A Lanthanide Phosphinidene Complex: Synthesis, Structure, and Phospha-Wittig Reactivity

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Supporting Information

General Synthetic Considerations. All reactions and manipulations were carried out using a Vacuum Atmospheres (MO 40-2 Dri-train) recirculating nitrogen atmosphere drybox, or using standard Schlenk and high vacuum line techniques. Glassware was dried at 150 °C before use. ^{1}H, $^{13}C\{^{1}H\}$, DEPT-90 and DEPT-135 spectra were collected using a Bruker Avance 300 MHz spectrometer. ^{1}H NMR chemical shifts were referenced to the protio solvent impurity in benzene-d_6 at δ 7.16 ppm or THF-d_8 at δ 3.58 ppm. $^{13}C\{^{1}H\}$ NMR chemical shifts were referenced to the solvent signal in benzene-d_6 at δ 128.39 ppm or in THF-d_8 at δ 67.40 ppm. For ^{31}P NMR spectra, H_3PO_4 was used as an external reference at δ 0.00 ppm. $^{13}C\{^{1}H\}$ NMR assignments were confirmed through the use of DEPT-90 and DEPT-135 NMR experiments.

Melting points were determined with a Mel-Temp II capillary melting point apparatus equipped with a Fluke 51 II K/J thermocouple using capillary tubes flame-sealed under nitrogen; values are uncorrected. Elemental Analyses were performed at the University of California, Berkeley Microanalytical Facility on a Perkin-Elmer Series II 2400 CHNS analyzer.

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich), 4 Å molecular sieves (Aldrich), and alumina (Brockman I, Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Anhydrous toluene (Aldrich), anhydrous hexanes (Aldrich), anhydrous diethyl ether (Aldrich), anhydrous THF (Aldrich) and hexamethyldisiloxane (Aldrich) were dried over KH for 24 hours, passed through a column of activated alumina and stored over activated 4 Å molecular sieves prior to use. Benzene-d_6 (Aldrich) and $CDCl_3$ were dried over activated 4 Å molecular sieves prior to use. THF-d_8 (CIL) was dried over a Na mirror prior to use. $LiCH_2SiMe_3$ was purchased as a solution (1.0M in pentane, Aldrich), which was filtered through Celite and isolated as a

white powder upon removal of volatiles under dynamic vacuum. [{2-Br-4-Me-C_6H_3}$_2$N]H and [{2-(^{i}Pr$_2$P)-4-Me-C_6H_3}$_2$N]H (**1**) were prepared according to literature procedures.[1]

Synthesis of Lu(CH_2SiMe_3)$_3$(THF)$_2$. This procedure is slightly modified from the one presented by Okuda and co-workers.[2] A 125 mL side-arm flask was charged with $LuCl_3$ (4.99 g, 17.74 mmol), THF (50 mL) and a magnetic stir bar. The suspension was stirred and heated to 60°C for 30 minutes, after which the stirring was stopped and the suspension was allowed to cool to ambient temperature. The mixture was then cooled to -35°C and to the stirring mixture was added $LiCH_2SiMe_3$ (5.01 g, 53.21 mmol) and the mixture allowed to warm to ambient temperature and stirred overnight to yield a clear, colorless solution. The volatiles were removed under reduced pressure to give a white colored oil. The oil was stirred with pentane (75 mL) for one hour and the pentane solution was filtered through a sintered glass filter frit topped with a layer of Celite. The remaining white oil was washed again with pentane (50 mL) and the solution was filtered again. Removal of pentane under reduced pressure gave Lu(CH_2SiMe_3)$_3$(THF)$_2$ as a fluffy, white solid (5.856 g, 57%). ^{1}H NMR data match those reported in the literature.[2] ^{1}H NMR (C_6D_6, 298K): δ 3.95 (m, 8H, THF), 1.31 (m, 8H, THF), 0.29 (s, 27H, $CH_2Si\mathit{Me}_3$), -0.90 (s, 6H, $C\mathit{H}_2SiMe_3$). ^{13}C{^{1}H} NMR (C_6D_6, 298K): δ 71.28 (s, CH_2-THF), 42.11 (s, $\mathit{C}H_2SiMe_3$), 25.42 (s, CH_2-THF), 5.15 (s, $CH_2Si\mathit{Me}_3$).

Synthesis of MesPH$_2$. This is a modification of an earlier published procedure.[3] To a cooled (-78 °C) suspension of $LiAlH_4$ (5.27 g, 0.139 mol) in Et_2O (150 mL) was added dropwise a solution of $MesPCl_2$[4] (38.40 g, 0.173 mol) in Et_2O (150 mL). After the addition was complete (ca. 1 h), the reaction was warmed to room temperature (ca. 1 h). ^{31}P NMR spectroscopy of an aliquot removed from the reaction mixture confirmed that the phosphine had been formed quantitatively. Degassed water (ca. 200 mL) was added to quench residual aluminum hydrides.

(***CAUTION:*** *extreme care should be taken when adding the first few mL of water since the quenching is highly exothermic and H_2 is evolved*). The Et_2O layer was separated and the aqueous layer was extracted with a further 150 mL of Et_2O. The organic layers were combined, filtered, dried with $MgSO_4$, and the Et_2O was removed under reduced pressure. The product was purified by vacuum distillation (65–75 °C, 1 mm Hg). Yield: 17.72 g (67 %). ***CAUTION:*** *The product is pyrophoric and very malodorous.* ^{31}P NMR (C_6D_6): δ –155.4 (t, $^1J_{PH}$ = 204 Hz); ^{1}H NMR (C_6D_6): δ 6.70 (s, 2H, *m*-Mes), 3.60 (d, $^1J_{PH}$ = 203 Hz, 2H, -PH_2), 2.21 (s, 6H, *o*-CH_3), 2.09 (s, 3H, *p*-CH_3).

