

Supporting Information

**Binuclear Rare-Earth Polyhydride Complexes Bearing both
Terminal and Bridging Hydride Ligands**

Jianhua Cheng, Haiyu Wang, Masayoshi Nishiura and Zhaomin Hou*

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General Methods.

All reactions were carried out under a dry and oxygen-free argon atmosphere using Schlenk techniques and an Mbraun glovebox. The argon was purified by being passed through a Dryclean column (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4 Å) catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by O₂/H₂O Combi-Analyzer (Mbraun) to ensure both were always below 0.1 ppm. THF, toluene, hexane were obtained from Kanato Kagaku Co. and purified by use of an Mbraun SPS-800 solvent purification system, and dried over fresh Na chips in the glovebox. Cyclohexane, hexamethyldisiloxane (HMDSO) and THF-*d*₈ were distilled from Na/K alloy/benzophenone ketyl, degassed by the freeze-pump-thaw method (three times), and dried over fresh Na chips in the glovebox. LnCl₃ (Ln = Y, Lu) were purchased from Strem Chemicals Ltd. LiCH₂SiMe₃ (1.0 M in pentane) was purchased from Aldrich. The pentane solvent was removed under vacuum and the so obtained solid LiCH₂SiMe₃ was used without further purification. H₂ gas was purchased from Suzuki Shokan Co., Ltd. and used without further purification. Other commercially available reagents were purchased and used without purification. The complexes (NCN)Ln(CH₂SiMe₃)₂(THF) (Ln = Y, Lu; NCN = PhC(NC₆H₃^{*i*}Pr₂-2,6)₂)^[1] were synthesized according to the published procedures.

Samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes. (¹H, ¹³C) NMR spectra were recorded on JNM-EX 300 or JNM-EX 400. ¹H and ¹³C NMR spectra of complexes were recorded using TMS as an internal standard. The elemental analyses were performed on a MICRO CORDER JM10 apparatus.

[(NCN)YH₂]₂(THF)₃ (1-Y): In the glovebox, (NCN)Y(CH₂SiMe₃)₂(THF) (420 mg, 0.54 mmol) in THF (4 mL) was charged into a glass tube in a medium-pressure autoclave with a magnetic stirring bar. The autoclave was transferred outside of the glovebox and pressurized with H₂ to 10 atm. The mixture was stirred at 0 °C for 24 h. Pressure was released and the autoclave was quickly returned to the glovebox. After filtration, the solution was concentrated to ~1 mL, layered with hexane (4 mL), and kept at -30 °C to give **1-Y** (280 mg, 0.22 mmol, 81% yield) as colorless crystalline solid. Single crystals of **1-Y**·C₆H₁₄, suitable for X-ray analysis, were grown from THF/hexane solution at -30 °C. ¹H NMR (300 MHz, THF-*d*₈, 25 °C): δ = 0.76 (br, 24H, CH(CH₃)₂), 1.17 (d, *J* = 6.8 Hz, 24H, CH(CH₃)₂), 1.69 (br, THF), 3.51 (m, 8H, CH(CH₃)₂), 3.55 (br, THF), 6.34 (t, *J*_{Y-H} = 25.2 Hz, 4H, Y-H), 6.72~6.90 (m, 10H + 12H, Ph-H + Ar-H). ¹³C NMR (75 MHz, THF-*d*₈, 25 °C): δ = 23.84 (s, CH(CH₃)₂), 25.92 (s, THF), 26.45 (s, CH(CH₃)₂), 28.85 (s, CH(CH₃)₂), 68.38 (s, THF), 123.58 (s), 123.93 (s), 127.46 (s), 129.05 (s), 131.61 (s), 134.86 (s), 142.64 (s), 147.11 (s), (NCN signal was not observed). Anal. Calcd. for (**1-Y**) C₇₄H₁₀₆N₄O₃Y₂ (1277.49): C, 69.58; H, 8.36; N, 4.39. Found: C,

69.60; H, 8.53; N, 4.11.

[(NCN)LuH₂]₂(THF)₃ (1-Lu): In the glovebox, (NCN)Lu(CH₂SiMe₃)₂(THF) (405 mg, 0.47 mmol) in THF (4 mL) was charged into a glass tube in a medium-pressure autoclave with a magnetic stirring bar. The autoclave was transferred outside of the glovebox and pressurized with H₂ to 10 atm. The mixture was stirred at 0 °C for 30 h. Pressure was released and the autoclave was quickly returned to the glovebox. After filtration, the solution was concentrated to ~1 mL, layered with hexane (4 mL), and kept at -30°C to give **1-Lu** (287 mg, 0.198 mmol, 84% yield) as colorless crystalline solid. Single crystals of **1-Lu**·(C₇H₈ + C₄H₁₀O), suitable for X-ray analysis, were grown from THF/hexane solution (containing drops of toluene and Et₂O) at -30°C. ¹H NMR (300 MHz, THF-*d*₈, 25°C): δ = 0.73 (br, 24H, CH(CH₃)₂), 1.17 (d, *J* = 6.8 Hz, 24H, CH(CH₃)₂), 1.69 (br, THF), 3.54 (m, 8H, CH(CH₃)₂), 3.56 (br, THF), 6.72–6.90 (m, 10H + 12H, Ph-*H* + Ar-*H*), 8.72 (br, 4H, Lu-*H*). ¹³C NMR (75 MHz, THF-*d*₈, 25°C): δ = 23.96 (s, CH(CH₃)₂), 25.81 (s, THF), 26.45 (s, CH(CH₃)₂), 28.75 (s, CH(CH₃)₂), 68.38 (s, THF), 123.98 (br), 127.49 (s), 129.20 (s), 131.80 (s), 135.16 (s), 142.87 (s), 147.16 (s), (NCN signal was not observed). Anal. Calcd. for (**1-Lu**) C₇₄H₁₀₆N₄O₃Lu₂ (1449.62): C, 61.31; H, 7.37; N, 3.86; (**1-Lu**·toluene) C₈₁H₁₁₄N₄O₃Lu₂ (1541.76): C, 63.10; H, 7.45; N, 3.63; Found: C, 62.76; H, 7.83; N, 3.73.

[(NCN)₂YH₃(OC₄H₉)](THF)₃ (2-Y): At room temperature, [(NCN)YH₂]₂(THF)₃ (1-Y) in the THF solution decomposed gradually to **1-Y'** with ring-opening a THF molecular. Single crystals of **2-Y**·(1/2HMDSO), suitable for X-ray analysis, were grown from Et₂O/HMDSO solution at -30°C. ¹H NMR (400 MHz, C₆D₆, 60°C): δ = 1.04 (br, 24H, CH(CH₃)₂), 1.13 (t, *J* = 7.4 Hz, 3H, -OCH₂CH₂CH₂CH₃), 1.35 (br, 24H, CH(CH₃)₂), 1.42 (br, 12H, THF), 1.64 (pseudo sextet, *J* = 7.2 Hz, 2H, -OCH₂CH₂CH₂CH₃), 1.81 (pseudo quintet, *J* = 6.8 Hz, 2H, -OCH₂CH₂CH₂CH₃), 3.67 (br, 8H + 12H, CH(CH₃)₂ + THF), 4.33 (t, *J* = 6.7 Hz, 2H, -OCH₂CH₂CH₂CH₃), 6.21 (t, *J*_{Y-H} = 23.7 Hz, 3H, Y-*H*), 6.69 (m, 6H, Ar-*H*), 6.94 (m, 10H + 2H, Ph-*H* + Ar-*H*), 7.14 (br, 4H, Ar-*H*). Anal. Calcd. for (**2-Y**) C₇₈H₁₁₄N₄O₄Y₂ (1248.80): C, 69.42; H, 8.51; N, 4.15; **2-Y**·(1/2HMDSO) C₈₁H₁₂₃N₄O_{4.5}Si₁Y₂ (1349.59): C, 68.00; H, 8.66; N, 3.92; Found: C, 68.27; H, 8.31; N, 4.39.

