ /°	108.7700(10)	69.550(5)	69.4640(10)
Volume /Å^3	2223.03(8)	2647(2)	2625.9(3)
Z	2	2	2
D_{calc} /g·cm^{-3}	1.048	1.308	1.328
μ /mm^{-1}	0.129	1.727	2.023
Crystal size /mm	0.30 × 0.30 × 0.10	0.47 × 0.09 × 0.07	0.31 × 0.22 × 0.13
Crystal colour	colourless	pale pink	colourless
Crystal habit	block	needle	prism
θ range /°	1.63 to 27.54	1.71 to 26.37	1.79 to 27.10
N	36845	34897	37480
N_{ind}	10171	10778	11526
Data/restraints/parameters	10171 / 42 / 439	10778 / 0 / 548	11526 / 0 / 548
GoF on F^2	1.045	1.022	1.023
R_1 (I>2σ(I))[b]	0.0709	0.0365	0.0300
wR_2 (I>2σ(I))[c]	0.1723	0.0818	0.0721
R_1 (all data)[b]	0.0950	0.0484	0.0346
wR_2 (all data)[c]	0.1821	0.0868	0.0746
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ /e·Å^{-3}	0.491 and −0.431	0.827 and −0.814	1.124 and −0.853

Notes: [a]A highly disordered solvent molecule was removed from the reflection file using the SQUEEZE subroutine of PLATON; [b]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [c]$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