Synthesis of [{2-(Ph_2P)-4-Me-C_6H_3}$_2$N]H (2).[5] To a solution of [2-Br-4-Me-C_6H_3]$_2$NH (710 mg, 2.0 mmol) in Et_2O (50 mL) at –35 ºC was slowly added *n*-BuLi (2.5 mL of 2.5M solution in hexanes, 6.25 mmol). The mixture was allowed to warm up to ambient temperature and stirred for 3 h, and then it was cooled down to –35ºC. Ph_2PCl (1.13 mL, 6.30 mmol) was slowly added to the mixture and it was allowed to warm up to ambient temperature while stirring. After 20 hours, excess aqueous HCl (2 mL) was added to the reaction mixture and the mixture was allowed to stir 0.5 h. Na_2CO_3 solid was added to mixture until the *pH* value of organic phrase equaled 7. All of the volatiles were removed under reduced pressure, and the residue was extracted with toluene (50 mL) and the precipitate was filtered off. The filtrate was collected, and the volatiles were removed under reduced pressure. The resulting solid was washed with 2 x 5 mL cold ethanol and then dried under dynamic vacuum to afford a white solid (760 mg, 68 % yield). ^{1}H NMR (C_6D_6, 298K): δ 7.34 (m, 8H, Ar-*H*), 7.26 (m, 2H, Ar-*H*), 7.08 (t, 1H, J = 6 Hz, N-*H*), 7.01 (m, 12H, Ar-*H*), 6.92 (m, 2H, Ar-*H*), 6.84 (d, 2H, J = 8 Hz, Ar-H), 1.92 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298K): δ 144.97 (d, 21.0 Hz, quat C_{Ar}), 136.38 (d, 9.1 Hz, quat C_{Ar}),

134.56 (s, C_{Ar}), 133.70 (d, 20.5 Hz, C_{Ar}), 130.79 (s, quat C_{Ar}), 130.72 (s, C_{Ar}), 128.69 (m, C_{Ar}), 118.76 (s, C_{Ar}), 21.95 (s, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 298K): δ –18.9.

Synthesis of [{2-(^{i}Pr$_2$P)-4-Me-C$_6$H$_3$}$_2$N]Lu(CH$_2$SiMe$_3$)$_2$ (3). A scintillation vial was charged with [{2-(^{i}Pr$_2$P)-4-Me-C_6H_3}$_2$N]H (**1**) (1.353 g, 3.150 mmol), a magnetic stir bar, and 5 mL pentane. To the stirring suspension of **2** was added $Lu(CH_2SiMe_3)_3(THF)_2$ (1.8276 g, 3.150 mmol) as a solution in pentane (5 mL). Upon addition the solution began to turn yellow and was stirred overnight to give a yellow solution. The pentane was removed under dynamic vacuum to give a yellow, foamy solid. This was then dissolved in 20 mL of hot $(Me_3Si)_2O$ and filtered through a glass fiber plug to give a clear yellow solution. Upon cooling to ambient temperature and sitting overnight large, yellow blocks formed. The solution was decanted and the crystals were washed with 5 mL of cold (-35°C) pentane and dried under dynamic vacuum (1.379g, 1.773 mmo, 56%). ^1H NMR (C_6D_6, 298 K): δ 7.08 (dd, 4.3 and 8.5 Hz, 2H, C_{Ar}-*H*), 6.89 (dd, 6.9 and 8.7 Hz, 2H, C_{Ar}-*H*), 6.79 (br m, 2H, C_{Ar}-*H*), 2.17 (m, 2H, C*H*Me$_2$, obscured by the peak at δ 2.14 ppm), 2.14 (s, 6H, C*H*$_3$), 2.01 (sept, 6.9 Hz, C*H*Me$_2$), 1.17 (m, 18H, CH*Me*$_2$), 0.84 (m, 6H, CH*Me*$_2$), 0.36 (s, 18H, CH$_2$Si*Me*$_3$), -0.34 (d, 2.6 Hz, 4H, C*H*$_2$SiMe$_3$). $^{13}C\{H\}$ NMR (C_6D_6, 298 K): δ 161.01 (pseudo t, 9.8 Hz, quat C_{Ar}), 133.7 (C_{Ar}), 133.6 (C_{Ar}), 127.88 (pseudo t, 1.8 Hz, quat C_{Ar}), 121.48 (pseudo t, 3.1Hz, C_{Ar}), 115.83 (dd, 9.7 and 11.3 Hz, quat C_{Ar}), 56.70 (t, 7.5 Hz, *C*H$_2$SiMe$_3$), 25.12 (t, 3.3 Hz, ^{i}Pr), 21.12 (s, CH_3), 20.58 (t, 3.6 Hz, ^{i}Pr), 20.14 (t, 4.2 Hz, ^{i}Pr), 20.01 (t, 6.5 Hz, ^{i}Pr), 19.47 (t, 6.1 Hz, ^{i}Pr), 16.82 (t, 2.8 Hz, ^{i}Pr), 5.34 (s, CH$_2$Si*Me*$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): δ 14.5 (s). Anal. Calcd. for $C_{34}H_{62}LuNP_2Si_2$ (777.95 g/mol): C, 52.49; H, 8.03; N, 1.80. Found: C, 52.44; H, 8.35; N, 1.75. Mp = 130-131 °C.

