

Electronic Supplementary Information

**Reduction of carbodiimides by a dialumane through insertion and
cycloaddition**

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S1. Experimental details

General procedures

All of the reactions and manipulations of air- and moisture-sensitive compounds were carried out under argon or nitrogen with standard Schlenk or dry box techniques. The solvents (toluene and THF) were dried using appropriate methods and were distilled under argon prior to use. Benzene-*d*₆ and THF-*d*₈ were dried over Na/K alloy. The α -diimine ligand L was prepared according to literature procedures.¹ Sodium metal, anhydrous aluminum chloride (AlCl₃) and carbodiimides were purchased from Alfa Aesar. NMR spectra were recorded on a Mercury Plus-400 spectrometer. Elemental analyses were performed with an Elementar VarioEL III instrument. IR spectra were recorded using a Nicolet AVATAR 360 FT-IR spectrometer.

Synthesis of [LAl(CyNCNCy)Al(THF)L] (2)

N,N'-Dicyclohexylcarbodiimide (DCC, 0.206 g, 1.0 mmol) was added to a solution of [L(THF)Al–Al(THF)L] (1)² (1.0 mmol) in 30 mL of toluene, and the mixture was stirred at r.t. for 12h, upon which the color changed from deep-red to orange. The mixture was filtered, and the brownish yellow filtrate was concentrated to about 5 mL. Yellow crystals were grown from a toluene-THF solution at –20 °C for 1 week (0.680 g, 56 %). ¹H NMR (400 MHz, THF-*d*₈, 293 K): δ /ppm: 0.00 (m, 2H, CH₂-Cy), 0.59 (m, 2H, CH₂-Cy), 0.71 (m, 4H, CH₂-Cy), 0.89 (m, 2H, CH₂-Cy), 1.00 (m, 2H, CH₂-Cy), 1.05 (d, *J* = 6.8 Hz, 6H, CH(CH₃)₂), 1.08 (d, *J* = 6.8 Hz, 6H, CH(CH₃)₂), 1.11 (d, 12H, CH(CH₃)₂), 1.12 (m, 2H, CH₂-Cy), 1.13 (d, *J* = 6.8 Hz, 6H, CH(CH₃)₂), 1.17 (d, 12H, CH(CH₃)₂), 1.22 (m, 4H, CH₂-Cy), 1.23 (d, *J* = 6.8 Hz, 6H, CH(CH₃)₂), 1.34 (s, 6H, N-CCH₃), 1.52 (s, 6H, N-CCH₃), 1.56 (m, 2H, CH₂-Cy), 2.30 (toluene), 1.77 (THF), 2.63 (m, 2H, CH-Cy), 3.30 (sept, *J* = 6.8 Hz, 2H, CH(CH₃)₂), 3.38 (sept, *J* = 6.8 Hz, 2H, CH(CH₃)₂), 3.62 (THF), 3.67 (overlap with THF, 4H, CH(CH₃)₂), 6.90–7.10 (m, Ar). ¹³C NMR (100.6 MHz, THF-*d*₈, 298 K): δ /ppm: 15.2 (NCCH₃), 21.3 (toluene), 24.3 (CH₂-Cy), 24.4 (CH₂-Cy), 24.7 (CH₂-Cy), 24.8 (CH₂-Cy), 24.9 (CH(CH₃)₂), 25.1 (CH(CH₃)₂), 25.2 (CH₂-Cy), 25.3 (CH₂-Cy), 25.4 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 25.6 (CH₂-Cy), 25.7 (CH(CH₃)₂), 26.2 (CH(CH₃)₂), 28.4 (THF), 36.6 (CH₂-Cy), 38.4 (CH₂-Cy), 54.6 (CH-Cy), 119.8–138.4 (Ar), 145.7 (N-CCH₃), 146.8 (N-CCH₃), 147.9 (N-CCH₃), 148.8 (CyNCNCy). IR (Nujol, cm⁻¹): 2957 s, 2931 s, 2920 s, 2783 w, 2718 w, 2685 w, 1662 w, 1604 w, 1558 w, 1472 s, 1429 s, 1389 s, 1366 s, 1230 s, 1176 m, 944 m, 923 m, 727 m, 694 w, 463 w. Elemental analysis calcd. for C₇₃H₁₁₀Al₂N₆O·THF (C₇₇H₁₁₈Al₂N₈O₂ 1213.73): C 76.19; H 9.80; N 6.92. Found: C 76.52, H 9.70 N 7.16%.

Synthesis of [LAl(*i*PrNCN*i*Pr)Al(*i*PrNCN*i*Pr)] (3)

N,N'-Diisopropylcarbodiimide (DIC, 0.252 g, 2.0 mmol) was added to a solution of 1.0 mmol of **1** in

30 mL toluene. The resultant orange solution was stirred at ambient temperature for 3 days. The mixture was filtered, and the brownish yellow filtrate was concentrated to about 5 mL. Red crystals were grown from a toluene solution at $-20\text{ }^{\circ}\text{C}$ for 1 week (0.780 g, 70 %). ^1H NMR (400 MHz, THF- d_8 , 298 K): δ/ppm : 0.26 (s, 6H, N-CCH₃), 0.60 (s, 6H, N-CCH₃), 1.02 (d, $J = 4.4$ Hz, 6H, CH(CH₃)₂), 1.08 (d, $J = 4.4$ Hz, 6H, CH(CH₃)₂), 1.08-1.14 (br, 30H, CH(CH₃)₂), 1.17 (dd, $J = 4.4$ Hz, 12H, CH(CH₃)₂), 1.20 (d, $J = 4.4$ Hz, 6H, CH(CH₃)₂), 1.46 (br, 12H, CH(CH₃)₂), 2.92 (sept, $J = 4.4$ Hz, 2H, CH(CH₃)₂), 3.28 (sept, $J = 4.4$ Hz, 2H, CH(CH₃)₂), 3.41 (sept, $J = 4.4$ Hz, 2H, CH(CH₃)₂), 3.49 (sept, $J = 4.4$ Hz, 2H, CH(CH₃)₂), 3.55 (br, 2H, CH(CH₃)₂), 3.63 (br, 2H, CH(CH₃)₂), 6.91-7.05 (m, Ar). ^{13}C NMR (100.6 MHz, THF- d_8 , 298 K): δ/ppm : 15.2 (N-CCH₃), 23.8 (N-CCH₃), 24.8 (N-CCH₃), 24.9(CH(CH₃)₂), 25.0 (CH(CH₃)₂), 25.2 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 25.6 (N-CCH₃), 28.2 (CH(CH₃)₂), 28.3(CH(CH₃)₂), 49.3 (NCH(CH₃)₂), 49.3 (NCH(CH₃)₂), 67.7 (N-CCH₃), 119.7–125.4 (Ar), 145.0 (N-CCH₃), 146.9 (N-CCH₃), 146.9 (*i*Pr-NCN-*i*Pr), 148.9 (*i*Pr-NCN-*i*Pr). IR (Nujol, cm^{-1}): 3026 m, 2954 s, 2923 s, 2854 s, 2727 w, 2669 w, 1605 w, 1574 m, 1543 m, 1495 m, 1456 s, 1377 s, 1325 m, 1304 m, 1254 m, 1211 w, 1176 w, 1057 w, 1029 w, 935 w, 918 w, 887 w, 833 w, 787 m, 757 w, 727 s, 694 m, 626 m, 604 m, 578 m, 465 m, 449 w. Elemental analysis calcd for C₇₀H₁₀₈Al₂N₈ (1115.60): C 75.36; H 9.76; N 10.04; found: C 75.64, H 9.79 N, 9.76%.