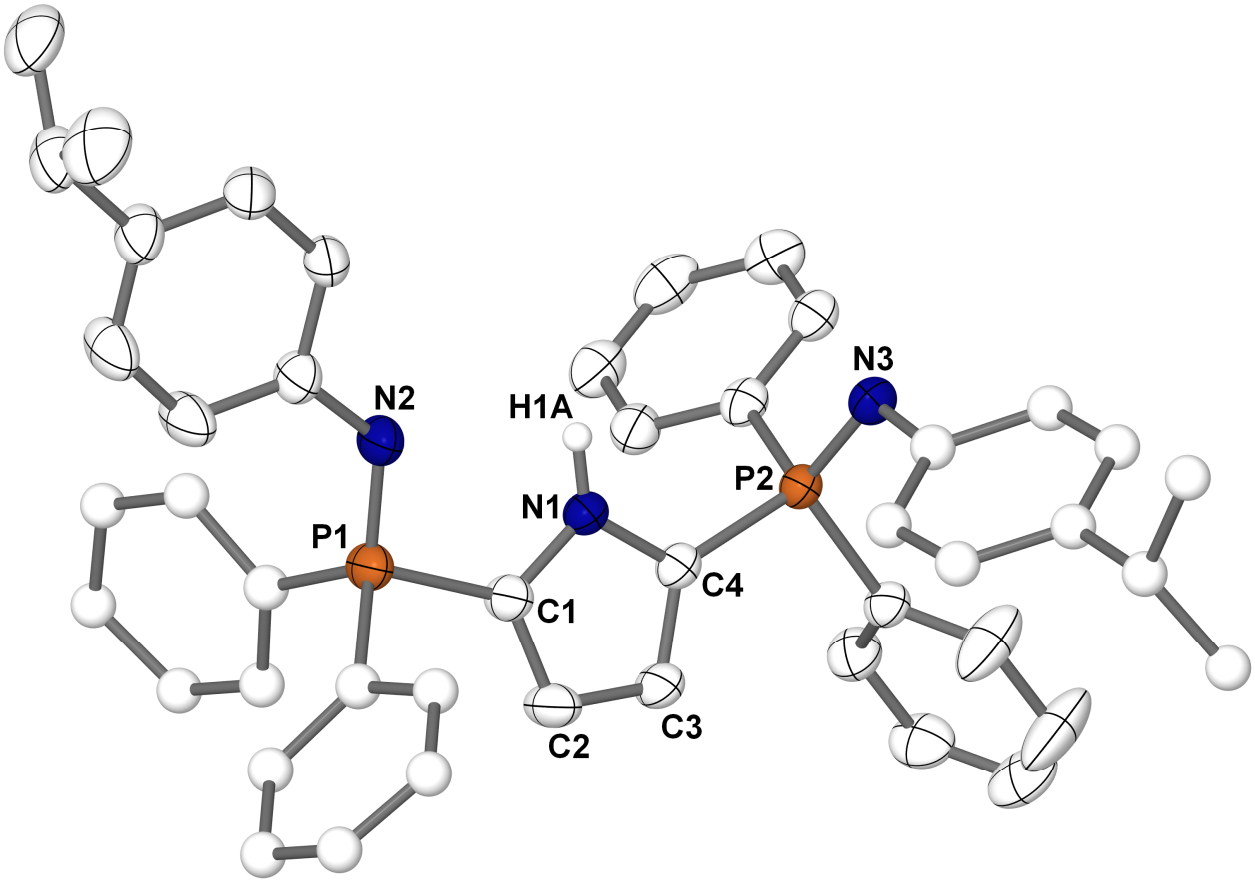


Figure S1. Thermal ellipsoid plot (50% probability) of H**L** (**6**) with hydrogen atoms (except H1A) omitted for clarity. Disordered atoms are depicted as spheres of arbitrary radius.