Synthesis of [{2-(Ph$_2$P)-4-Me-C$_6$H$_3$}$_2$N]Lu(CH$_2$SiMe$_3$)$_2$ (4). A 125 mL side-arm flask was charged with $Lu(CH_2SiMe_3)_3(THF)_2$ (0.293 g, 0.518 mmol), a magnetic stir bar, and 20 mL of

toluene. To the stirring solution, a suspension of [{2-(Ph_2P)-4-Me-C_6H_3}$_2$N]H (**2**) (1.8276 g, 3.150 mmol) in toluene (20 mL) was added portion-wise. The reaction mixture immediately became yellow in color and after two hours the solvent was removed under dynamic vacuum. The yellow solids were triturated with pentane (10 mL), the pentane decanted and the yellow powder was dried under dynamic vacuum (0.340 g, 0.372 mmol, 72%). ^{1}H NMR (C_6D_6, 298 K): δ 7.58 (m, 8H, *o*-Ph_2P), 6.81-7.09 (m, 18H, Ar-*H*), 0.22 (s, 18H, $CH_2Si\mathit{Me}_3$), -0.08 (s, 4H, $C\mathit{H}_2SiMe_3$). ^{13}C{H} NMR (C_6D_6, 298 K): δ 158.32 (pseudo t, 11.2 Hz, quat C_{Ar}), 134.96 (s, C_{Ar}), 134.50 (pseudo t, 7.3 Hz, C_{Ar}), 134.27 (s, C_{Ar}), 132.97 (pseudo t, 9.4 Hz, quat C_{Ar}), 130.38 (s, C_{Ar}), 129.52 (pseudo t, 2.1 Hz, quat C_{Ar}), 129.34 (pseudo t, 17.9 Hz, C_{Ar}), 128.65 (s,C_{Ar}), 121.26 (pseudo t, 2.8 Hz, C_{Ar}), 120.79 (pseudo t, 13.1 Hz, quat C_{Ar}), 50.81 (t, 7.8 Hz, $\mathit{C}H_2SiMe_3$), 20.88 (s, $\mathit{C}H_3$), 5.02 (s, $CH_2Si\mathit{Me}_3$). ^{31}P{^{1}H} NMR (C_6D_6, 298 K): δ -4.8. Anal. Calcd. for $C_{46}H_{54}LuNP_2Si_2$ (914.01 g/mol): C, 60.45; H, 5.95; N, 1.53. Found: C, 60.75; H, 5.96; N, 1.92. Mp = >230 °C.

Synthesis of [{2-(^{i}Pr$_2$P)-4-Me-C$_6$H$_3$}$_2$NLu]$_2$(μ-PMes)$_2$ (5). A 50-mL thick-walled Schlenk tube equipped with Teflon valve was charged with a magnetic stir bar, [{2-(^{i}Pr$_2$P)-4-Me-C_6H_3}$_2$N]Lu(CH_2SiMe_3)$_2$ (**3**) (0.9645g, 1.336 mmol), and a solution of $MesPH_2$ (0.2034 g, 1.336 mmol) in toluene (5 mL). The yellow solution was then stirred overnight in a silicone oil bath (80°C) to yield a cherry red colored solution. Removal of volatiles afforded a red solid, which was then triturated with hexanes (2x5 mL) to yield a fine red precipitate upon drying using dynamic vacuum. The free flowing red powder was dissolved in hot toluene (5 mL). Upon cooling, the toluene solution was layered with pentane (5 mL) yielding red crystals of compound **5** (0.5203g, 0.3452 mmol, 52%). ^{1}H NMR (C_6D_6, 298 K): δ 6.95-7.25 (m, 12H, C_{Ar}-*H*), 6.79 (s, 4H, C_{Ar}-*H*), 2.26 (m, 8H, C*H*Me$_2$), 2.19 (s, 12H, CH_3), 2.14 (s, 12H, CH_3), 2.12 (s, 6H, CH_3),

1.39 (pseudo pentet, 24H, CH*Me*$_2$), 1.13 (pseudo q, 24H, CH*Me*$_2$), 0.94 (pseudo q, 12H, CH*Me*$_2$). ^{13}C{H} NMR (THF-d_8, 298 K): δ 162.18 (pseudo t, 11.2 Hz, quat C_{Ar}), 153.67 (br s, quat C_{Ar}), 139.64 (s, quat C_{Ar}), 138.42 (s, quat C_{Ar}), 133.63 (s, C_{Ar}), 133.14 (s, C_{Ar}), 129.66 (s, C_{Ar}), 129.6 (s, quat C_{Ar}), 128.9 (s, C_{Ar}), 127.43 (s, quat C_{Ar}), 127.32 (s, quat C_{Ar}), 126.04 (s, C_{Ar}), 121.56 (s, C_{Ar}), 119.03 (pseudo t, 10.4 Hz, quat C_{Ar}), 26.59 (pseudo t, 5.2 Hz, C*H*$_3$), 26.05 (br s, C*H*Me$_2$), 21.50 (s, C*H*$_3$), 21.18 (pseudo t, 6.0 Hz, C*H*Me$_2$), 20.82 (s, C*H*$_3$), 20.77 (s, C*H*$_3$), 20.52 (br s, C*H*$_3$), 20.08 (pseudo t, 4.9 Hz, C*H*$_3$), 19.34 (br s, C*H*$_3$), 17.92 (br s, C*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 298 K): δ 186.8 (pentet, $^2J_{PP}$ = 14.6 Hz), 18.11 (t, $^2J_{PP}$ = 14.6 Hz). Anal. Calcd. for $C_{84}H_{118}Lu_2N_2P_6$ (1691.63 g/mol): C, 59.64; H, 7.03; N, 1.66. Found: C, 59.77; H, 7.16; N,1.67. Mp = 245-246 °C.