[(NCN)YH]₂(CH₂NAr*)(THF)₃ (3-Y): Solid 2,6-dimethylphenylisocyanide (C≡NAr*) (10 mg, 0.076 mmol) was added in one portion to the THF solution (2 mL) of [(NCN)YH₂]₂(THF)₃ (**1-Y**) (97 mg, 0.076 mmol) at 0 °C. The yellow mixture was stirred for at room temperature 3 h. After removal of all the volatiles under vacuum, the residue was extracted with hexane (3 x 3 mL). The filtration was concentrated to 1 mL and kept at -30°C to give **3-Y** (75 mg, 0.053 mmol, 70% yield) as yellow solid. Single crystals of **3-Y**·(2.5xC₇H₈ + C₆H₁₄), suitable for X-ray analysis, were grown from toluene/hexane solution at -30°C. ¹H NMR (300 MHz, C₆D₆, 40°C): δ = 0.97 (m, 24H, CH(CH₃)₂),

1.29 (br, 24H + 12H, CH(CH₃)₂ + THF), 3.14 (s, 6H, Ar*-CH₃), 3.42 (br, 2H, CH₂NAr*), 3.70 (br, 8H + 12H, CH(CH₃)₂ + THF), 6.08 (t, *J* = 24.8 Hz, 2H, Y-H), 6.69 (m, 7H, Ar-H + Ar*-H), 6.97 (m, 13H, Ph-H + Ar-H + Ar*-H), 7.20 (m, 5H, Ar-H + Ar*-H). ¹³C NMR (75 MHz, C₆D₆, 25°C): δ = 23.97 (br, CH(CH₃)₂), 25.68 (s, THF), 26.99 (br, CH(CH₃)₂), 28.40 (br, CH(CH₃)₂), 68.70 (d, *J* = 30.3 Hz), 70.44 (s, THF), 113.53 (s), 124.06 (br), 126.03 (s), 127.35 (s), 129.66 (s), 131.66 (s), 132.04 (s), 133.52 (s), 134.41 (s), 138.24 (s), 142.36 (br), 147.21 (br), 155.42 (s), 171.63 (s), 175.72 (s, NCN). Anal. Calcd. for (3-Y) C₈₃H₁₁₅N₅O₃Y₂ (1408.67): C, 70.77; H, 8.23; N, 4.97. Found: C, 71.31; H, 8.33; N, 4.79.

[(NCN)₂Lu₂H₃(THF)₃](PhC≡CHPh) (4-Lu-a): Solid diphenylacetylene (PhC≡CPh) (13 mg, 0.073 mmol) was added in one portion to the THF solution (2 mL) of [(NCN)LuH₂]₂(THF)₃ (1-Lu) (106 mg, 0.073 mmol) at 0 °C. The light yellow mixture was stirred at room temperature for 1 h. After filtration, the solution was concentrated to 0.5 mL, layered with 2 mL hexane, and kept at -30°C to give 4-Lu-a (74 mg, 0.0454 mmol, 62% yield) as pale yellow crystalline materials. Single crystals of 4-Lu-a•(1/2C₆H₁₄), suitable for X-ray analysis, were grown from THF/hexane solution at -30°C. ¹H NMR (300M Hz, THF-*d*₈, 25°C): δ = 0.74 (br, 24H, CH(CH₃)₂), 1.06 (br, 12H, CH(CH₃)₂), 1.20 (d, *J* = 6.6 Hz, 12H, CH(CH₃)₂), 1.70 (br, THF), 3.31 (br, 4H, CH(CH₃)₂), 3.56 (br, THF), 3.75 (br, 4H CH(CH₃)₂), 6.67~7.04 (m, 32H, Ph-H + Ar-H), 7.71 (s, 1H, PhC=CHPh), 8.83 (s, 3H, Lu-H). ¹³C NMR (75 MHz, THF-*d*₈, 25°C): δ = 24.19 (s, CH(CH₃)₂), 24.44 (s, CH(CH₃)₂), 26.44 (s, THF), 28.61 (s, CH(CH₃)₂), 28.83 (s, CH(CH₃)₂), 68.38 (s, THF), 121.37 (s), 123.73 (s), 124.36 (s), 124.48 (s), 124.76 (s), 126.17 (s), 127.40 (s), 127.50(s), 127.90 (s), 128.44 (s), 128.79 (s), 129.48 (s), 130.36 (s), 131.96 (s), 132.23 (s), 132.52 (s), 132.70 (s), 134.72(s), 136.14 (s), 141.49 (s), 142.93 (s), 143.89 (s), 146.80 (s), 147.98 (s), 157.12 (s), 175.44 (s, NCN), 177.22 (s, PhC=CHPh), 210.64 (s, PhC=CHPh). Anal. Calcd. for (4-Lu-a) C₈₈H₁₁₆N₄O₂Lu₂ (1627.85): C, 64.93; H, 7.18; N, 3.44. Found: C, 65.21; H, 7.39; N, 3.57.

[(NCN)LuH(THF)]₂(PhCH-CHPh) (4-Lu-b): Solid diphenylacetylene (PhC≡CPh) (13 mg, 0.073 mmol) was added in one portion to the THF solution (2 mL) of [(NCN)LuH₂]₂(THF)₃ (1-Lu) (106 mg, 0.073 mmol) at 0 °C. The mixture was stirred at room temperature for 24 h. After filtration, the orange solution was concentrated to 0.5 mL, layered with 2 mL hexane, and kept at -30°C to give 4-Lu-b (97 mg, 0.062 mmol, 85% yield) as red orange crystalline materials. Single crystals of 4-Lu-b•(1.5C₆H₁₄), suitable for X-ray analysis, were grown from THF/hexane solution at -30°C. ¹H NMR (300M Hz, THF-*d*₈, 60°C): δ = 0.49 (br, 12H, CH(CH₃)₂), 0.97 (br, 36H, CH(CH₃)₂), 1.68 (br, THF), 2.56 (br, 2H, PhCH-CHPh), 3.21 (br, 8H, CH(CH₃)₂), 3.54 (br, THF), 6.22 (t, *J* = 7.0 Hz, 2H, Ph-H), 6.69~6.91 (m, 30H, Ph-H + Ar-H), 9.14 (s, 2H, Lu-H). ¹³C NMR (75 MHz, THF-*d*₈, 25°C): δ = 23.40 (br, CH(CH₃)₂), 26.48 (s, THF), 28.24 (s, CH(CH₃)₂), 28.57 (br, CH(CH₃)₂), 68.39 (s,

THF), 117.52 (s), 122.07 (br), 124.51 (br), 127.41 (s), 129.61 (s), 132.27 (s), 134.05 (s), 142.43 (s), 142.88 (s), 146.19 (br), 158.53 (s), 175.73 (s, NCN), (attempts to assign the carbons of PhCH–CHPh were failed). Anal. Calcd. for (**4-Lu-b**) C₈₄H₁₀₈N₄O₂Lu₂ (1555.74): C, 64.85; H, 7.00; N, 3.60; (**4-Lu-b**•1.5C₆H₁₄) C₉₃H₁₂₉N₄O₂Lu₂ (1685.01): C, 66.29; H, 7.72; N, 3.33. Found: C, 66.34; H, 7.62; N, 3.02.

[(NCN)₂Lu₂H₂(THF)] (PhCH–CHPh) (4-Lu-c): Dissolution of complex **4-Lu-b** in benzene to give a deep purple solution immediately. After removal of all the solvents, the residue was washed with hexane and dried under vacuum to give **4-Lu-c** as purple solid quantitatively. Single crystals of **4-Lu-c**•(3C₆H₁₂), suitable for X-ray analysis, were grown from evaporation of HMDSO/cyclohexane solution at room temperature. ¹H NMR (300M Hz, C₆D₆, 60°C): δ = 0.67 (d, *J* = 5.3 Hz, 12H, CH(CH₃)₂), 0.91 (d, *J* = 5.4 Hz, 12H, CH(CH₃)₂), 1.06 (br, 12H, CH(CH₃)₂), 1.28 (d, *J* = 6.7 Hz, 12H, CH(CH₃)₂), 1.45 (br, 4H, THF), 3.27 (br, 4H, CH(CH₃)₂), 3.55 (br, 4H, CH(CH₃)₂), 3.72 (br, 4H, THF), 3.86 (br, 1H, PhCH–CHPh), 5.79 (br, 1H, PhCH–CHPh), {6.41 (br, 7H), 6.64 (m, 7H), 6.92~7.06 (m, 18H), Ar-*H* + Ph-*H*}, 10.96 (s, 2H, Lu-*H*). ¹³C NMR (75 MHz, C₆D₆, 25°C): δ = 23.19 (br, CH(CH₃)₂), 24.46 (br, CH(CH₃)₂), 25.79 (s, THF), 28.64 (br, CH(CH₃)₂), 71.87 (s, THF), 124.05 (s), 124.61 (s), 127.29 (s), 131.36 (s), 132.27 (s), 133.73 (s), 142.24 (s), (NCN signal was not observed), (attempts to assign the carbons of PhCH–CHPh were failed).. Anal. Calcd. for (**4-Lu-c**) C₈₀H₁₀₀N₄O₁Lu₂ (1483.64): C, 64.77; H, 6.79; N, 3.78. Found: C, 65.31; H, 7.18; N, 3.66.