Synthesis of [LAl(CyNCNCy)AlL^H(CyNCNHCy)] (4)

N,N'-Dicyclohexylcarbodiimide (DCC, 0.413 g, 2.0 mmol) was added to a solution of 1.0 mmol of **1** in 30 mL toluene. Or N,N'-Dicyclohexylcarbodiimide (DCC, 0.206 g, 1.0 mmol) was added to a solution of 1.0 mmol of **2** in 30 mL of toluene. The resultant orange solution was stirred at ambient temperature for 3 days. The mixture was filtered, and the brownish yellow filtrate was concentrated to about 5 mL. Orange crystals were grown from a toluene-THF solution at $-20\text{ }^{\circ}\text{C}$ for 1 week (0.705 g, 53 %). ^1H NMR (400 MHz, THF- d_8 , 298 K): δ/ppm : -0.63 (m, 1H, CH₂-Cy), -0.25 (m, 1H, CH₂-Cy), 0.24 (m, 1H, CH₂-Cy), 0.55 (m, 3H, CH₂-Cy), 0.74 (m, 1H, CH₂-Cy), 0.88 (m, 4H, CH₂-Cy), 0.98 (d, $J = 4.4$ Hz, 3H, CH(CH₃)₂), 1.01 (m, 1H, CH₂-Cy), 1.05 (d, $J = 4.4$ Hz, 3H, CH(CH₃)₂), 1.10 (m, 2H, CH₂-Cy), 1.11 (d, $J = 4.4$ Hz, 6H, CH(CH₃)₂), 1.12 (d, $J = 4.4$ Hz, 6H, CH(CH₃)₂), 1.14 (m, 4H, CH₂-Cy), 1.17 (m, 12H, CH(CH₃)₂), 1.21 (m, 12H, CH(CH₃)₂), 1.27 (d, $J = 4.4$ Hz, 3H, CH(CH₃)₂), 1.31 (d, $J = 4.4$ Hz, 3H, CH(CH₃)₂), 1.35 (m, 5H, CH₂-Cy), 1.43 (s, 3H, N-CCH₃), 1.48 (s, 3H, N-CCH₃), 1.54 (m, 2H, CH₂-Cy), 1.58 (m, 1H, CH₂-Cy), 1.60 (m, 2H, CH₂-Cy), 1.67 (m, 3H, CH₂-Cy), 1.78 0.24 (m, 3H, CH₂-Cy), 1.87 (m, 3H, CH₂-Cy), 1.96 (m, 1H, CH₂-Cy), 2.02 (m, 1H, CH₂-Cy), 2.22 (m, 1H, CH₂-Cy), 2.30 (s, 3H, N-CCH₃), 2.47 (m, 1H, CH-Cy), 2.74 (br, 2H, C=CH₂), 3.04 (m, 1H, CH-Cy), 3.38 (m, 1H, CH-Cy), 3.40 (sept, $J = 4.4$ Hz, 1H, CH(CH₃)₂), 3.44 (sept, $J = 4.4$ Hz, 1H, CH(CH₃)₂), 3.54 (sept, $J = 4.4$ Hz, 1H, CH(CH₃)₂), 3.63 (m, sept, $J = 4.4$ Hz, 2H, CH(CH₃)₂), 3.65 (m, 1H, CH-Cy), 3.73 (sept, $J = 4.4$ Hz, 1H, CH(CH₃)₂), 3.84 (sept, $J = 4.4$ Hz, 1H, CH(CH₃)₂), 3.88 (sept, 1H, CH(CH₃)₂), 5.77 (br, 1H, CyNCNHCy), 6.90–7.10 (m, Ar). ^{13}C NMR (100.6 MHz, THF- d_8 , 298 K): δ/ppm : 14.9 (N-CCH₃), 15.6 (N-CCH₃), 23.6 (N-CCH₃), 24.0, 24.0, 24.4, 24.6, 24.6,

25.3, 25.4, 25.7, 25.8, 25.9, 26.5, 26.6, 26.8, 27.0, 27.5, 27.6, 27.6, 27.9, 28.0, 28.2, 28.3, 28.6, 28.7, 29.1 (CH(CH₃)₂, CH(CH₃)₂ or CH₂-Cy), 35.1 (CH₂-Cy), 35.2 (CH₂-Cy), 35.3 (CH₂-Cy), 36.3 (CH₂-Cy), 38.3 (CH₂-Cy), 38.7 (CH₂-Cy), 53.6 (CH-Cy), 55.8 (CH-Cy), 55.8 (CH-Cy), 57.7 (CH-Cy), 67.7 (NCCH₃), 69.1 (NC=CH₂), 119.6–147.0 (Ar), 147.9 (NC=CH₂), 148.7 (NC=CN), 149.8 (NC=CN), 151.6 (Cy-NCN-Cy), 160.7 (Cy-NCN-Cy). IR (Nujol, cm⁻¹): 3155 m (NH), 2974 s, 2864 s, 2683 w, 1630 w, 1497 w, 1460 s, 1365 m, 1290 m, 1246 m, 1213 m, 1178 m, 1070 s, 1029 s, 912 s, 873 s, 731 w, 696 m, 679 m, 669 w, 660 w, 466 w. Elemental analysis calcd for C₈₂H₁₂₄Al₂N₈·1/2toluene (1321.91): C 77.68; H 9.76; N 8.48; found: C 77.20, H 9.81, N 8.58%.

Synthesis of [LAl(CyNCNCy)AlI^{-H}(CyNCNCy)][Na(THF)₂] (**5**)

N,N'-Dicyclohexylcarbodiimide (DCC, 0.413 g, 2.0 mmol) was added to a solution of 1.0 mmol of **1** and 1.0 mmol of Na metal in 30 mL toluene. Or 1.0 mmol of Na metal was added to a solution of 1.0 mmol of **3** in 30 mL of toluene. The resultant orange solution was stirred at ambient temperature for 3 days, upon which the color changed to yellow. The mixture was filtered, and the brownish yellow filtrate was concentrated to about 5 mL. Yellow crystals were grown from a toluene solution at -20 °C for 1 week (0.865 g, 52 %). ¹H NMR (400 MHz, C₆D₆, 298 K): δ/ppm: -0.20 (m, 1H, CH₂-Cy), 0.28 (m, 1H, CH₂-Cy), 0.63 (m, 1H, CH₂-Cy), 0.72 (m, 1H, CH₂-Cy), 0.79 (m, 1H, CH₂-Cy), 0.96 (d, *J* = 4.6 Hz, 3H, CH(CH₃)₂), 0.96–1.12 (m, 4H, CH₂-Cy), 1.12 (s, 3H, CCH₃), 1.21 (d, *J* = 4.6 Hz, 3H, CH(CH₃)₂), 1.23–1.34 (m, 4H, CH₂-Cy), 1.36–1.38 (m, 2H, CH₂-Cy), 1.37 (m, 6H, CH(CH₃)₂), 1.41 (s, 3H, CCH₃), 1.39–1.42 (m, 1H, CH₂-Cy), 1.40 (m, 6H, CH(CH₃)₂), 1.45 (d, *J* = 4.6 Hz, 6H, CH(CH₃)₂), 1.50 (m, 6H, CH(CH₃)₂), 1.48–1.53 (m, 7H, CH₂-Cy), 1.53 (m, 6H, CH(CH₃)₂), 1.59 (m, 6H, CH(CH₃)₂), 1.58–1.60 (m, 3H, CH₂-Cy), 1.63 (m, 6H, CH₂-Cy), 1.74 (m, 2H, CH₂-Cy), 1.81 (d, *J* = 4.5 Hz, 6H, CH(CH₃)₂), 1.90 (m, 2H, CH₂-Cy), 2.01 (m, 2H, CH₂-Cy), 2.11 (s, 3H, CCH₃), 2.17 (m, 1H, CH₂-Cy), 2.45 (s, 1H, C=CH₂), 2.51 (m, 1H, CH₂-Cy), 2.74 (m, 1H, CH-Cy), 2.95 (s, 1H, C=CH₂), 3.10 (sept, *J* = 4.6 Hz, 1H, CH(CH₃)₂), 3.36 (sept, *J* = 4.6 Hz, 1H, CH(CH₃)₂), 3.39 (m, 1H, CH-Cy), 3.55 (m, 1H, CH-Cy), 3.70 (sept, *J* = 4.6 Hz, 1H, CH(CH₃)₂), 3.90 (m, THF), 3.90 (m, 1H, CH-Cy), 3.95 (sept, *J* = 4.6 Hz, 1H, CH(CH₃)₂), 4.14 (sept, *J* = 4.6 Hz, 1H, CH(CH₃)₂), 4.17 (sept, *J* = 4.6 Hz, 1H, CH(CH₃)₂), 4.25 (sept, *J* = 4.6 Hz, 1H, CH(CH₃)₂), 4.27 (sept, *J* = 4.6 Hz, 1H, CH(CH₃)₂), 6.99–7.25 (m, Ar). ¹³C NMR (100.6 MHz, C₆D₆, 298 K): δ/ppm: 15.6 (N-CCH₃), 16.0 (N-CCH₃), 21.4 (N-CCH₃), 23.7, 24.2, 24.5, 24.8, 24.8, 25.1, 25.1, 25.2, 25.3, 25.4, 25.5, 25.6, 25.7, 25.7, 25.8, 25.9, 25.9, 26.3, 26.6, 26.7, 26.8, 27.0, 27.2, 27.5, 27.5, 27.7, 27.9, 28.2, 28.2, 28.3, 28.4, 28.6 (CH(CH₃)₂, CH(CH₃)₂ or CH₂-Cy), 35.4 (CH₂-Cy), 36.3 (CH₂-Cy), 37.2 (CH₂-Cy), 37.4 (CH₂-Cy), 38.1 (CH₂-Cy), 38.1 (CH₂-Cy), 38.7 (CH₂-Cy), 39.1 (CH₂-Cy), 53.4 (CH-Cy), 54.9 (CH-Cy), 56.0 (CH-Cy), 56.3 (CH-Cy), 62.4 (NCCH₃), 70.5 (NC=CH₂) 119.9–148.5 (Ar), 150.7 (NC=CH₂), 151.3 (NC=CN), 170.5 (CyNCNCy), 173.7 (CyNCNCy). IR (Nujol, cm⁻¹): 3026 m, 2957 s, 2923 s, 2854 s, 2727 w, 2671 w, 2180 w, 1605 w, 1495 m, 1458 s, 1377 s, 1251 m, 1211 w, 1177 w, 1124 w, 1080 w, 995 w, 939 w, 788 w, 727 s, 694 w, 462 w. Elemental analysis calcd for (C₈₂H₁₂₃Al₂N₈·Na(THF)₂·2.5(toluene)