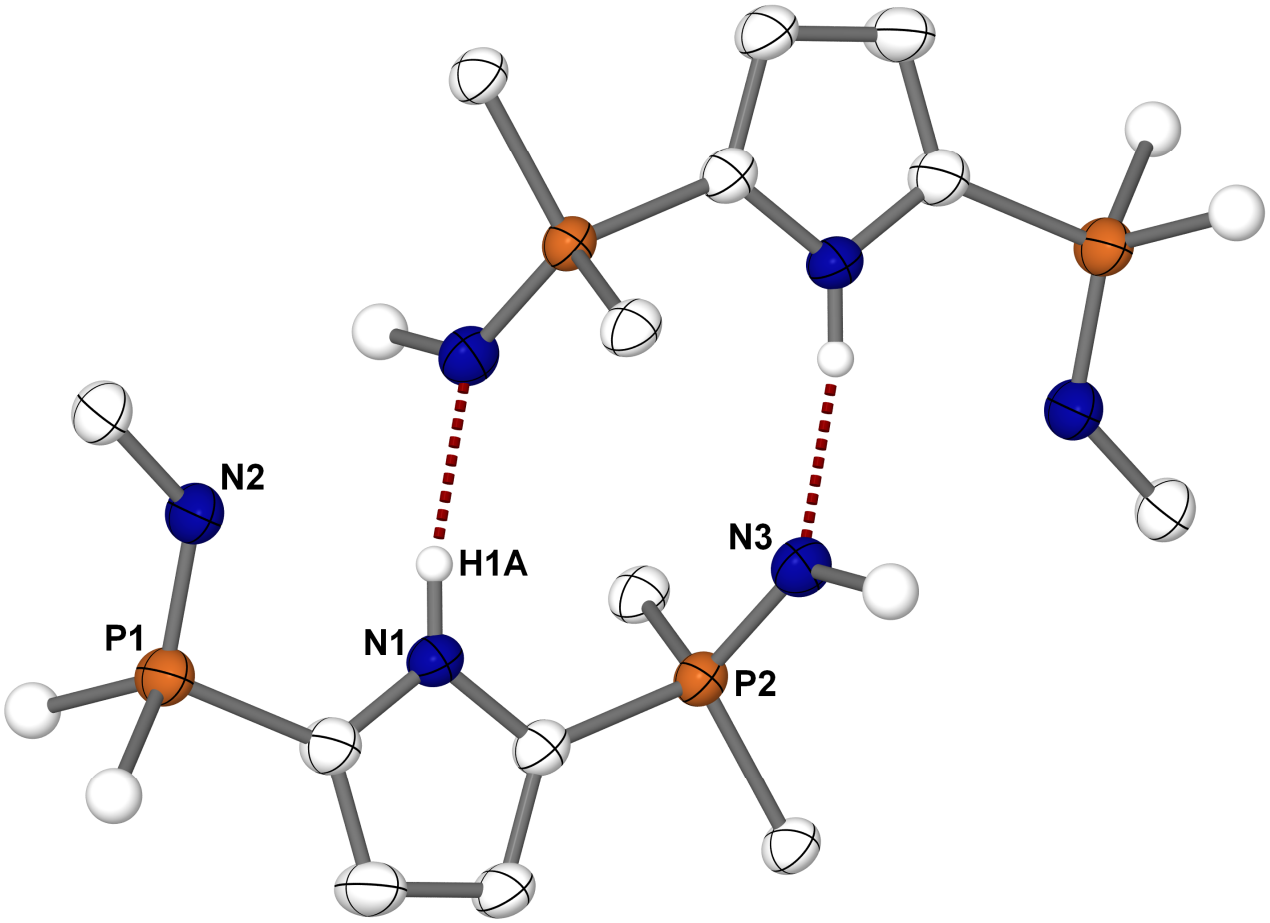


Figure S2. Packing diagram of H**L** (**6**) with hydrogen atoms (except H1A), phenyl and para-isopropylphenyl rings (except for ipso carbons) omitted for clarity.

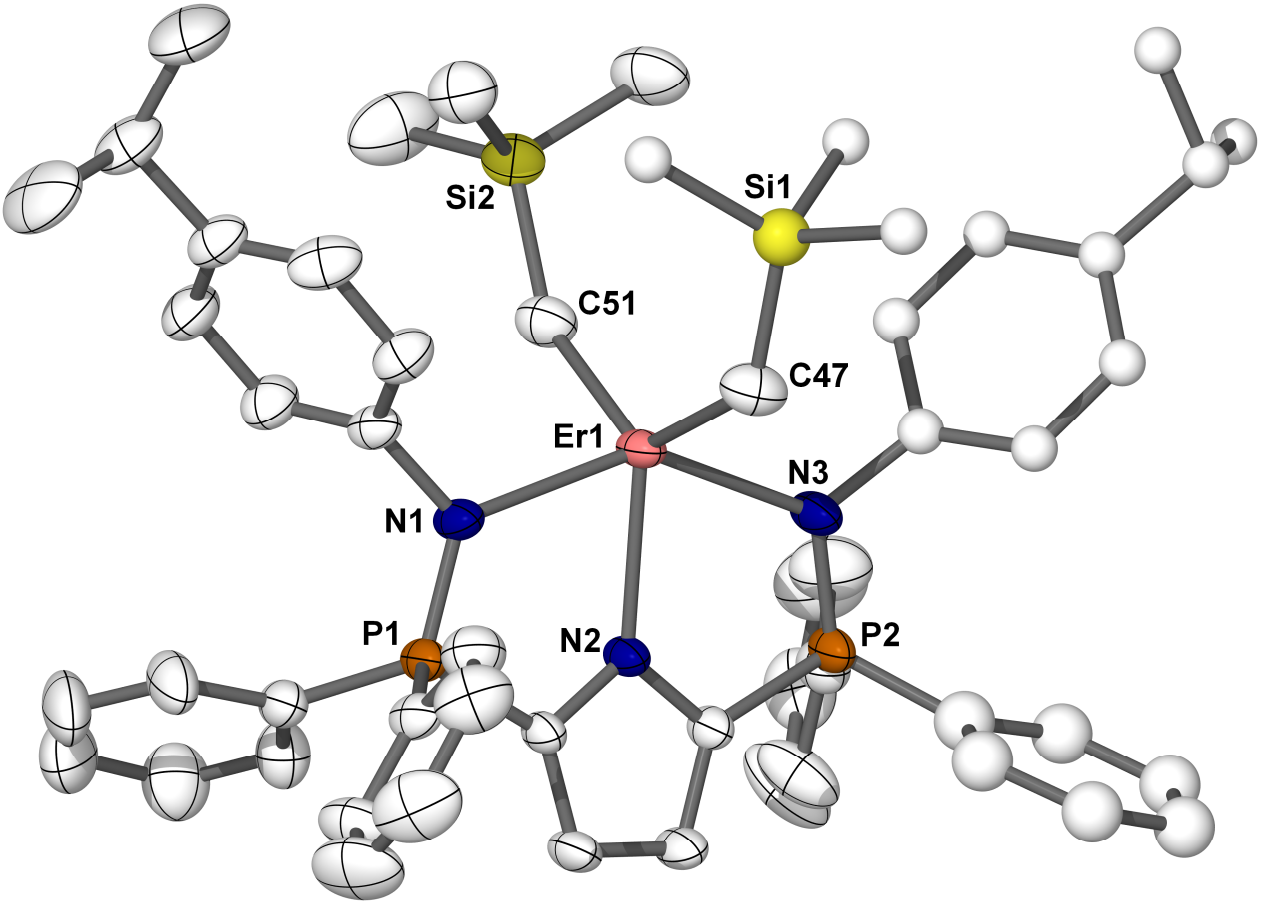


Figure S3. Thermal ellipsoid plot (50% probability) of **L**Er(CH_2SiMe_3)$_2$ (**7a**) with hydrogen atoms omitted for clarity. Disordered atoms are depicted as spheres of arbitrary radius.