Procedure for Generation of *E*-MesP=C(H)^{t}Bu. A J-Young NMR tube was charged with [{2-(^{i}Pr$_2$P)-4-Me-C$_6$H$_3$}$_2$NLu]$_2$(μ-PMes)$_2$ (**5**) (29.4 mg, 0.0195 mmol) and 0.6 mL of C_6D_6. Pivalaldehyde (4.2 μL, 3.36mg, 0.0390 mmol) was injected using a syringe and the tube was agitated. Yields were determined by ^{1}H NMR spectroscopy, using diphenyl methane as an internal standard. ^{1}H and ^{31}P NMR spectra confirmed the formation of *E*-MesP=C(H)^{t}Bu (48% yield, ^{31}P NMR δ 227.1 ppm, lit. (C_6D_6) δ 228.4 ppm).[6]

Procedure for Generation of MesP=CPh$_2$. A J-Young NMR tube was charged with [{2-(^{i}Pr$_2$P)-4-Me-C$_6$H$_3$}$_2$NLu]$_2$(μ-PMes)$_2$ (**5**) (37.3 mg, 0.02474 mmol) and 0.4 mL of C_6D_6. Benzophenone (9.0 mg, 0.04948 mmol) was added as a solution in C_6D_6 (0.2 mL) and the tube was agitated. Yields were determined by ^{1}H NMR spectroscopy, using diphenyl methane as an internal standard. ^{1}H and ^{31}P NMR spectra confirmed the formation of MesP=CPh$_2$ (72% yield, ^{31}P NMR δ 234.0 ppm, lit. ($CDCl_3$) δ 233.06 ppm).[7]

Generation of Phosphaindole 6. A J-Young NMR tube was charged with [{2-(^{i}Pr$_2$P)-4-Me-C$_6$H$_3$}$_2$N]Lu(CH$_2$SiMe$_3$)$_2$ (**3**) (58.5 mg, 0.0640 mmol) and a solution of H$_2$P-2,4,6-^{t}Bu$_3$-C$_6$H$_2$ (15.9 mg, 0.0640 mmol) in C$_6$D$_6$ (0.6 mL) was added. The mixture was heated to 80°C for 7 hours to give quantitative formation of **6** as monitored by ^{31}P NMR spectroscopy (^{31}P NMR δ 79.14 ppm (dm, $^{1}J_{PH}$ = 181.1 Hz), lit. (C$_6$D$_6$) δ 78.4 ppm (dm, $^{1}J_{PH}$ = 181.9 Hz). ^{1}H and ^{31}P NMR spectroscopic data match the literature.[8]

Crystallographic Details for Complexes 3 and 5 (Tables S1-S7).

Single crystals of complexes **3** and **5** were mounted from Paratone N oil (Hampton Research) onto a nylon cryoloop under argon gas flow and placed on a Bruker SMART APEX II CCD diffractometer (Compund **3**), or a Bruker Platform with 1k CCD, each equipped with a KRYO-FLEX liquid nitrogen vapor cooling device. The instruments were equipped with a graphite monochromatized MoKα X-ray source (λ = 0.71073 Å). A hemisphere of data was collected using ω scans, with 5 second frame exposure (**3**) or 10 second frame exposure times (**5**) and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using APEX II software.[9] Frame integration, including Lorentz-polarization corrections and final cell parameter calculations were carried out using SAINT+ software.[10] The data were corrected for absorption using the SADABS program.[11] Decay of reflection intensity was monitored by analysis of redundant frames. The structures of **3** and **5** were solved using direct methods. Structure solution and refinement were performed using SHELXTL.[12] The figures for both complexes were made using ORTEP-3 for Windows.[13]

All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions. Two ^{i}Pr groups (C19-C21, C22-C24) of **5** were disordered and refined in two one-half occupancy positions. Hydrogen atoms were not included on these atoms for refinement. The SQUEEZE feature in Platon[14] was implemented to take into account the disordered solvent in compound **5** (2 equivalents of toluene).

Table S1. Crystal Data and Structure Refinement for [2-(^{i}Pr$_2$P)-4-Me-C$_6$H$_3$}$_2$N]Lu(CH$_2$SiMe$_3$)$_2$ (**3**).

Identification code	apx525	
Empirical formula	C_{34} H_{62} Lu N P_2 Si_2	
Formula weight	777.94	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 11.8412(16) Å	α= 93.120(2)°
	b = 12.0344(17) Å	β= 109.3100(1)°
	c = 15.568(2) Å	γ = 112.1280(1)°
Volume	1898.3(5) Å^3	
Z	2	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	2.770 mm^{-1}	
F(000)	804	
Crystal size	0.18 x 0.12 x 0.04 mm^3	
Θ Range for data collection	2.01 to 24.59°.	
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18	
Reflections collected	17078	
Independent reflections	6353 [R(int) = 0.0583]	
Completeness to Θ = 24.59°	99.4 %	
Max. and min. transmission	0.8973 and 0.6355	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6353 / 0 / 377	
Goodness-of-fit on F^2	0.967	
Final R indices [I>2σ(I)]	R1 = 0.0409, wR2 = 0.0827	
R indices (all data)	R1 = 0.0575, wR2 = 0.0882	
Largest diff. peak and hole	1.689 and -1.503 e.Å^{-3}	

Table S2. Bond Lengths [Å] for [2-(^{i}Pr$_2$P)-4-Me-C$_6$H$_3$}$_2$N]Lu(CH$_2$SiMe$_3$)$_2$ (**3**).