1672.36): C 77.30; H 9.47; N 6.71; found: C 76.90, H 9.56, N 7.14 %.

Synthesis of [LAl(dippNCHNdipp)] (6)

Bis(2,6-diisopropylphenyl)carbodiimide (0.724, 2.0 mmol) was added to a solution of 1.0 mmol of **1** in 30 mL toluene. The resultant orange solution was stirred at ambient temperature for 3 days. The mixture was filtered, and the brownish yellow filtrate was concentrated to about 5 mL. Red crystals were grown from a toluene solution at $-20\text{ }^{\circ}\text{C}$ for 1 week (0.715 g, 45 %). ^1H NMR (400 MHz, THF- d_8 , 298 K): δ /ppm: 0.80 (d, $J = 6.8$ Hz, 12H, CH(CH $_3$) $_2$), 0.95 (d, $J = 6.8$ Hz, 24H, CH(CH $_3$) $_2$), 1.16 (d, $J = 6.8$ Hz, 12H, CH(CH $_3$) $_2$), 1.16 (s, 6H, N-CCH $_3$), 2.31 (toulene), 3.06 (sept, $J = 6.8$ Hz, 4H, CH(CH $_3$) $_2$), 3.48 (sept, $J = 6.8$ Hz, 4H, CH(CH $_3$) $_2$), 6.98–7.07 (m, Ar), 8.09 (s, 1H, dipp-NC(H)N-dipp). ^{13}C NMR (100.6 MHz, THF- d_8 , 298 K): δ /ppm: 15.0 (N-CCH $_3$), 21.3 (toulene), 24.2 (CH(CH $_3$) $_2$), 24.5 (CH(CH $_3$) $_2$), 24.7 (CH(CH $_3$) $_2$), 29.4 (CH(CH $_3$) $_2$), 29.5 (CH(CH $_3$) $_2$), 121.1–129.5 (Ar), 138.4 (toulene), 145.3 (N-CCH $_3$), 147.2 (N-CCH $_3$), 176.0 (dipp-NC(H)N-dipp). IR (Nujol, cm^{-1}): 2958 s, 2901 s, 2731 s, 2716 s, 2180 w, 1661 w, 1474 s, 1389 s, 1366 s, 1261 m, 1231 s, 1165 m, 1099 w, 1078 w, 1030, 981 w, 951 m, 923 m, 891 w, 804 m, 727 m, 694 w, 460 w. Elemental analysis calcd for C $_{53}$ H $_{75}$ AlN $_4$ (795.15): C 80.05; H 9.51; N 7.05; found: C 81.00, H 9.40, N 6.54%.

Synthesis of [LAl(*t*BuNCHN*t*Bu)] (7)

N,N'-Di-*tert*-butylcarbodiimide (0.299 g, 2.0 mmol) was added to a solution of 1.0 mmol of **1** in 30 mL toluene. The deep-red solution was stirred at ambient temperature for 3 days, upon which the color changed to yellow. The mixture was filtered, and the brownish yellow filtrate was concentrated to about 5 mL. Yellow crystals were grown from a toluene solution at $-20\text{ }^{\circ}\text{C}$ for 1 week (0.575 g, 49 %). ^1H NMR (400 MHz, THF- d_8 , 298 K): δ /ppm: 1.16 (s, 18H, C(CH $_3$) $_3$), 1.17 (d, $J = 6.8$ Hz, 12H, CH(CH $_3$) $_2$), 1.21 (d, $J = 6.8$ Hz, 12H, CH(CH $_3$) $_2$), 1.50 (s, 6H, N-CCH $_3$), 3.67 (sept, $J = 6.8$ Hz, 4H, CH(CH $_3$) $_2$), 6.95 (t, $J = 7.5$ Hz, 2H, *p*-C $_6$ H $_3$), 7.03 (d, $J = 7.5$ Hz, 4H, *m*-C $_6$ H $_3$), 8.54 (s, 1H, *t*Bu-NC(H)N-*t*Bu). ^{13}C NMR (100.6 MHz, THF- d_8 , 298 K): δ /ppm: 15.0 (N-CCH $_3$), 24.8 (CH(CH $_3$) $_2$), 25.7 (CH(CH $_3$) $_2$), 27.7 (CH(CH $_3$) $_2$), 31.5 (C(CH $_3$) $_3$), 51.6 (C(CH $_3$) $_3$), 120.9 (*p*-C $_6$ H $_3$), 123.7 (*m*-C $_6$ H $_3$), 123.7 (*o*-C $_6$ H $_3$), 144.2 (N-CCH $_3$), 146.4 (N-CCH $_3$), 169.8 (*t*Bu-NC(H)N-*t*Bu). IR (Nujol, cm^{-1}): 3053 m, 2957 s, 2926 s, 2855 s, 1614 w, 1588 s, 1521 m, 1462 s, 1377 s, 1321 w, 12546 m, 1213 m, 1175 m, 1115 w, 1040 w, 1029 w, 995 w, 943 m, 926 w, 789 m, 744 w, 727 m, 638 w, 578 w. Elemental analysis calcd for C $_{37}$ H $_{59}$ AlN $_4$ (586.86): C 75.72; H 10.13; N 9.55; found: C 76.02, H 9.96, N 9.34%.

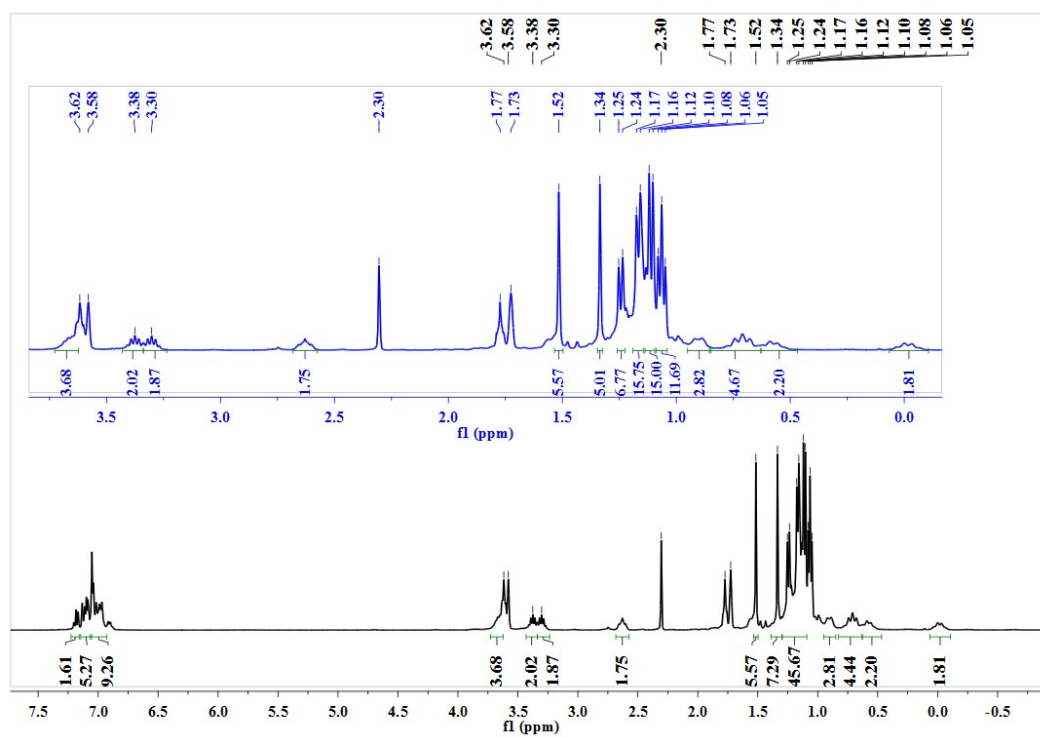


Fig. S1. ^1H NMR spectrum of complex **2** at 293 K in $\text{THF-}d_8$.