[(NCN)YH(THF)]₂(PhCH–CHPh) (4-Y-b): A procedure analogous to **4-Lu-b** using diphenylacetylene (PhC≡CPh) (13 mg, 0.073 mmol) and [(NCN)YH₂]₂(THF)₃ (**1-Y**) (93 mg, 0.073 mmol) gave **4-Y-b** (56 mg, 0.0568 mmol, 71% yield) as red orange crystalline materials. Single crystals of **4-Y-b**•(C₄H₈O+C₆H₁₄), suitable for X-ray analysis, were grown from THF/hexane solution at -30°C. *Although the quality of crystals prevented us from obtaining the precise bond lengths, the structure data showed that complex 4-Y-b is isostructural to complex 4-Lu-b.* ¹H NMR (300M Hz, THF-*d*₈, 60°C): δ = 0.60 (d, *J* = 5.3 Hz, 12H, CH(CH₃)₂), 0.91 (d, *J* = 5.6 Hz, 12H, CH(CH₃)₂), 1.02 (d, *J* = 5.5 Hz, 24H, CH(CH₃)₂), 1.69 (br, THF), 2.86 (br, 2H, PhCH–CHPh), 3.29 (br, 4H, CH(CH₃)₂), 3.47 (br, 4H, CH(CH₃)₂), 3.55 (br, THF), 5.92 (t, *J* = 29.2 Hz, 2H, Y-*H*), 6.20 (t, *J* = 6.8 Hz, 2H, Ph-*H*), 6.61~6.92 (m, 30H, Ph-*H* + Ar-*H*). ¹³C NMR (100 MHz, THF-*d*₈, 25°C): δ = 23.71 (br, CH(CH₃)₂), 24.29 (br, CH(CH₃)₂), 26.49 (s, THF), 28.90 (br, CH(CH₃)₂), 68.39 (s, THF), 117.26 (s), 121.08 (br), 124.13 (s), 124.35 (s), 127.36 (s), 129.47 (s), 131.22 (br), 132.08 (s), 133.78 (s), 142.16 (s), 142.29 (s), 146.22 (br), 157.47 (s), 175.91 (s, NCN), (attempts to assign the carbons of PhCH–CHPh were failed). Anal. Calcd. for (**4-Y-b**) C₈₄H₁₀₈N₄O₂Y₂ (1383.61): C, 72.92; H, 7.87; N, 4.05; (**4-Y-b**•(C₄H₈O+C₆H₁₄)) C₉₄H₁₃₀N₄O₃Y₂ (1541.90): C, 73.22; H, 8.50; N, 3.63. Found: C, 72.95; H, 8.39; N, 3.38.

[(NCN)YH(THF)]₂(PhCHC≡CCHPh) (5-Y): Solid 1,4-diphenyl-1,3-butadiyne (PhC≡C–C≡CPh) (14 mg, 0.069 mmol) was added in one portion to the THF solution (2 mL) of [(NCN)YH₂]₂(THF)₃ (**1-Y**) (88 mg, 0.069 mmol) at 0 °C. The brown mixture was stirred for at room temperature 2 h. After removal of all the volatiles under vacuum, the residue was extracted with toluene (2 x 2 mL). The filtration was concentrated to 1 mL, layered with 3 mL hexane, and kept at -30°C to give **5-Y** (79 mg, 0.056 mmol, 81% yield) as yellow brown solids. Single crystals of **5-Y**•(3C₆H₆), suitable for X-ray analysis, were grown from benzene solution at room temperature. ¹H NMR (300M Hz, THF-*d*₈, 25°C): δ = -0.28 (d, *J* = 6.1 Hz, 6H, CH(CH₃)₂), 0.12 (d, *J* = 5.9 Hz, 6H, CH(CH₃)₂), 0.18 (d, *J* = 6.3 Hz, 6H, CH(CH₃)₂), 0.28 (d, *J* = 6.3 Hz, 6H, CH(CH₃)₂), 1.40 (m, 18H, CH(CH₃)₂), 1.61 (d, *J* = 6.3 Hz, 6H, CH(CH₃)₂), 1.69 (br, THF), 2.38 (m, 2H, CH(CH₃)₂), 2.95 (m, 2H, CH(CH₃)₂), 3.50 (m, 2H, CH(CH₃)₂), 3.54 (br, THF), 3.92 (s, 2H, PhCHC≡CCHPh), 4.25 (m, 2H, CH(CH₃)₂), 6.18 (t, *J* = 30.1 Hz, 2H, Y–H), {6.36 (t, *J* = 7.2 Hz, 2H), 6.42 (d, *J* = 7.5 Hz, 2H), 6.62 (t, *J* = 6.4 Hz, 4H), 6.68 (t, *J* = 7.6 Hz, 2H), 6.77 (m, 12H), 6.90 (m, 6H), 7.09 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), Ph–H + Ar–H}. ¹³C NMR (75 MHz, THF-*d*₈, 25°C): δ = 21.98 (s, CH(CH₃)₂), 23.14 (s, CH(CH₃)₂), 24.39 (s, CH(CH₃)₂), 26.49 (s, THF), 26.57 (s, CH(CH₃)₂), 28.72 (s, CH(CH₃)₂), 28.84 (s, CH(CH₃)₂), 28.94 (s, CH(CH₃)₂), 29.56 (s, CH(CH₃)₂), 62.21 (br, PhCHC≡CCHPh), 68.39 (s, THF), 119.70 (s), 122.64 (br), 123.54 (s), 124.00 (s), 124.24 (s), 124.34 (s), 124.73 (s), 125.20 (s), 126.30 (s), 127.59 (s), 128.78 (s), 129.18 (s), 129.40 (s), 129.94 (s), 131.51(s), 134.19(s), 141.86 (s), 141.99 (s), 142.48 (s), 143.55(s), 144.91 (s), 145.79 (s), 148.15 (s), 178.73 (s, NCN). Anal. Calcd. for (**5-Y**) C₈₆H₁₀₈N₄O₂Y₂ (1407.58): C, 73.38; H, 7.73; N, 3.98; Found: C, 73.86; H, 7.67; N, 4.05.

X-ray Crystallographic Studies

Single crystals suitable for X-ray analysis were obtained as described in the preparation. The crystals were manipulated in the glovebox under a microscope in the glovebox. Data collection was performed at -110°C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo K_α radiation (λ = 0.71073 Å). The determination of the crystal class and unit cell parameters was carried out by the SMART program package.^[2] The raw frame data were processed using SAINT^[3] and absorption corrections using SADABS^[4] to yield the reflection data file. The structures were solved by using SHELXS-97^[5] or SUPERFLIP.^[6] Refinements were performed on *F*² anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method using SHELXL-97 program.^[5] The SQUEEZE^[7] routine of the program PLATON^[8] was implemented to remove the contributions of the disordered solvents (hexane in **1-Y**; Et₂O in **1-Lu**; hexane and toluene in **3-Y**; hexane in **4-Lu-a**; hexane in **4-Lu-b**; cyclohexane in **4-Lu-c**; and benzene in **5-Y**) to the observed structure factors. The hydrides in **1-Y**, **1-Lu**, **2-Y**, **3-Y**, **4-Lu-a**, **4-Lu-b**, **4-Lu-c** and **5-Y**; two hydrogen atoms of CH₂NAr* unit in **3-Y**; hydrogen atom of

PhC=CHPh unit in **4-Lu-a**; two hydrogen atoms of the (PhCH-CHPh) unit in **4-Lu-b**; seven hydrogen atoms of (C₆H₅-CH-CHPh) unit in **4-Lu-c**; and two hydrogen atoms in PhCHC≡CCPh unit in **5-Y** were located by difference Fourier syntheses and refined. Other hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Crystal data and analysis results are listed in STable 1–6.