Lu(1)-N(1)	2.244(5)	C(9)-C(11)	1.515(8)
Lu(1)-C(5)	2.307(6)	C(12)-C(13)	1.509(8)
Lu(1)-C(1)	2.322(6)	C(12)-C(14)	1.514(8)
Lu(1)-P(1)	2.8534(15)	C(15)-C(16)	1.516(8)
Lu(1)-P(2)	2.8547(15)	C(15)-C(17)	1.528(8)
N(1)-C(33)	1.395(7)	C(18)-C(19)	1.510(8)
N(1)-C(26)	1.400(7)	C(18)-C(20)	1.522(7)
P(1)-C(21)	1.823(6)	C(21)-C(22)	1.394(7)
P(1)-C(9)	1.839(6)	C(21)-C(26)	1.402(8)
P(1)-C(12)	1.846(6)	C(22)-C(23)	1.378(7)
P(2)-C(28)	1.809(6)	C(23)-C(24)	1.383(8)
P(2)-C(15)	1.842(6)	C(23)-C(27)	1.493(7)
P(2)-C(18)	1.856(6)	C(24)-C(25)	1.372(7)
Si(1)-C(1)	1.817(6)	C(25)-C(26)	1.397(7)
Si(1)-C(3)	1.863(7)	C(28)-C(29)	1.386(8)
Si(1)-C(4)	1.865(6)	C(28)-C(33)	1.407(7)
Si(1)-C(2)	1.873(7)	C(29)-C(30)	1.392(8)
Si(2)-C(5)	1.835(6)	C(30)-C(31)	1.378(7)
Si(2)-C(6)	1.862(6)	C(30)-C(34)	1.494(7)
Si(2)-C(7)	1.864(7)	C(31)-C(32)	1.370(7)
Si(2)-C(8)	1.867(6)	C(32)-C(33)	1.409(7)
C(9)-C(10)	1.508(8)		

Table S3. Bond Angles [°] for [2-(^{i}Pr$_2$P)-4-Me-C$_6$H$_3$}$_2$N]Lu(CH$_2$SiMe$_3$)$_2$ (**3**).

N(1)-Lu(1)-C(5)	112.82(18)	C(5)-Si(2)-C(8)	110.4(3)
N(1)-Lu(1)-C(1)	128.69(19)	C(6)-Si(2)-C(8)	107.0(3)
C(5)-Lu(1)-C(1)	118.0(2)	C(7)-Si(2)-C(8)	107.3(3)
N(1)-Lu(1)-P(1)	70.37(12)	Si(1)-C(1)-Lu(1)	126.2(3)
C(5)-Lu(1)-P(1)	103.06(15)	Si(2)-C(5)-Lu(1)	127.6(3)
C(1)-Lu(1)-P(1)	103.93(14)	C(10)-C(9)-C(11)	111.5(5)
N(1)-Lu(1)-P(2)	69.31(11)	C(10)-C(9)-P(1)	109.7(4)
C(5)-Lu(1)-P(2)	101.75(15)	C(11)-C(9)-P(1)	112.1(4)
C(1)-Lu(1)-P(2)	93.13(14)	C(13)-C(12)-C(14)	112.1(5)
P(1)-Lu(1)-P(2)	138.32(4)	C(13)-C(12)-P(1)	111.0(4)
C(33)-N(1)-C(26)	117.3(4)	C(14)-C(12)-P(1)	113.4(4)
C(33)-N(1)-Lu(1)	126.4(3)	C(16)-C(15)-C(17)	110.6(5)
C(26)-N(1)-Lu(1)	116.2(3)	C(16)-C(15)-P(2)	111.6(4)
C(21)-P(1)-C(9)	104.9(3)	C(17)-C(15)-P(2)	108.6(4)
C(21)-P(1)-C(12)	105.1(3)	C(19)-C(18)-C(20)	110.3(5)
C(9)-P(1)-C(12)	104.2(3)	C(19)-C(18)-P(2)	114.7(4)
C(21)-P(1)-Lu(1)	90.10(17)	C(20)-C(18)-P(2)	110.3(4)
C(9)-P(1)-Lu(1)	127.3(2)	C(22)-C(21)-C(26)	119.9(5)
C(12)-P(1)-Lu(1)	120.4(2)	C(22)-C(21)-P(1)	122.5(4)
C(28)-P(2)-C(15)	106.4(3)	C(26)-C(21)-P(1)	117.5(4)
C(28)-P(2)-C(18)	103.9(3)	C(23)-C(22)-C(21)	122.5(5)
C(15)-P(2)-C(18)	104.4(3)	C(22)-C(23)-C(24)	117.1(5)
C(28)-P(2)-Lu(1)	96.59(18)	C(22)-C(23)-C(27)	121.4(5)
C(15)-P(2)-Lu(1)	125.9(2)	C(24)-C(23)-C(27)	121.5(5)
C(18)-P(2)-Lu(1)	116.63(18)	C(25)-C(24)-C(23)	121.8(5)
C(1)-Si(1)-C(3)	111.9(3)	C(24)-C(25)-C(26)	121.6(5)
C(1)-Si(1)-C(4)	115.2(3)	C(25)-C(26)-N(1)	122.5(5)
C(3)-Si(1)-C(4)	105.2(3)	C(25)-C(26)-C(21)	117.1(5)
C(1)-Si(1)-C(2)	108.4(3)	N(1)-C(26)-C(21)	120.3(5)
C(3)-Si(1)-C(2)	107.9(3)	C(29)-C(28)-C(33)	120.4(5)
C(4)-Si(1)-C(2)	108.0(3)	C(29)-C(28)-P(2)	123.5(4)
C(5)-Si(2)-C(6)	112.5(3)	C(33)-C(28)-P(2)	116.1(4)
C(5)-Si(2)-C(7)	113.3(3)	C(28)-C(29)-C(30)	122.2(5)
C(6)-Si(2)-C(7)	106.0(3)	C(31)-C(30)-C(29)	116.9(5)

C(31)-C(30)-C(34)	120.7(5)
C(29)-C(30)-C(34)	122.3(5)
C(32)-C(31)-C(30)	122.2(5)
C(31)-C(32)-C(33)	121.4(5)
N(1)-C(33)-C(28)	120.3(5)
N(1)-C(33)-C(32)	123.0(5)
C(28)-C(33)-C(32)	116.6(5)

Table S4. Crystal Data and Structure Refinement for $[\{2\text{-}(^{i}Pr_2P)\text{-}4\text{-}Me\text{-}C_6H_3\}_2NLu]_2(\mu\text{-}PMes)_2$ (**5**).