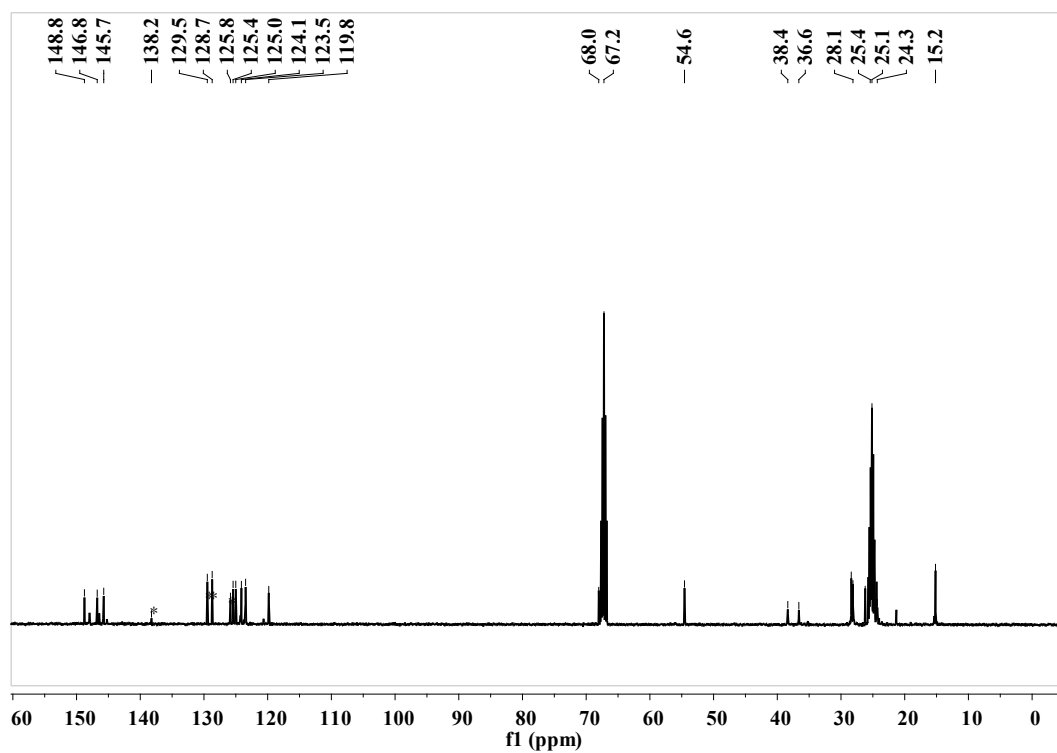


Fig. S2. ^{13}C NMR spectrum of complex **2** at 293 K in $\text{THF-}d_8$.

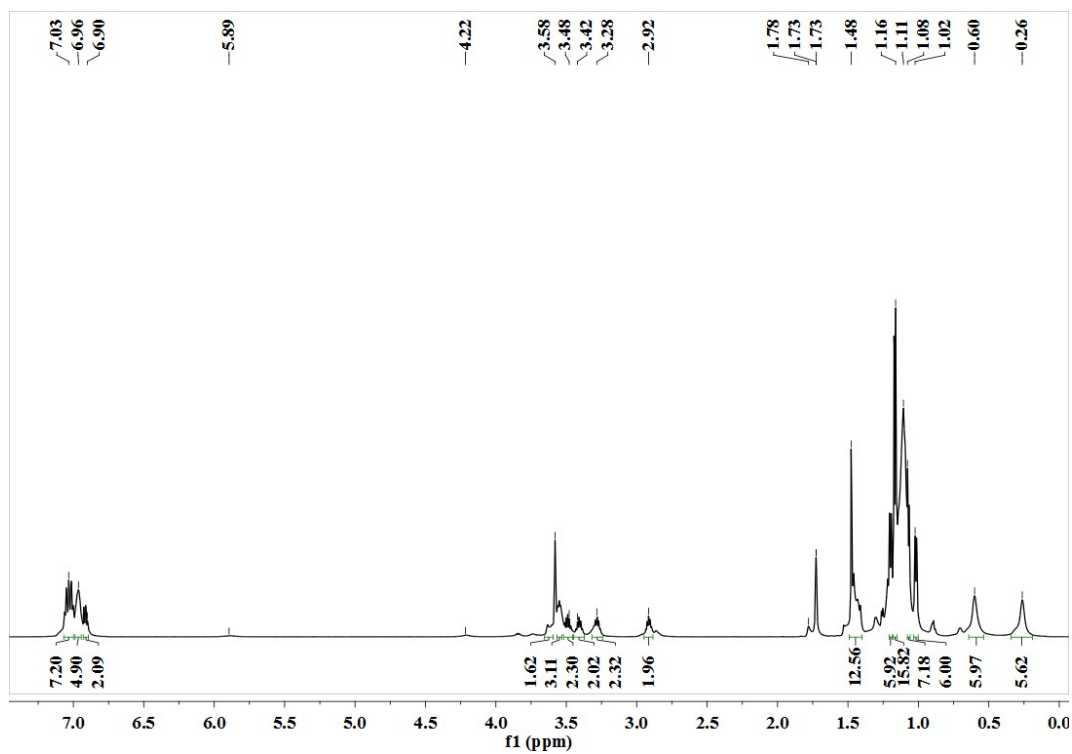


Fig. S3. ^1H NMR spectrum of complex **3** at 293 K in THF-d_8

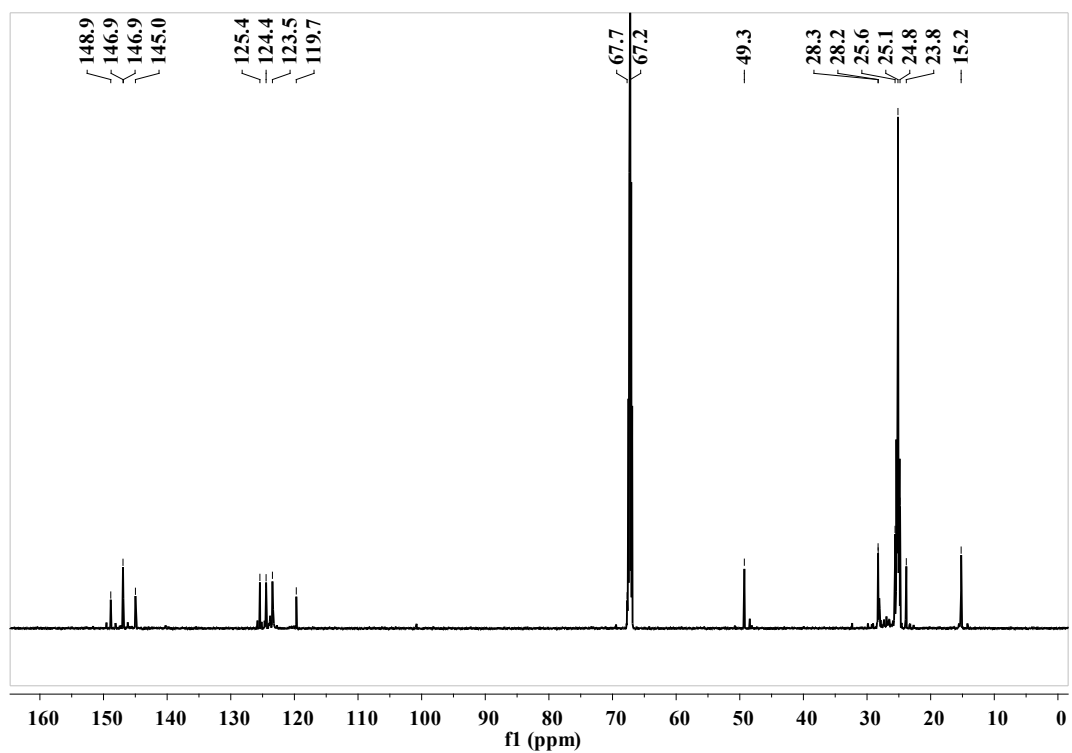


Fig. S4. ^{13}C NMR spectrum of complex **3** at 293 K in THF-d_8 .