CCDC numbers 859483 (**1-Y**), 859484 (**1-Lu**), 859485 (**2-Y**), 859486 (**3-Y**), 859487 (**4-Lu-a**) 859488 (**4-Lu-b**), 859489 (**4-Lu-c**) and 859490 (**5-Y**) 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.

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Table 1. Crystal data and structure refinement for **1-Ln**

Identification code	1-Y (II-035-02)	1-Lu (II-044)
Empirical formula	C ₇₄ H ₁₀₆ N ₄ O ₃ Y ₂	C ₈₁ H ₁₁₄ N ₄ O ₃ Lu ₂ (1-Lu ·C ₇ H ₈)
Formula weight	1277.45	1541.70
Temperature	163(2) K	163(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, P-1	Triclinic, P-1
a	12.5958(16) Å	13.2117(18) Å
b	15.800(2) Å	14.827(2) Å
c	20.902(3) Å	23.057(3) Å
α	76.137(2)°	81.780(2)°
β	76.659(2)°	73.628(2)°
γ	83.229(2)°	66.103(2)°
Volume	3921.1(9) Å ³	3960.1(9) Å ³
Z, Calculated density	2, 1.082 Mg/m ³	2, 1.293 Mg/m ³
Absorption coefficient	1.515 mm ⁻¹	2.524 mm ⁻¹
F(000)	1360	1588
Crystal size	0.40 x 0.35 x 0.32 mm	0.35 x 0.21 x 0.15 mm
Theta range for data collection	1.33 to 25.00°	1.74 to 25.04°
Limiting indices	-14<=h<=14, -18<=k<=18, -24<=l<=17	-14<=h<=15, -15<=k<=17, -21<=l<=27
Reflections collected / unique	21111 / 13507 [R(int) = 0.0311]	21538 / 13729 [R(int) = 0.0266]
Completeness to theta	(25.00°) 97.9 %	(25.04°) 98.0 %
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.6429 and 0.5825	0.7033 and 0.4720
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	13507 / 44 / 735	13729 / 6 / 798
Goodness-of-fit on F ²	0.953	1.064
Final R indices [I>2σ(I)]	R1 = 0.0580, wR2 = 0.1398	R1 = 0.0498, wR2 = 0.1252
R indices (all data)	R1 = 0.0935, wR2 = 0.1518	R1 = 0.0620, wR2 = 0.1317
Largest diff. peak and hole	0.861 and -0.561 e. Å ⁻³	3.566 and -1.041 e. Å ⁻³

STable 2. Crystal data and structure refinement for **2-Y**

Identification code	2-Y· (1/2HMDSO) (I-175-03)
Empirical formula	C ₈₁ H ₁₂₃ N ₄ O _{4.5} Si ₁ Y ₂ (C ₇₈ H ₁₁₄ N ₄ O ₄ Y ₂ ·0.5C ₆ H ₁₈ O ₁ Si ₂)
Formula weight	1430.74
Temperature	163(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/n
a	13.0663(19) Å
b	38.724(6) Å
c	15.781(2) Å
α	90°
β	93.796(3)°
γ	90°
Volume	7967(2) Å ³
Z, Calculated density	4, 1.193 Mg/m ³
Absorption coefficient	1.513 mm ⁻¹
F(000)	3060
Crystal size	0.28 x 0.20 x 0.15 mm
Theta range for data collection	1.40 to 25.07°
Limiting indices	-10 ≤ h ≤ 15, -46 ≤ k ≤ 46, -18 ≤ l ≤ 18
Reflections collected / unique	43453 / 14111 [R(int) = 0.1123]
Completeness to theta	(25.07°) 99.7 %
Absorption correction	Empirical
Max. and min. transmission	0.8048 and 0.6766
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	14111 / 0 / 842
Goodness-of-fit on F ²	0.966
Final R indices [I > 2σ(I)]	R1 = 0.0629, wR2 = 0.1162
R indices (all data)	R1 = 0.1443, wR2 = 0.1430
Largest diff. peak and hole	0.491 and -0.428 e. Å ⁻³

STable 3. Crystal data and structure refinement for **3-Y**

Identification code	3-Y (II-141-02)
Empirical formula	C ₈₃ H ₁₁₅ N ₅ O ₃ Y ₂
Formula weight	1408.62
Temperature	163(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/c
a	11.898(3) Å
b	23.121(6) Å
c	35.564(9) Å
α	90 °
β	90.028(4) °
γ	90 °
Volume	9784(4) Å ³
Z, Calculated density	4, 0.956 Mg/m ³
Absorption coefficient	1.219 mm ⁻¹
F(000)	3000
Crystal size	0.48 x 0.45 x 0.42 mm
Theta range for data collection	1.44 to 25.00 °
Limiting indices	-9<=h<=14, -26<=k<=27, -39<=l<=42
Reflections collected / unique	49823 / 17087 [R(int) = 0.0663]
Completeness to theta	(25.00 °) 99.2 %
Absorption correction	Empirical
Max. and min. transmission	0.6284 and 0.5922
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	17087 / 7 / 857
Goodness-of-fit on F ²	0.935
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.1301
R indices (all data)	R1 = 0.0881, wR2 = 0.1407
Largest diff. peak and hole	0.685 and -0.444 e. Å ⁻³

STable 4. Crystal data and structure refinement for **4-Lu-a**

Identification code	4-Lu-a (II-139-03)
Empirical formula	C ₈₈ H ₁₁₆ N ₄ O ₃ Lu ₂
Formula weight	1627.79
Temperature	163(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	13.437(2) Å
b	14.939(3) Å
c	22.326(4) Å
α	107.399(3)°
β	102.549(3)°
γ	100.158(3)°
Volume	4031.9(12) Å ³
Z, Calculated density	2, 1.341 Mg/m ³
Absorption coefficient	2.483 mm ⁻¹
F(000)	1676
Crystal size	0.30 x 0.28 x 0.25 mm
Theta range for data collection	1.48 to 25.00 °
Limiting indices	-15<=h<=10, -17<=k<=17, -24<=l<=26
Reflections collected / unique	21877 / 13956 [R(int) = 0.0364]
Completeness to theta	(25.00°) 98.3 %
Absorption correction	Empirical
Max. and min. transmission	0.5757 and 0.5229
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	13956 / 0 / 890
Goodness-of-fit on F ²	0.952
Final R indices [I>2σ(I)]	R1 = 0.0452, wR2 = 0.0937
R indices (all data)	R1 = 0.0710, wR2 = 0.1015
Largest diff. peak and hole	1.931 and -0.550 e. Å ⁻³

Table 5. Crystal data and structure refinement for **4-Lu-b** and **4-Lu-c**

Identification code	4-Lu-b (II-139-01)	4-Lu-c (II-139-02)
Empirical formula	C ₈₄ H ₁₀₈ N ₄ O ₂ Lu ₂	C ₈₀ H ₁₀₀ N ₄ O ₁ Lu ₂
Formula weight	1555.68	1483.58
Temperature	163(2) K	163(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, P-1	Triclinic, P-1
a	12.530(5) Å	15.161(2) Å
b	16.733(5) Å	17.449(3) Å
c	22.194(5) Å	18.270(3) Å
α	107.824(5)°	76.958(3)°
β	103.291(5)°	76.864(3)°
γ	91.970(5)°	70.969(3)°
Volume	4284(2) Å ³	4388.8(12) Å ³
Z, Calculated density	2, 1.206 Mg/m ³	2, 1.123 Mg/m ³
Absorption coefficient	2.333 mm ⁻¹	2.274 mm ⁻¹
F(000)	1596	1516
Crystal size	0.28 x 0.20 x 0.15 mm	0.36 x 0.28 x 0.15 mm
Theta range for data collection	1.35 to 25.00°	1.69 to 25.00°
Limiting indices	-14 ≤ h ≤ 13, -19 ≤ k ≤ 18, -25 ≤ l ≤ 26	-18 ≤ h ≤ 10, -20 ≤ k ≤ 19, -21 ≤ l ≤ 21
Reflections collected / unique	23135 / 14821 [R(int) = 0.0441]	23847 / 15180 [R(int) = 0.0448]
Completeness to theta	(25.00°) 98.2 %	(25.00°) 98.2 %
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.7210 and 0.5611	0.7267 and 0.4949
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	14821 / 3 / 851	15180 / 0 / 811
Goodness-of-fit on F ²	0.928	0.939
Final R indices [I > 2σ(I)]	R1 = 0.0475, wR2 = 0.1006	R1 = 0.0445, wR2 = 0.0844
R indices (all data)	R1 = 0.0756, wR2 = 0.1081	R1 = 0.0667, wR2 = 0.0895
Largest diff. peak and hole	1.642 and -0.833 e. Å ⁻³	1.051 and -0.498 e. Å ⁻³