Identification code	xpl041s	
Empirical formula	$C_{84}\ H_{118}\ Lu_2\ N_2\ P_6$	
Formula weight	1691.56	
Temperature	141(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 19.993(3) Å	α= 90°
	b = 24.746(4) Å	β= 110.892(2)°
	c = 17.489(3) Å	γ = 90°
Volume	8084(2) $Å^3$	
Z	4	
Density (calculated)	1.390 Mg/m^3	
Absorption coefficient	2.590 mm^{-1}	
F(000)	3472	
Crystal size	0.10 x 0.08 x 0.05 mm^3	
Θ Range for data collection	1.49 to 25.02°.	
Index ranges	$-23 \le h \le 23$, $-29 \le k \le 29$, $-20 \le l \le 20$	
Reflections collected	77845	
Independent reflections	14243 [R(int) = 0.0794]	
Completeness to Θ = 25.00°	99.9 %	
Max. and min. transmission	0.8880 and 0.7799	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14243 / 82 / 797	
Goodness-of-fit on F^2	0.946	
Final R indices [I>2σ(I)]	R1 = 0.0367, wR2 = 0.0758	
R indices (all data)	R1 = 0.0629, wR2 = 0.0826	
Largest diff. peak and hole	0.759 and -0.787 $e.Å^{-3}$	

Table S5. Bond Lengths [Å] for [{2-(^{i}Pr$_2$P)-4-Me-C$_6$H$_3$}$_2$NLu]$_2$(μ-PMes)$_2$ (**5**).

Lu(1)-N(1)	2.296(4)	C(2)-C(7)	1.500(7)
Lu(1)-P(1)	2.6029(15)	C(3)-C(4)	1.383(7)
Lu(1)-P(2)	2.6723(14)	C(4)-C(5)	1.371(8)
Lu(1)-P(3)	2.8467(18)	C(4)-C(8)	1.506(7)
Lu(1)-P(4)	2.8562(15)	C(5)-C(6)	1.382(8)
Lu(1)-Lu(2)	3.9352(5)	C(6)-C(9)	1.519(8)
Lu(2)-N(2)	2.296(4)	C(10)-C(11)	1.416(7)
Lu(2)-P(2)	2.5976(14)	C(10)-C(15)	1.424(7)
Lu(2)-P(1)	2.6526(15)	C(11)-C(12)	1.382(7)
Lu(2)-P(6)	2.8303(14)	C(11)-C(16)	1.507(7)
Lu(2)-P(5)	2.8780(14)	C(12)-C(13)	1.389(7)
P(1)-C(1)	1.809(5)	C(13)-C(14)	1.385(7)
P(2)-C(10)	1.823(5)	C(13)-C(17)	1.513(7)
P(3)-C(22')	1.769(15)	C(14)-C(15)	1.381(7)
P(3)-C(36)	1.821(5)	C(15)-C(18)	1.511(7)
P(3)-C(19')	1.82(2)	C(19)-C(20)	1.513(17)
P(3)-C(19)	1.945(15)	C(19)-C(21)	1.514(15)
P(3)-C(22)	2.002(14)	C(19')-C(20')	1.498(18)
P(4)-C(43)	1.821(5)	C(19')-C(21')	1.487(17)
P(4)-C(25)	1.846(5)	C(22)-C(24)	1.531(16)
P(4)-C(28)	1.871(6)	C(22)-C(23)	1.557(15)
P(5)-C(62)	1.822(5)	C(22')-C(23')	1.474(16)
P(5)-C(54)	1.839(6)	C(22')-C(24')	1.519(14)
P(5)-C(51)	1.864(5)	C(25)-C(27)	1.524(7)
P(6)-C(69)	1.810(5)	C(25)-C(26)	1.531(8)
P(6)-C(45)	1.862(5)	C(28)-C(29)	1.530(7)
P(6)-C(48)	1.869(5)	C(28)-C(30)	1.533(7)
N(1)-C(31)	1.406(6)	C(31)-C(36)	1.392(7)
N(1)-C(38)	1.425(6)	C(31)-C(32)	1.398(7)
N(2)-C(64)	1.408(6)	C(32)-C(33)	1.380(7)
N(2)-C(57)	1.418(6)	C(33)-C(34)	1.386(8)
C(1)-C(2)	1.416(7)	C(34)-C(35)	1.383(7)
C(1)-C(6)	1.423(7)	C(34)-C(37)	1.531(7)
C(2)-C(3)	1.391(7)	C(35)-C(36)	1.400(7)