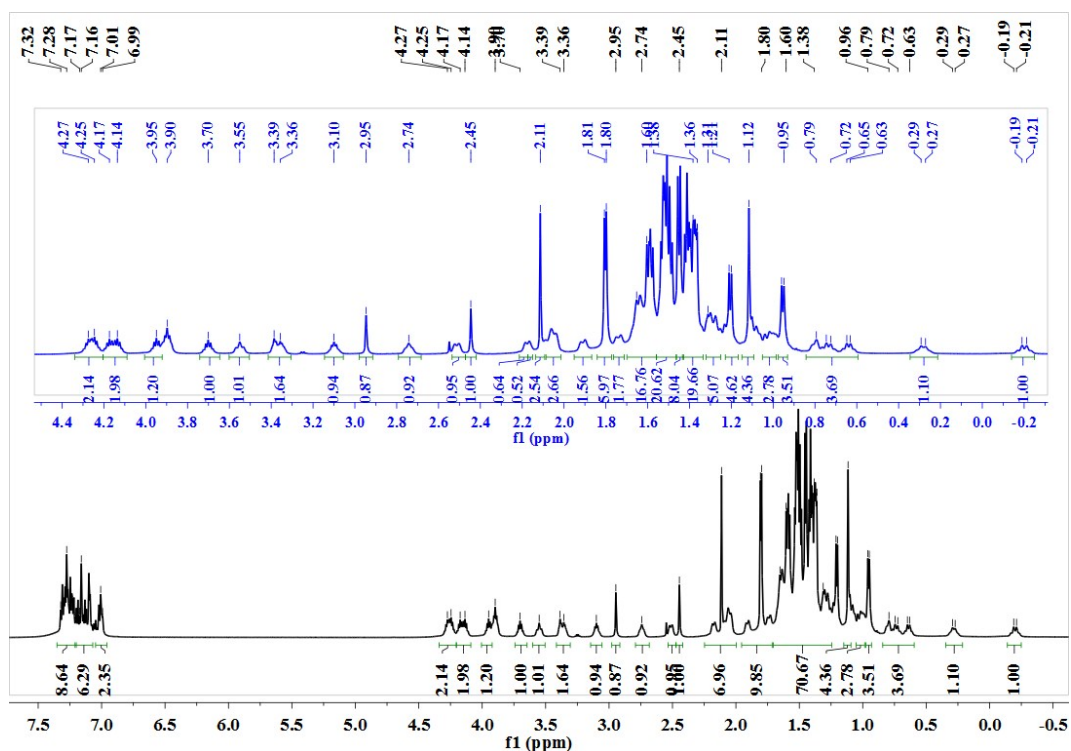


Fig. S7. ^1H NMR spectrum of complex **5** at 293 K in C_6D_6

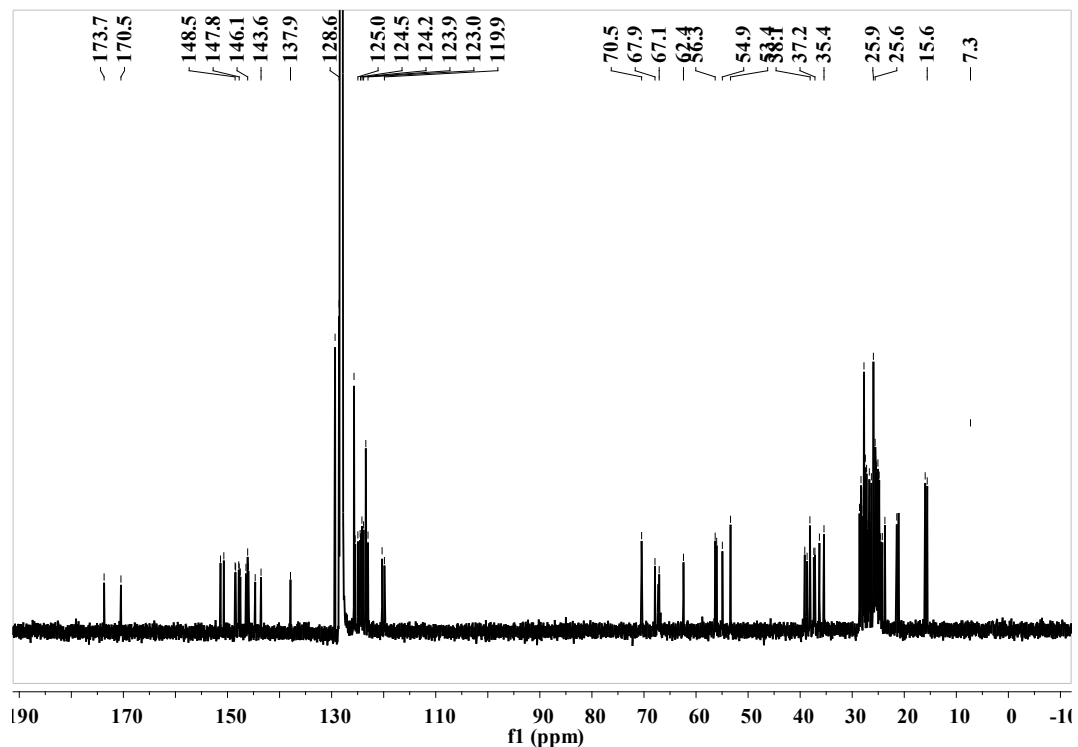


Fig. S8. ^{13}C NMR spectrum of complex **5** at 293 K in C_6D_6

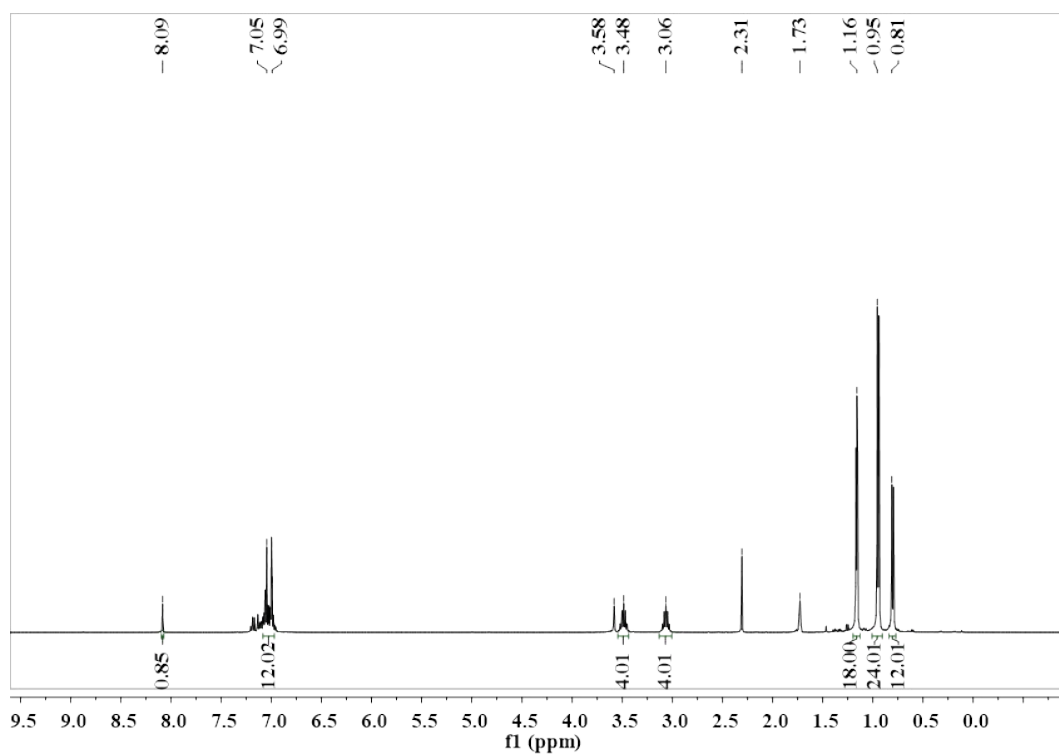


Fig. S9. ^1H NMR spectrum of complex **6** at 293 K in THF-d_8 .