STable 6. Crystal data and structure refinement for **5-Y**

Identification code	5-Y (II-140-02)
Empirical formula	C ₈₆ H ₁₀₈ N ₄ O ₂ Y ₂
Formula weight	1407.58
Temperature	163(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	13.731(3) Å
b	15.277(3) Å
c	22.821(5) Å
α	97.855(3)°
β	98.334(3)°
γ	99.894(3)°
Volume	4601.5(17) Å ³
Z, Calculated density	2, 1.016 Mg/m ³
Absorption coefficient	1.295 mm ⁻¹
F(000)	1492
Crystal size	0.48 x 0.45 x 0.43 mm
Theta range for data collection	1.53 to 25.00 °
Limiting indices	-11<=h<=16, -17<=k<=18, -27<=l<=25
Reflections collected / unique	24189 / 15874 [R(int) = 0.0347]
Completeness to theta	(25.00°) 97.8 %
Absorption correction	Empirical
Max. and min. transmission	0.6059 and 0.5753
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	15874 / 0 / 867
Goodness-of-fit on F ²	0.944
Final R indices [I>2σ(I)]	R1 = 0.0475, wR2 = 0.1089
R indices (all data)	R1 = 0.0727, wR2 = 0.1171
Largest diff. peak and hole	0.524 and -0.322 e. Å ⁻³

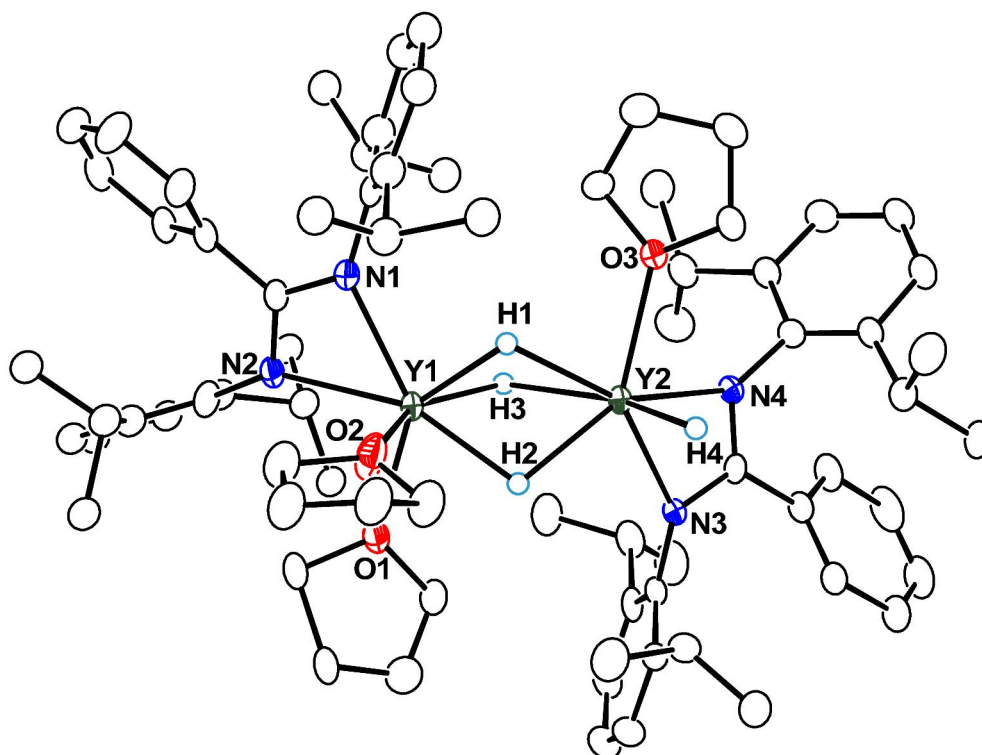


Figure 1. Ortep drawing of $[(\text{NCN})\text{YH}_2]_2(\text{THF})_3$ (**1-Y**) with thermal ellipsoids at the 30% probability level. Selected bond distances [\AA] and angles [deg]: Y1–H1, 2.03(4); Y1–H2, 2.15(4); Y1–H3, 2.00(4); Y1–N1, 2.374(3); Y1–N2, 2.466(3); Y1–O1, 2.403(3); Y1–O2, 2.342(3); Y2–H1, 2.21(4); Y2–H2, 2.15(4); Y2–H3, 2.32(4); Y2–H4, 2.40(4); Y2–N3, 2.403(3); Y2–N4, 2.404(3); Y2–O3, 2.415(3); Y1---Y2, 3.3614(6); Y1–H1–Y2, 104.4(11); Y1–H2–Y2, 103.1(11); Y1–H3–Y2, 101.9(11).

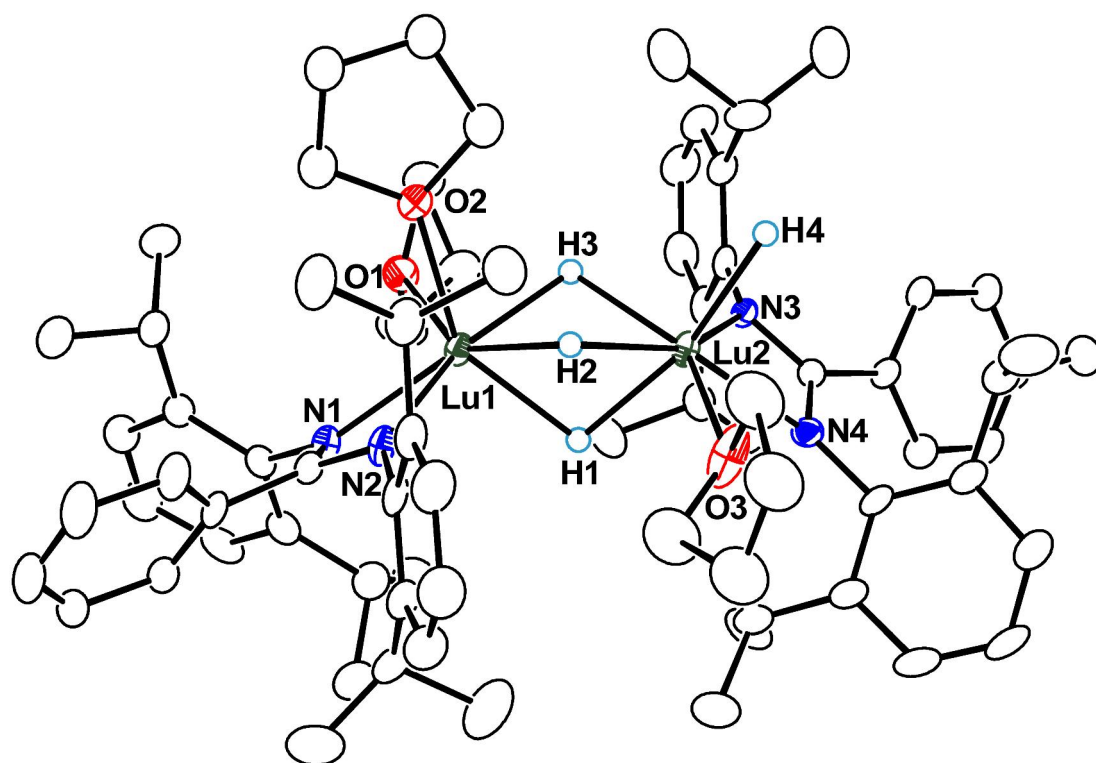


Figure 2. Ortep drawing of $[(\text{NCN})\text{LuH}_2]_2(\text{THF})_3$ (**1-Lu**) with thermal ellipsoids at the 30% probability level. Selected bond distances [\AA] and angles [deg]: Lu1–H1, 2.1766(3); Lu1–H2, 2.06(6); Lu1–H3, 2.06(6); Lu1–N1, 2.373(5); Lu1–N2, 2.345(5); Lu1–O1, 2.368(4); Lu1–O2, 2.322(4); Lu2–H1, 2.0405(3); Lu2–H2, 2.15(6); Lu2–H3, 2.09(6); Lu2–H4, 2.2900(3); Lu2–N3, 2.349(5); Lu2–N4, 2.369(5); Lu2–O3, 2.360(5); Lu1---Lu2, 3.2359(5); Lu1–H1–Lu2, 100.2(16); Lu1–H2–Lu2, 100.7(10); Lu1–H3–Lu2, 102.6(16).