C(38)-C(43)	1.405(7)	C(57)-C(58)	1.407(7)
C(38)-C(39)	1.414(7)	C(57)-C(62)	1.413(7)
C(39)-C(40)	1.370(7)	C(58)-C(59)	1.373(7)
C(40)-C(41)	1.391(7)	C(59)-C(60)	1.396(7)
C(41)-C(42)	1.387(7)	C(60)-C(61)	1.367(8)
C(41)-C(44)	1.503(7)	C(60)-C(63)	1.498(7)
C(42)-C(43)	1.388(7)	C(61)-C(62)	1.405(7)
C(45)-C(46)	1.512(7)	C(64)-C(65)	1.415(6)
C(45)-C(47)	1.519(7)	C(64)-C(69)	1.420(6)
C(48)-C(49)	1.523(7)	C(65)-C(66)	1.383(7)
C(48)-C(50)	1.525(7)	C(66)-C(67)	1.402(7)
C(51)-C(52)	1.533(7)	C(67)-C(68)	1.379(7)
C(51)-C(53)	1.534(7)	C(67)-C(70)	1.510(7)
C(54)-C(56)	1.523(8)	C(68)-C(69)	1.409(6)
C(54)-C(55)	1.533(8)		

Table S6. Bond Angles [°] for [{2-(^{i}Pr$_2$P)-4-Me-C$_6$H$_3$}$_2$NLu]$_2$(μ-PMes)$_2$ (**5**).

N(1)-Lu(1)-P(1)	132.57(10)	C(10)-P(2)-Lu(1)	118.46(17)
N(1)-Lu(1)-P(2)	144.50(10)	Lu(2)-P(2)-Lu(1)	96.61(4)
P(1)-Lu(1)-P(2)	82.91(4)	C(22')-P(3)-C(36)	111.4(5)
N(1)-Lu(1)-P(3)	67.99(11)	C(22')-P(3)-C(19')	75.3(9)
P(1)-Lu(1)-P(3)	100.76(6)	C(36)-P(3)-C(19')	107.5(7)
P(2)-Lu(1)-P(3)	112.26(5)	C(22')-P(3)-C(19)	97.9(8)
N(1)-Lu(1)-P(4)	69.00(10)	C(36)-P(3)-C(19)	106.6(6)
P(1)-Lu(1)-P(4)	110.07(5)	C(19')-P(3)-C(19)	23.9(7)
P(2)-Lu(1)-P(4)	101.02(4)	C(22')-P(3)-C(22)	29.1(6)
P(3)-Lu(1)-P(4)	136.91(5)	C(36)-P(3)-C(22)	95.7(5)
N(1)-Lu(1)-Lu(2)	174.49(10)	C(19')-P(3)-C(22)	103.4(8)
P(1)-Lu(1)-Lu(2)	42.00(3)	C(19)-P(3)-C(22)	126.7(6)
P(2)-Lu(1)-Lu(2)	40.97(3)	C(22')-P(3)-Lu(1)	131.4(6)
P(3)-Lu(1)-Lu(2)	110.49(4)	C(36)-P(3)-Lu(1)	94.66(17)
P(4)-Lu(1)-Lu(2)	112.58(3)	C(19')-P(3)-Lu(1)	135.7(8)
N(2)-Lu(2)-P(2)	125.49(10)	C(19)-P(3)-Lu(1)	113.5(5)
N(2)-Lu(2)-P(1)	149.83(10)	C(22)-P(3)-Lu(1)	112.1(4)
P(2)-Lu(2)-P(1)	83.39(4)	C(43)-P(4)-C(25)	105.6(2)
N(2)-Lu(2)-P(6)	69.20(10)	C(43)-P(4)-C(28)	104.4(2)
P(2)-Lu(2)-P(6)	109.48(4)	C(25)-P(4)-C(28)	104.4(3)
P(1)-Lu(2)-P(6)	94.67(5)	C(43)-P(4)-Lu(1)	97.33(17)
N(2)-Lu(2)-P(5)	68.24(10)	C(25)-P(4)-Lu(1)	123.00(19)
P(2)-Lu(2)-P(5)	109.42(4)	C(28)-P(4)-Lu(1)	119.33(17)
P(1)-Lu(2)-P(5)	113.75(5)	C(62)-P(5)-C(54)	106.4(3)
P(6)-Lu(2)-P(5)	133.75(4)	C(62)-P(5)-C(51)	104.6(2)
N(2)-Lu(2)-Lu(1)	166.87(10)	C(54)-P(5)-C(51)	103.5(3)
P(2)-Lu(2)-Lu(1)	42.42(3)	C(62)-P(5)-Lu(2)	92.25(17)
P(1)-Lu(2)-Lu(1)	41.04(3)	C(54)-P(5)-Lu(2)	122.4(2)
P(6)-Lu(2)-Lu(1)	107.75(3)	C(51)-P(5)-Lu(2)	123.94(17)
P(5)-Lu(2)-Lu(1)	117.74(3)	C(69)-P(6)-C(45)	104.9(2)
C(1)-P(1)-Lu(1)	135.85(18)	C(69)-P(6)-C(48)	102.3(2)
C(1)-P(1)-Lu(2)	126.11(18)	C(45)-P(6)-C(48)	104.9(2)
Lu(1)-P(1)-Lu(2)	96.97(5)	C(69)-P(6)-Lu(2)	99.27(16)
C(10)-P(2)-Lu(2)	141.46(18)	C(45)-P(6)-Lu(2)	126.76(16)