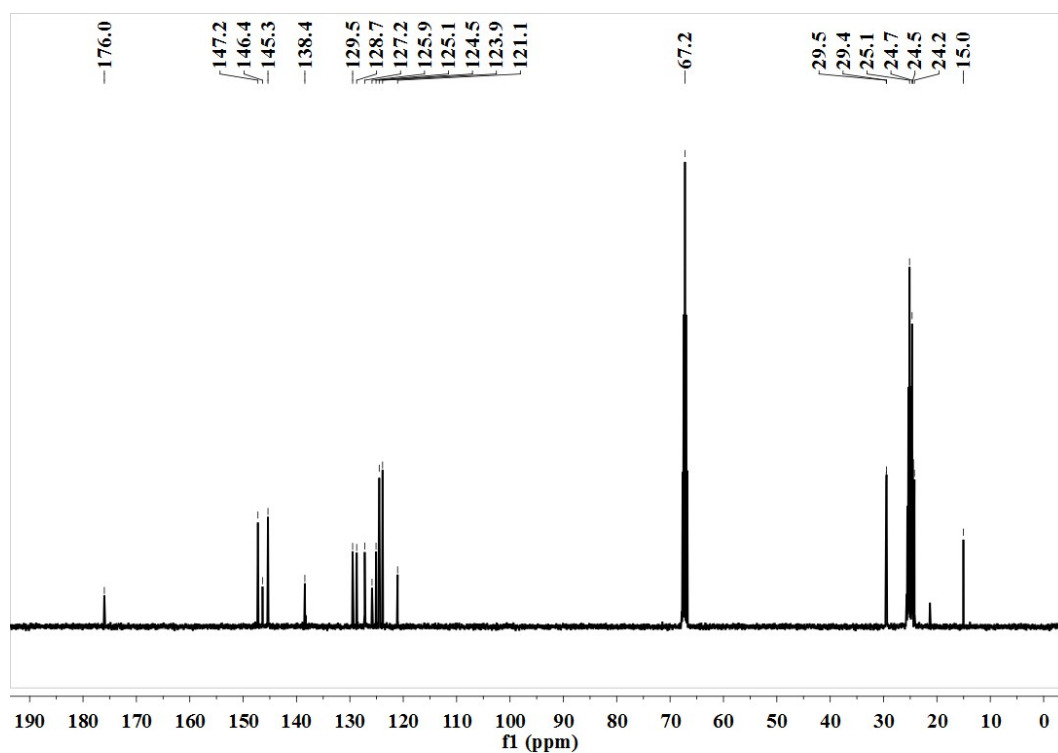


Fig. S10. ^{13}C NMR spectrum of complex **6** at 293 K in THF-d_8 .

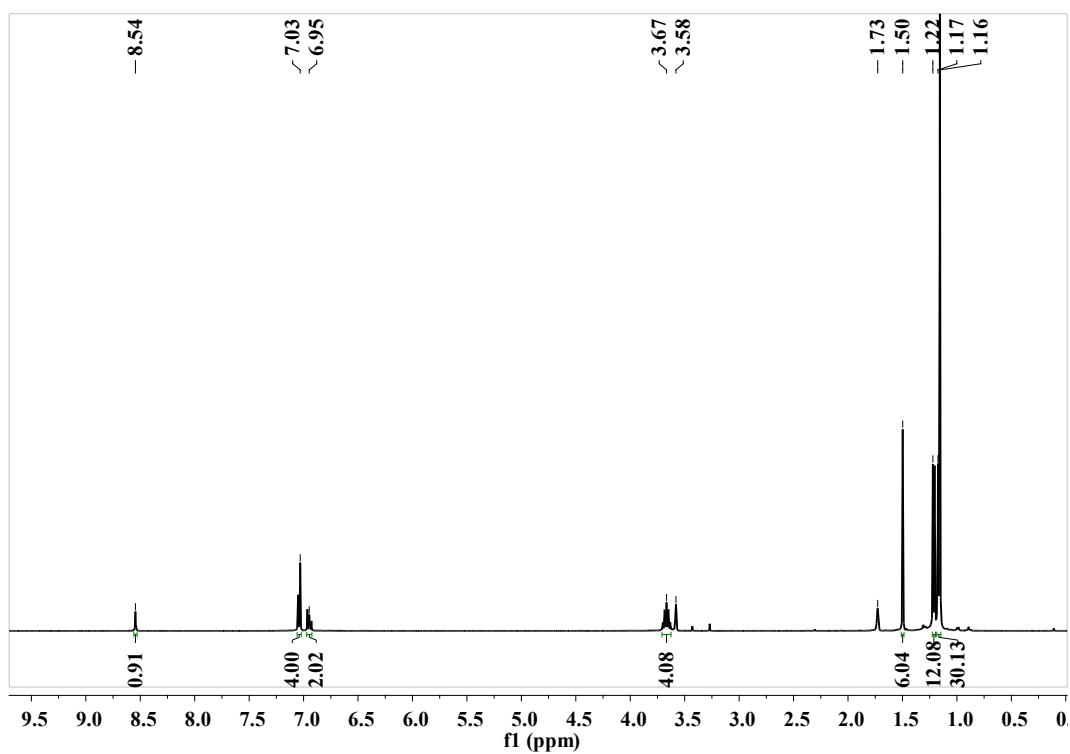


Fig. S11. ^1H NMR spectrum of complex 7 at 293 K in THF-d_8

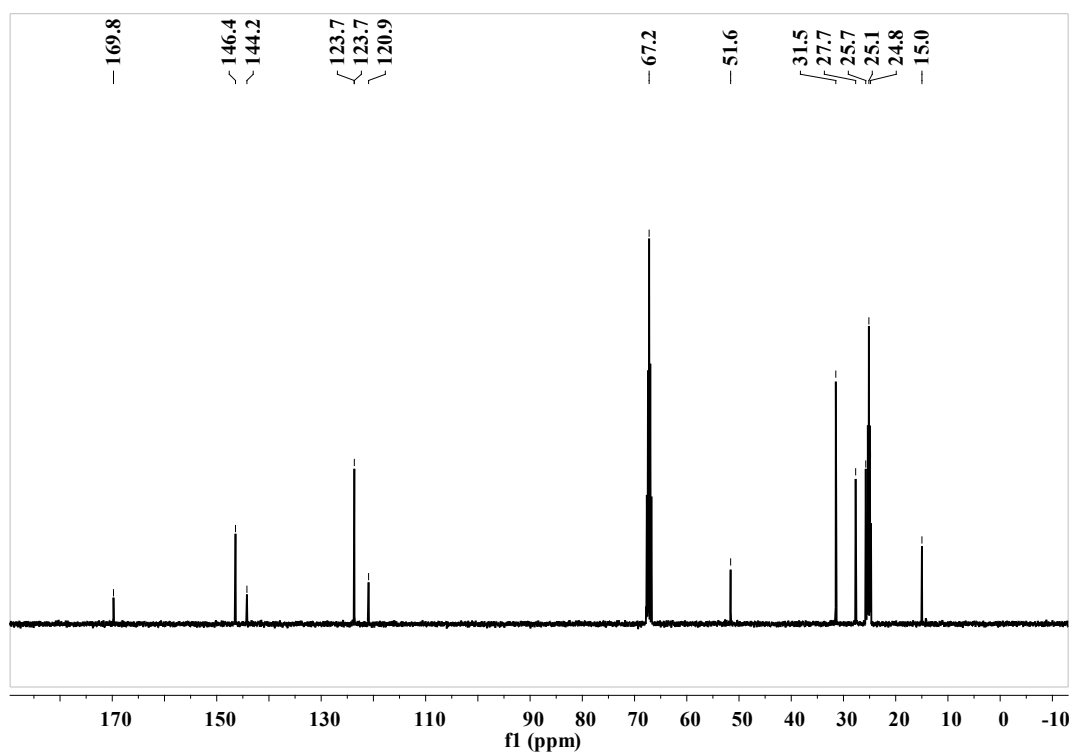


Fig. S12. ^{13}C NMR spectrum of complex 7 at 293 K in THF-d_8 .