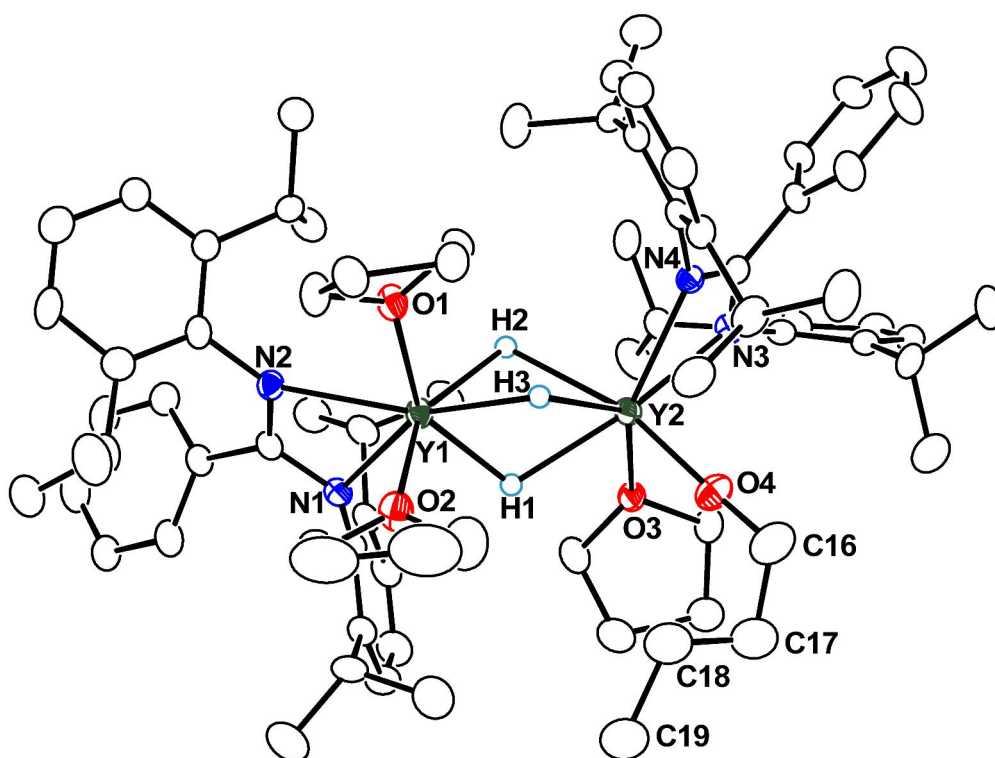


Figure 3. Ortep drawing of $[(\text{NCN})_2\text{Y}_2(\text{H})_3(\text{OC}_4\text{H}_9)](\text{THF})_3$ (**2-Y**) with thermal ellipsoids at the 30% probability level. Selected bond distances [Å] and angles [deg]: Y1–H1, 1.95(4); Y1–H2, 2.17(4); Y1–H3, 2.12(4); Y1–N1, 2.391(4); Y1–N2, 2.468(4); Y1–O1, 2.394(3); Y1–O2, 2.354(3); Y2–H1, 2.20(4); Y2–H2, 2.30(4); Y2–H3, 2.19(4); Y2–N3, 2.485(4); Y2–N4, 2.424(4); Y2–O3, 2.430(3); Y2–O4, 2.067(3); Y1---Y2, 3.3903(8); Y1–H1–Y2, 109.4(11); Y1–H2–Y2, 98.6(10); Y1–H3–Y2, 103.8(10).

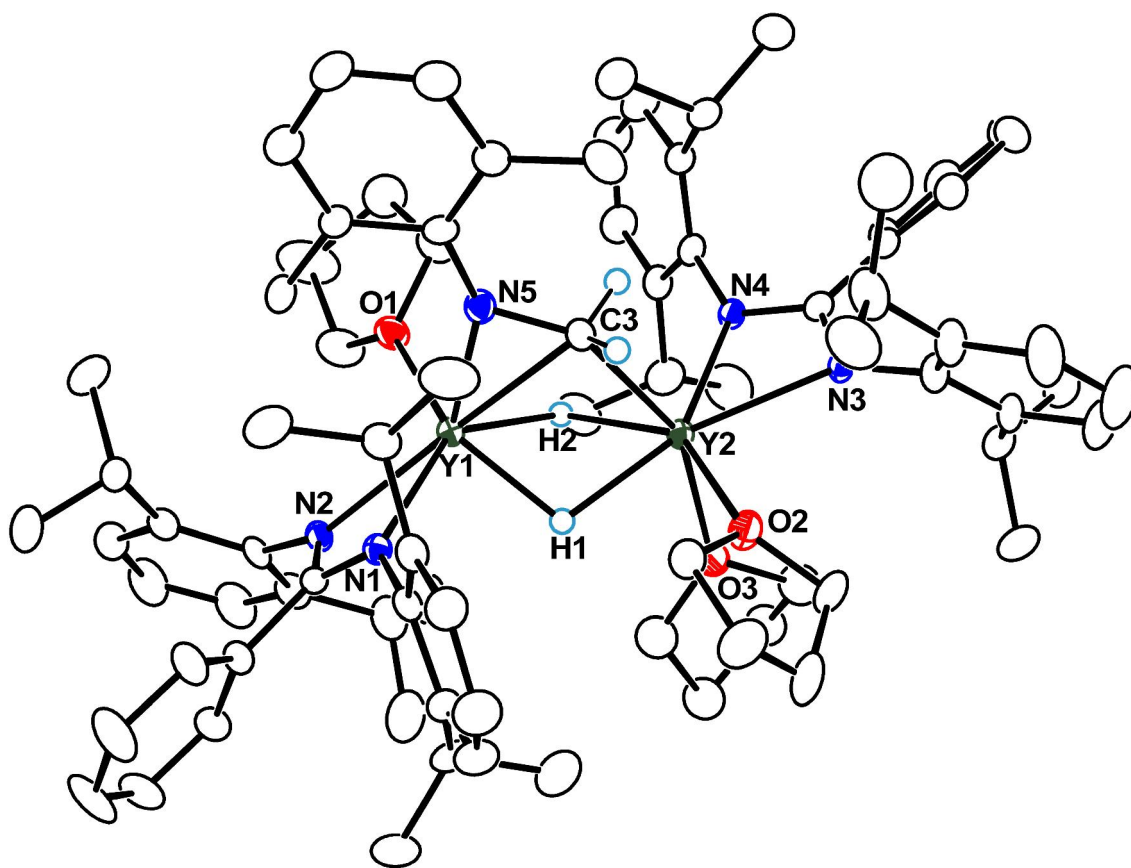


Figure 4. Ortep drawing of $[(\text{NCN})_2\text{Y}_2(\text{H})_2(\text{THF})_3](\text{NCH}_2\text{Ar}^*)$ (**3-Y**) with thermal ellipsoids at the 30% probability level. Selected bond distances [\AA] and angles [deg]: Y1–H1, 2.02(4); Y1–H2, 2.26(5); Y1–N5, 2.186(3); Y1–C3, 2.521(4); Y1–O1, 2.423(2); Y1–N1, 2.426(3); Y1–N2, 2.454(3); Y2–H1, 2.11(4); Y2–H2, 2.17(5); Y2–C3, 2.433(4); Y2–N3, 2.473(3); Y2–N4, 2.406(3); Y2–O2, 2.417(2); Y2–O3, 2.373(3); C3–N5, 1.446(5); Y1---Y2, 3.2699(8); Y1–H1–Y2, 104.9(12); Y1–H2–Y2, 95.1(13).