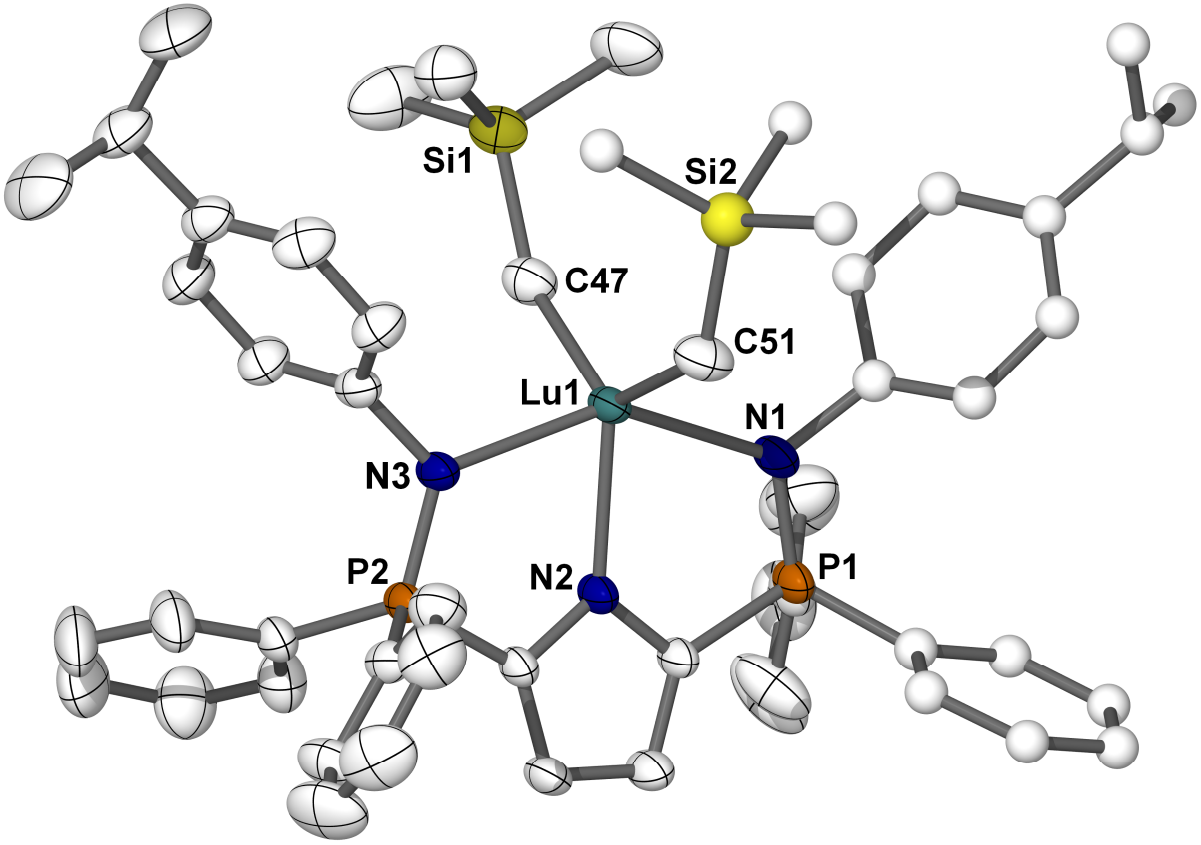


Figure S4. Thermal ellipsoid plot (50% probability) of **L**Lu(CH_2SiMe_3)$_2$ (**7b**) with hydrogen atoms omitted for clarity. Disordered atoms are depicted as spheres of arbitrary radius.

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