S2. X-ray Crystallographic Analysis

Diffraction data for complexes **2–7** were collected on a Bruker SMART APEX II diffractometer at 153 K with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). An empirical absorption correction using SADABS was applied for all data.³ The structures were solved and refined to convergence on F^2 for all independent reflections by the full-matrix least squares method using the SHELXL–2014 programs.⁴ **For compounds 2 and 4**, about 9.0 molecules of THF (about 1 THF molecule per formula, $Z = 8$) and about 1.0 molecules of toluene (about 0.5 toluene molecule per formula, $Z = 2$) are co-crystallized in **2** and **4** respectively, with the corresponding electron density (380 electrons in **2** and 58 electrons in **4**) being removed using the SQUEEZE routine implemented within the software program PLATON.⁵ Crystallographic data and refinement details for compounds **2–7** are given in Table S1 and S2. CCDC numbers 1990578–1990583 for **2–7**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data and refinement details for compounds **2–4**.

Compound	2	3	4
Empirical formula	C ₇₃ H ₁₁₀ Al ₂ N ₆ ·O·THF	C ₇₀ H ₁₀₈ Al ₂ N ₈	C ₈₂ H ₁₂₄ Al ₂ N ₈ ·1/2toluene
Fw	1213.73	1115.60	1321.91
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>C2/c</i>	<i>P</i> –1	<i>P</i> –1
<i>a</i> / \AA	23.926(5)	11.946(2)	12.9012(10)
<i>b</i> / \AA	13.520(3)	14.183(3)	15.4561(13)
<i>c</i> / \AA	47.134(9)	21.699(4)	22.31268(17)
α / $^\circ$	90	71.614(6)	100.431(3)
β / $^\circ$	98.006(3)	88.934(6)	95.380(3)
γ / $^\circ$	90	76.753(6)	110.218(3)
<i>V</i> / \AA^3	15098(5)	3390.1(11)	4046.7(6)
<i>Z</i>	8	2	2
<i>D</i> _{calc} /g cm ^{–3}	1.068	1.093	1.085
<i>F</i> (000)	5312	1220	1446
μ /mm ^{–1}	0.085	0.088	0.083
θ range	1.734 – 24.796	2.446–25.973	2.318–23.500
Reflns collected	45817	39706	32443
Independent reflns	12879	13216	11343
Reflns [<i>I</i> > 2 σ (<i>I</i>)]	7836	10616	8287
<i>R</i> _{int}	0.0613	0.0507	0.0369
<i>R</i> ₁ ; <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0761; 0.1972	0.0498; 0.1443	0.0548; 0.1270
<i>R</i> ₁ ; <i>wR</i> ₂ (all data)	0.1173; 0.2136	0.0648; 0.1623	0.0774; 0.1368
GOF (<i>F</i> ²)	1.107	1.005	1.021

Table S2. Crystallographic data and refinement details for compounds 4–7.

Compound	5	6	7
Empirical formula	[C ₈₂ H ₁₂₃ Al ₂ N ₈ ·Na(THF) ₂ ·5/2toluene]*2	C ₅₃ H ₇₅ AlN ₄	C ₃₇ H ₅₉ AlN ₄
Fw	3344.73	795.15	586.86
Crystal system	Triclinic	Orthorhombic	Tetragonal
Space group	<i>P</i> -1	<i>Pca</i> 21	<i>P</i> 41
<i>a</i> /Å	13.092(3)	20.250(3)	12.7376(9)
<i>b</i> /Å	17.852(4)	12.5817(17)	12.7376(9)
<i>c</i> /Å	21.332(5)	18.940(3)	22.3806(15)
α /°	90.530(3)	90	90
β /°	90.050(3)	90	90
γ /°	96.922(2)	90	90
<i>V</i> /Å ³	4949.1(19)	4825.4(11)	3631.2(6)
<i>Z</i>	1	4	4
<i>D</i> _{calc} /g cm ⁻³	1.122	1.095	1.073
<i>F</i> (000)	1826	1736	1288
μ /mm ⁻¹	0.086	0.080	0.088
θ range	1.501–24.999	2.151–25.020	2.446–25.973
Reflns collected	29251	29003	23345
Independent reflns	16660	8323	6641
Reflns [<i>I</i> > 2 σ (<i>I</i>)]	10400	7774	5987
<i>R</i> _{int}	0.0551	0.0348	0.0343
<i>R</i> ₁ ; <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0843; 0.1938	0.0321; 0.0669	0.0356; 0.0837
<i>R</i> ₁ ; <i>wR</i> ₂ (all data)	0.1368; 0.2259	0.0362; 0.0688	0.0427; 0.0881
GOF (<i>F</i> ²)	1.072	1.0035	1.060

Table S3. Selected bond lengths (Å) and angles (°) for compounds 3–5.

	2	3	4	5	6	7
Al1–N1	1.817(3)	1.825(1)	1.832(2)	1.838(4)	1.814(2)	1.811(2)
Al1–N2	1.838(3)	1.826(1)	1.825(2)	1.843(4)	1.816(2)	1.818(2)
Al1–N3					1.956(2)	1.935(2)
Al1–N4					1.952(2)	1.885(2)
Al1–N5	1.923(2)	1.936(1)	1.915(2)	1.920(4)		
Al1–N6	1.894(3)	1.912(1)	1.895(2)	1.909(4)		
Al2–N3	1.828(3)	1.825(1)	1.823(2)	1.826(4)		
Al2–N4	1.837(3)	1.978(2)	1.879(2)	1.912(4)		
Al2–N7		1.888(1)	1.978(2)	1.901(4)		
Al2–C57	2.058(3)	2.037(2)	2.057(3)	2.062(4)		
N1–C1	1.446(4)	1.434(2)	1.436(4)	1.427(5)	1.435(3)	1.438(3)
N2–C2	1.431(4)	1.436(2)	1.441(3)	1.434(6)	1.435(3)	1.443(3)
C1–C2	1.346(5)	1.344(2)	1.351(4)	1.341(7)	1.347(3)	1.342(4)
N5–C57	1.348(4)	1.342(2)	1.351(3)	1.335(5)		
N6–C57	1.351(4)	1.347(2)	1.354(3)	1.370(5)		
C29–N3	1.431(4)	1.498(2)	1.501(3)	1.502(5)	1.314(3)	1.318(3)
C29–N4					1.326(3)	1.328(3)
C29–C30	1.333(5)	1.536(2)	1.542(4)	1.540(6)		

C30–C32		1.457(2)	1.342(4)	1.356(6),		
C29–C31		1.518(2)	1.542(4)	1.520(6)		
C30–N4	1.439(4)	1.316(2)	1.394(4)	1.381(5)		
N7–C58		1.370(2)	1.322(4)	1.364(5)		
N8–C58		1.290(2)	1.343(4)	1.302(5)		
C29–C58		1.596(2)	1.583(4)	1.601(6)		
N1–Al1–N2	91.87(12)	91.23(6)	92.16(11)	91.28(17)	92.19(9)	94.29(9)
N3–Al1–N4					68.62(8)	70.12(9)
N3–C29–N4					113.1(2)	112.1(2)
N5–Al1–N6	69.17(11)	69.06(6)	69.36(10)	69.27(14)		
N3–Al2–N4	92.10(11)	87.35(6)	91.71(10)	90.46(16)		
N7–Al2–C57		127.20(6)	116.96(10)	114.49(16)		
C58–N7–Al2		104.43(11)	103.54(17)	103.7(3)		
N8–C58–N7		135.33(16)	121.0(3)	135.4(4)		

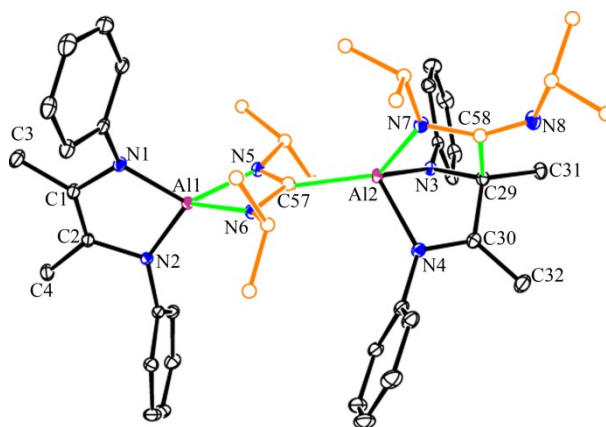


Fig. S13. Molecular structure of $[LAl(iPrNCNiPr)Al(iPrNCNiPr)]$ (**3**) (20% probability thermal ellipsoids). Hydrogen atoms, solvent molecules and isopropyl groups have been omitted for clarity.