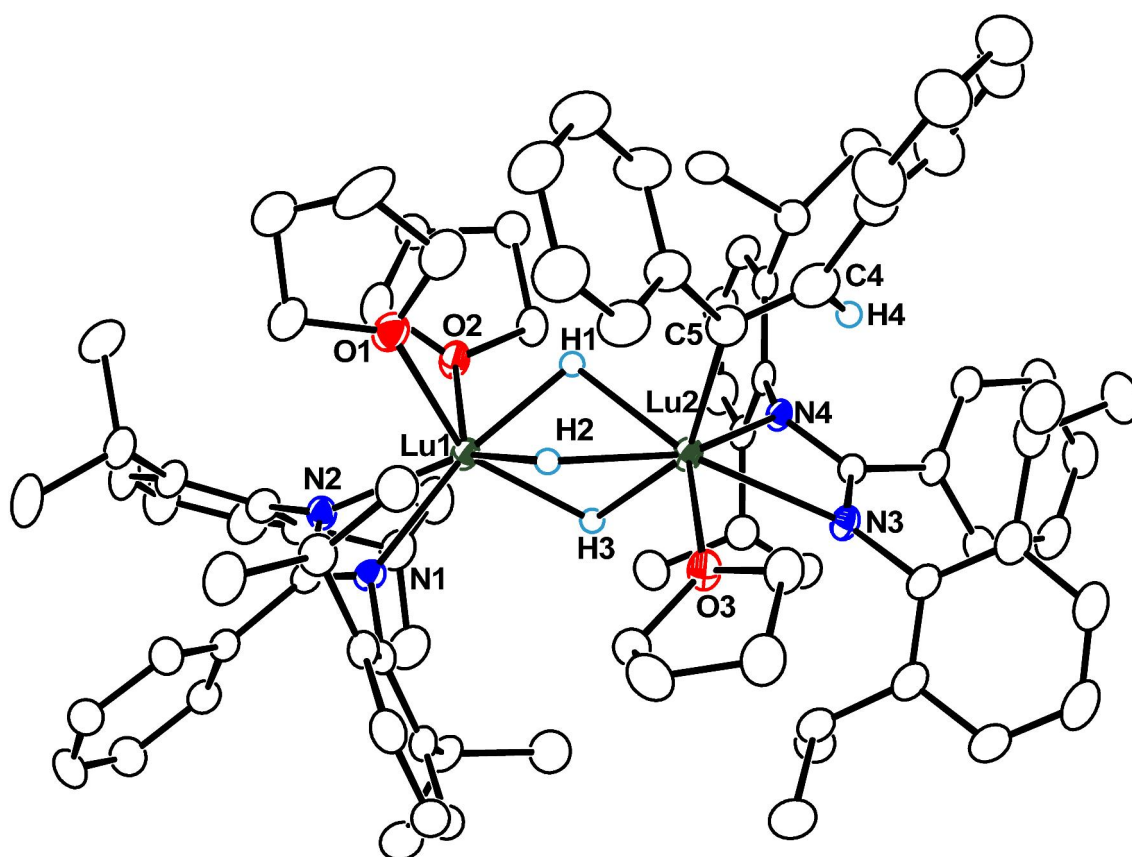
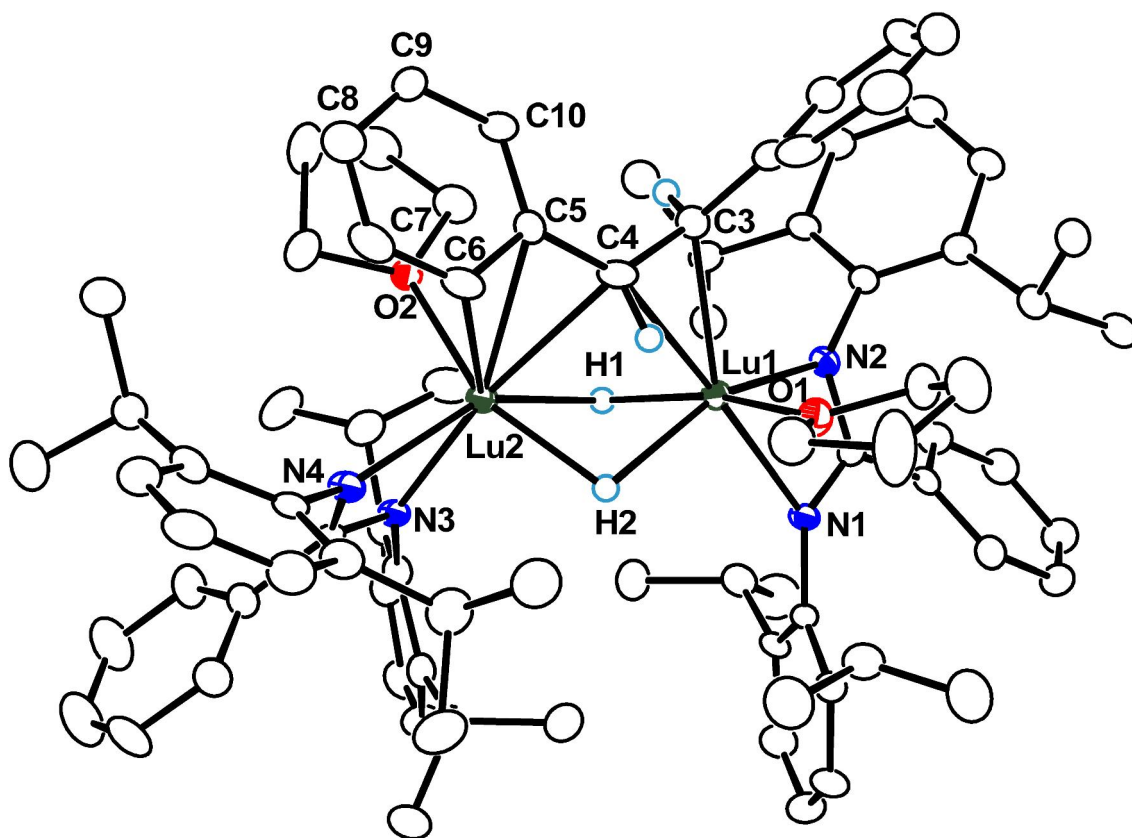


Figure 5. Ortep drawing of $[(\text{NCN})_2\text{Lu}_2(\text{H})_3(\text{THF})_3](\text{PhC}=\text{CHPh})$ (**4-Lu-a**) with thermal ellipsoids at the 30% probability level. Selected bond distances [Å] and angles [deg]: Lu1–H1, 1.98(5); Lu1–H2, 2.12(6); Lu1–H3, 2.11(6); Lu1–O1, 2.281(4); Lu1–O2, 2.361(4); Lu1–N1, 2.331(5); Lu1–N2, 2.474(5); Lu2–H1, 2.26(5); Lu2–H2, 2.10(6); Lu2–H3, 2.20(6); Lu2–N3, 2.470(5); Lu2–N4, 2.361(4); Lu2–C5, 2.371(7); Lu2–O3, 2.360(4); C4–C5, 1.347(10); Lu1---Lu2, 3.2808(6); Lu1–H1–Lu2, 100.9(14); Lu1–H2–Lu2, 102.3(17); Lu1–H3–Lu2, 99.3(15).



SFigure 6. Ortep drawing of $[(\text{NCN})\text{Lu}(\text{H})(\text{THF})_2](\text{PhCH}-\text{CHPh})$ (**4-Lu-b**) with thermal ellipsoids at the 30% probability level. Selected bond distances [\AA] and angles [deg]: Lu1–H1, 1.93(7); Lu1–H2, 2.14(6); Lu1–C3, 2.398(7); Lu1–C4, 2.483(7); Lu1–O1, 2.337(5); Lu1–N1, 2.381(5); Lu1–N2, 2.327(5); Lu2–H1, 2.28(7); Lu2–H2, 2.09(6); Lu2–C4, 2.604(7); Lu2–C5, 2.785(6); Lu2–C6, 2.775(7); Lu2–N3, 2.332(5); Lu2–N4, 2.317(5); Lu2–O2, 2.270(4); C3–C4, 1.503(9); C4–C5, 1.445(9); Lu1---Lu2, 3.2047(7); Lu1–H1–Lu2, 98.7(20); Lu1–H2–Lu2, 98.3(16).