C(48)-P(6)-Lu(2)	115.22(16)	C(20)-C(19)-P(3)	119.1(12)
C(31)-N(1)-C(38)	116.6(4)	C(21)-C(19)-P(3)	117.2(13)
C(31)-N(1)-Lu(1)	120.5(3)	C(20')-C(19')-C(21')	130(3)
C(38)-N(1)-Lu(1)	122.8(3)	C(20')-C(19')-P(3)	96.5(14)
C(64)-N(2)-C(57)	116.6(4)	C(21')-C(19')-P(3)	113.3(16)
C(64)-N(2)-Lu(2)	127.5(3)	C(24)-C(22)-C(23)	110.5(13)
C(57)-N(2)-Lu(2)	115.9(3)	C(24)-C(22)-P(3)	115.9(15)
C(2)-C(1)-C(6)	117.2(5)	C(23)-C(22)-P(3)	115.6(8)
C(2)-C(1)-P(1)	120.8(4)	C(23')-C(22')-C(24')	117.3(16)
C(6)-C(1)-P(1)	121.9(4)	C(23')-C(22')-P(3)	106.5(12)
C(3)-C(2)-C(1)	119.5(5)	C(24')-C(22')-P(3)	111.7(10)
C(3)-C(2)-C(7)	120.0(5)	C(27)-C(25)-C(26)	109.6(5)
C(1)-C(2)-C(7)	120.4(4)	C(27)-C(25)-P(4)	107.9(4)
C(4)-C(3)-C(2)	123.2(5)	C(26)-C(25)-P(4)	112.1(4)
C(5)-C(4)-C(3)	116.8(5)	C(29)-C(28)-C(30)	109.8(5)
C(5)-C(4)-C(8)	122.0(6)	C(29)-C(28)-P(4)	114.9(4)
C(3)-C(4)-C(8)	121.2(6)	C(30)-C(28)-P(4)	110.0(4)
C(4)-C(5)-C(6)	123.3(6)	C(36)-C(31)-C(32)	116.8(5)
C(5)-C(6)-C(1)	120.0(5)	C(36)-C(31)-N(1)	120.3(4)
C(5)-C(6)-C(9)	120.9(5)	C(32)-C(31)-N(1)	122.8(5)
C(1)-C(6)-C(9)	119.1(5)	C(33)-C(32)-C(31)	122.0(5)
C(11)-C(10)-C(15)	117.3(4)	C(32)-C(33)-C(34)	121.5(5)
C(11)-C(10)-P(2)	120.4(4)	C(35)-C(34)-C(33)	116.9(5)
C(15)-C(10)-P(2)	122.3(4)	C(35)-C(34)-C(37)	121.5(5)
C(12)-C(11)-C(10)	121.6(5)	C(33)-C(34)-C(37)	121.6(5)
C(12)-C(11)-C(16)	118.5(5)	C(34)-C(35)-C(36)	122.3(5)
C(10)-C(11)-C(16)	119.9(5)	C(31)-C(36)-C(35)	120.5(5)
C(11)-C(12)-C(13)	120.7(5)	C(31)-C(36)-P(3)	115.2(4)
C(14)-C(13)-C(12)	118.1(5)	C(35)-C(36)-P(3)	124.2(4)
C(14)-C(13)-C(17)	121.0(5)	C(43)-C(38)-C(39)	117.1(5)
C(12)-C(13)-C(17)	120.9(5)	C(43)-C(38)-N(1)	120.8(4)
C(15)-C(14)-C(13)	123.1(5)	C(39)-C(38)-N(1)	122.0(5)
C(14)-C(15)-C(10)	119.2(5)	C(40)-C(39)-C(38)	121.1(5)
C(14)-C(15)-C(18)	119.5(5)	C(39)-C(40)-C(41)	122.5(5)
C(10)-C(15)-C(18)	121.3(4)	C(42)-C(41)-C(40)	116.1(5)
C(20)-C(19)-C(21)	109.8(15)	C(42)-C(41)-C(44)	123.0(5)

C(40)-C(41)-C(44)	120.8(5)	C(66)-C(67)-C(70)	121.0(5)
C(41)-C(42)-C(43)	123.2(5)	C(67)-C(68)-C(69)	122.7(5)
C(42)-C(43)-C(38)	119.9(5)	C(68)-C(69)-C(64)	119.9(4)
C(42)-C(43)-P(4)	124.4(4)	C(68)-C(69)-P(6)	124.0(4)
C(38)-C(43)-P(4)	115.7(4)	C(64)-C(69)-P(6)	115.9(4)
C(46)-C(45)-C(47)	111.0(4)		
C(46)-C(45)-P(6)	110.6(4)		
C(47)-C(45)-P(6)	111.3(3)		
C(49)-C(48)-C(50)	110.2(4)		
C(49)-C(48)-P(6)	115.2(3)		
C(50)-C(48)-P(6)	109.2(3)		
C(52)-C(51)-C(53)	109.7(5)		
C(52)-C(51)-P(5)	111.1(4)		
C(53)-C(51)-P(5)	113.5(4)		
C(56)-C(54)-C(55)	111.5(5)		
C(56)-C(54)-P(5)	107.9(4)		
C(55)-C(54)-P(5)	110.4(4)		
C(58)-C(57)-C(62)	117.0(5)		
C(58)-C(57)-N(2)	123.0(5)		
C(62)-C(57)-N(2)	119.9(4)		
C(59)-C(58)-C(57)	121.8(5)		
C(58)-C(59)-C(60)	121.4(5)		
C(61)-C(60)-C(59)	117.5(5)		
C(61)-C(60)-C(63)	121.9(6)		
C(59)-C(60)-C(63)	120.6(5)		
C(60)-C(61)-C(62)	122.8(5)		
C(61)-C(62)-C(57)	119.5(5)		
C(61)-C(62)-P(5)	124.7(4)		
C(57)-C(62)-P(5)	115.8(4)		
N(2)-C(64)-C(65)	123.4(4)		
N(2)-C(64)-C(69)	119.7(4)		
C(65)-C(64)-C(69)	116.8(4)		
C(66)-C(65)-C(64)	121.6(5)		
C(65)-C(66)-C(67)	121.8(5)		
C(68)-C(67)-C(66)	117.1(5)		
C(68)-C(67)-C(70)	121.8(5)		

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