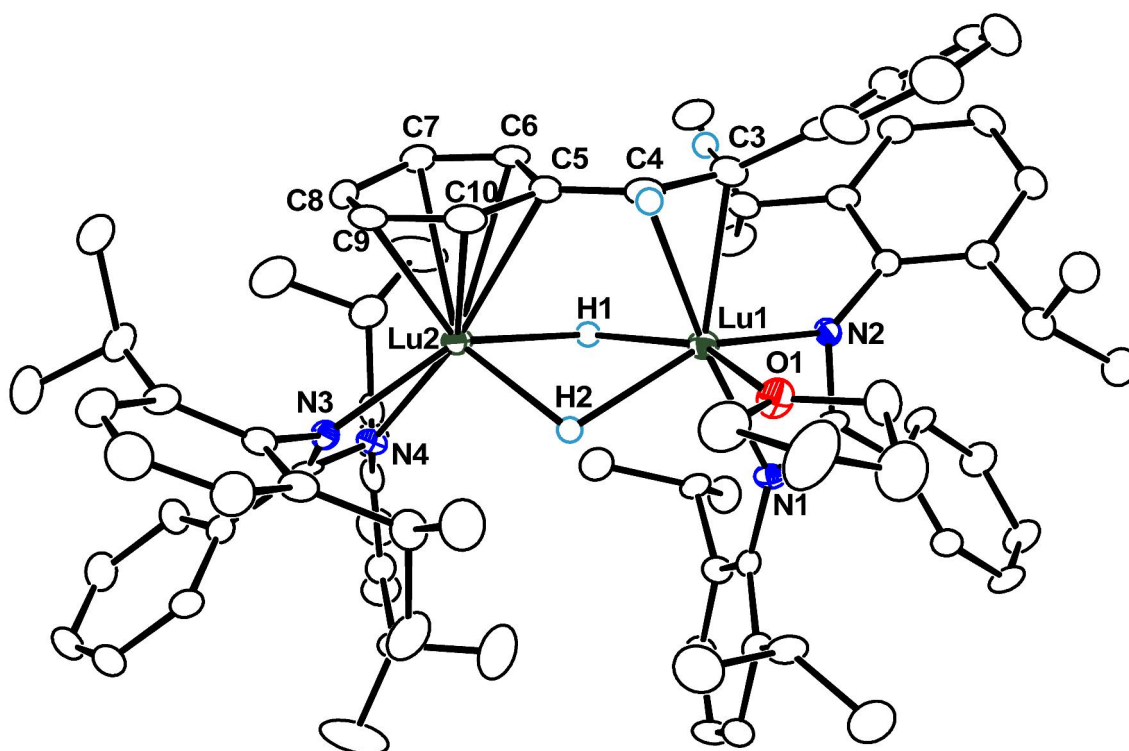


Figure 7. Ortep drawing of $[(\text{NCN})_2\text{Lu}_2(\text{H})_2(\text{THF})](\text{PhCH-CHPh})$ (**4-Lu-c**) with thermal ellipsoids at the 30% probability level. Selected bond distances [\AA] and angles [deg]: Lu1–H1, 2.00(5); Lu1–H2, 2.36(5); Lu1–C3, 2.474(6); Lu1–C4, 2.624(6); Lu1–O1, 2.300(4); Lu1–N1, 2.394(4); Lu1–N2, 2.324(4); Lu2–H1, 2.12(5); Lu2–H2, 2.22(5); Lu2–C5, 2.662(5); Lu2–C6, 2.687(6); Lu2–C7, 2.664(6); Lu2–C8, 2.571(6); Lu2–C9, 2.609(6); Lu2–C10, 2.622(6); Lu2–N3, 2.368(4); Lu2–N4, 2.282(4); C3–C4, 1.435(8); C4–C5, 1.385(8); C5–C6, 1.476(8); C6–C7, 1.355(8); C7–C8, 1.409(8); C8–C9, 1.388(9); C9–C10, 1.372(9); C10–C5, 1.461(8); Lu1---Lu2, 3.4224(5); Lu1–H1–Lu2, 111.7(15); Lu1–H2–Lu2, 96.2(14).

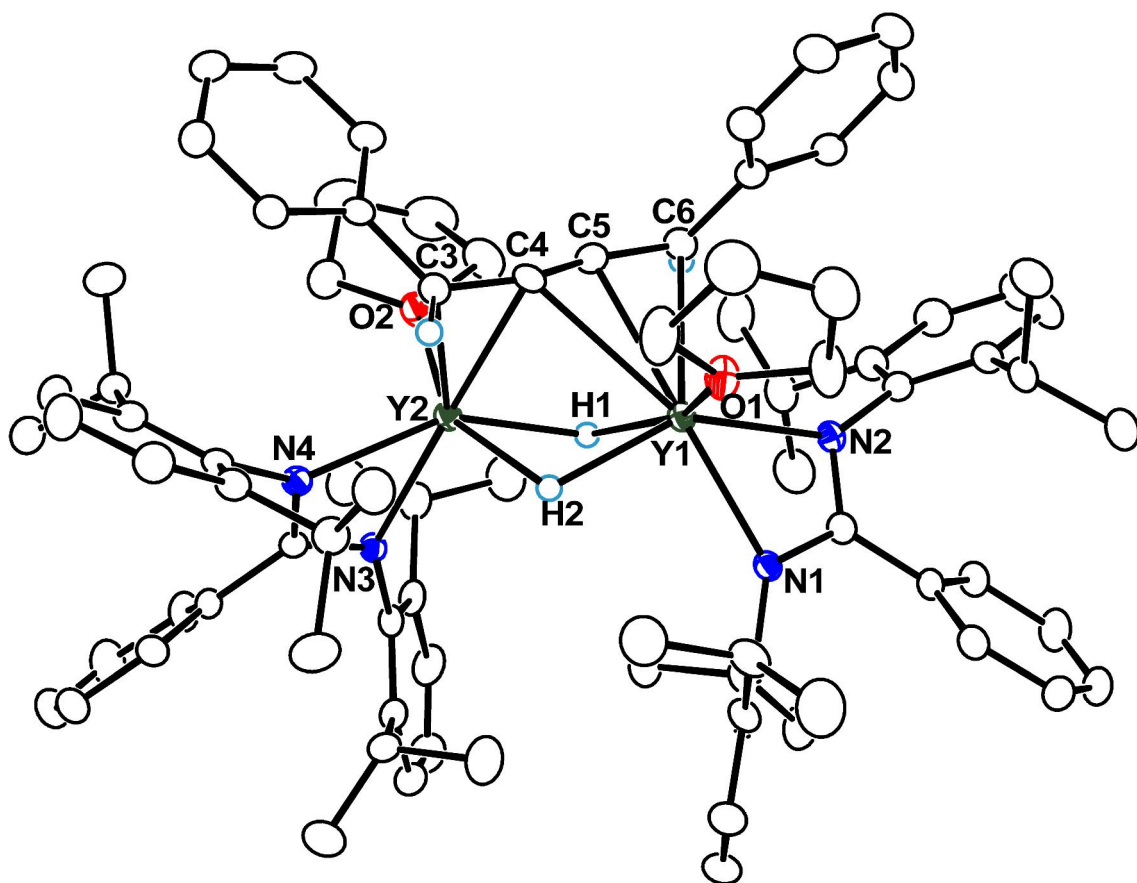


Figure 8. Ortep drawing of $[(\text{NCN})\text{Y}(\text{H})(\text{THF})]_2(\text{PhCHC}\equiv\text{CCHPh})$ (**5-Y**) with thermal ellipsoids at the 30% probability level. Selected bond distances [\AA] and angles [deg]: Y1–H1, 2.14(3); Y1–H2, 2.14(3); Y1–C4, 2.867(3); Y1–C5, 2.539(3); Y1–C6, 2.576(3); Y1–O1, 2.337(2); Y1–N1, 2.380(2); Y1–N2, 2.381(2); Y2–H1, 2.18(3); Y2–H2, 2.17(3); Y2–C3, 2.533(3); Y2–C4, 2.560(3); Y2–O2, 2.348(2); Y2–N3, 2.386(2); Y2–N4, 2.373(2); C3–C4, 1.403(4); C4–C5, 1.237(4); C5–C6, 1.393(4); Y1---Y2, 3.3404(7); Y1–H1–Y2, 101.3(8); Y1–H2–Y2, 101.8(8); C3–C4–C5, 158.6(3); C4–C5–C6, 160.1(3).