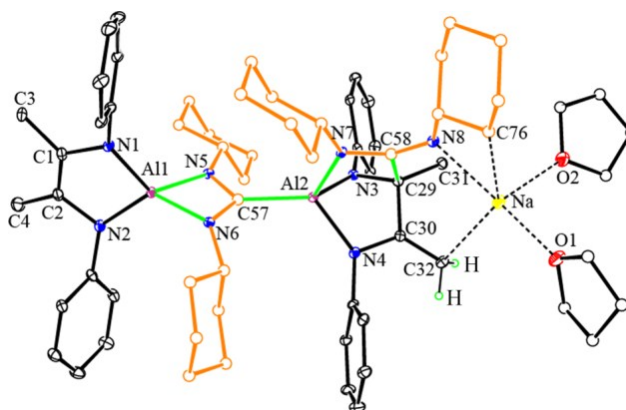


Fig. S14. Molecular structure of $[LAl(CyNCNCy)Al^{-H}(CyNCNCy)][Na(THF)_2]$ (**5**) (20% probability thermal ellipsoids). Hydrogen atoms, solvent molecules and isopropyl groups have been omitted for clarity.

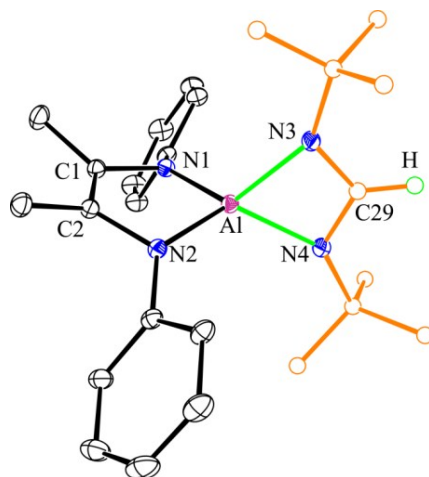


Fig. S15. Molecular structure of $[LAl(tBuNCHNtBu)]$ (**7**) (20% probability thermal ellipsoids). Hydrogen atoms, solvent molecules and isopropyl groups have been omitted for clarity.

The analogous insertion of DCC into a Mg–Mg bond has been reported.⁶ On the basis of these results, we propose the following mechanism for the formation of **2**: This reaction occurs via an initial coordination of one N-center of the carbodiimide at an aluminum center via a dative bond instead of THF. Then the other part (Al2L) migrates from the metal to the sp-hybridized carbon of the carbodiimide with Al–Al bond cleavage. The second nitrogen of the carbodiimide coordinates to the Al1 center to form the product (Chart S1).

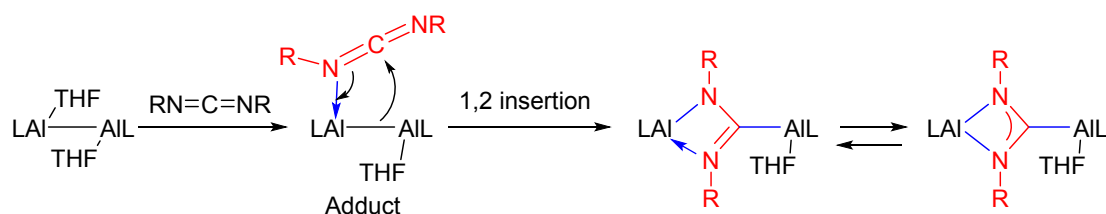


Chart S1. The possible mechanism of carbodiimide insertion into Al–Al Bond.

S3. Theoretical Calculations

Structure optimization for the model compounds $[L'^2-Al^{III}(CyNCNCy)^2-Al^{III}(THF)L'^2]$ (**2H**, $L' = (PhNCMe)_2$), $[L'^2-Al^{III}(iPrNCNiPr)^2-Al^{III}(L'(iPrNCNiPr))^2]$ (**3H**), $[L'^2-Al^{III}(CyNCNCy)^2-Al^{III}(L'^H(CyNCNHCy))^2]$ (**4H**) ($[L'^2-Al^{III}(CyNCNCy)^2-Al^{III}(L'^H(CyNCNCy))^3][Na(THF)_2]$ (**5H**) $[L'^2-Al^{III}(RNCHNR)]$ (**6H**, $R = Ph$ and **7H**, $R = tBu$), in which the 2,6-*i*Pr₂C₆H₃ groups were replaced by Ph groups, was carried out at the DFT (B3LYP) level with a 6-31G*^{7,8} basis set using the Gaussian 09 program.⁹ Fig. S16 shows the optimized geometries, which reproduce the experimental data of **2–7**

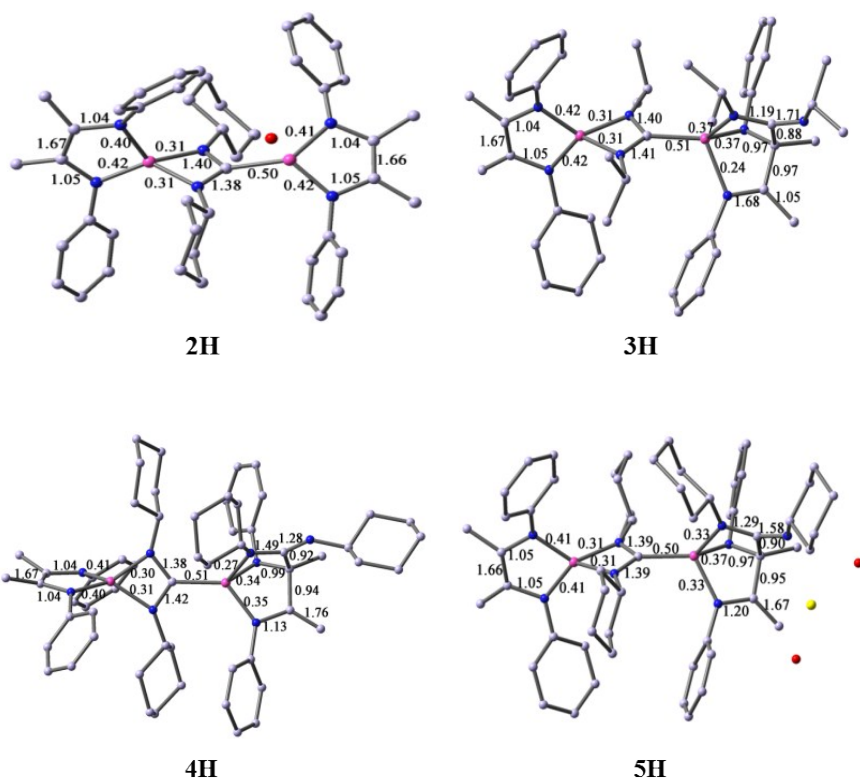
reasonably well. The atomic populations, bonding orbitals and Wiberg bond orders were obtained with NBO method.¹⁰⁻¹²

Table S4. Natural charges (e) of the model compounds **2–4**.

Compound	2	3	4
Al	1.9835, 1.9275	1.9789, 1.9010	1.9927, 1.9263
L	-1.4399, -1.4115	-1.4268, -0.6472	-1.4443, -1.3989
(NCN)	-1.1683	-1.1487, -0.6573	-1.1527, 0.0769

Table S5. Natural charges (e) of the model compounds **5–7**.

Compound	5	6	7
Al	1.9807, 1.9010	1.9932	1.9996
L	-1.4400, -1.4832	-1.3860	-1.4254
(NCN)	-1.1590, -0.7309	-0.6073	-0.5742



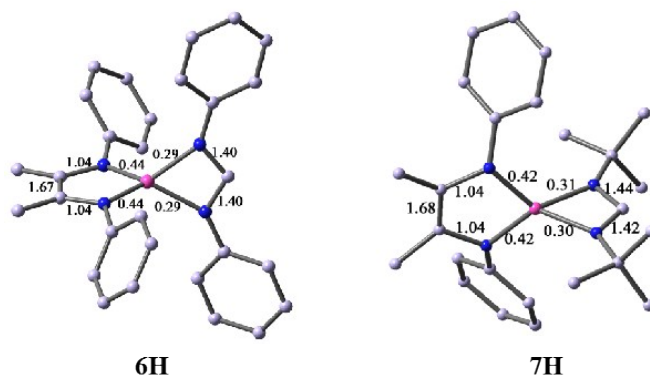


Fig. S16. Optimized structures of 2–7 labeled with selected bond orders.

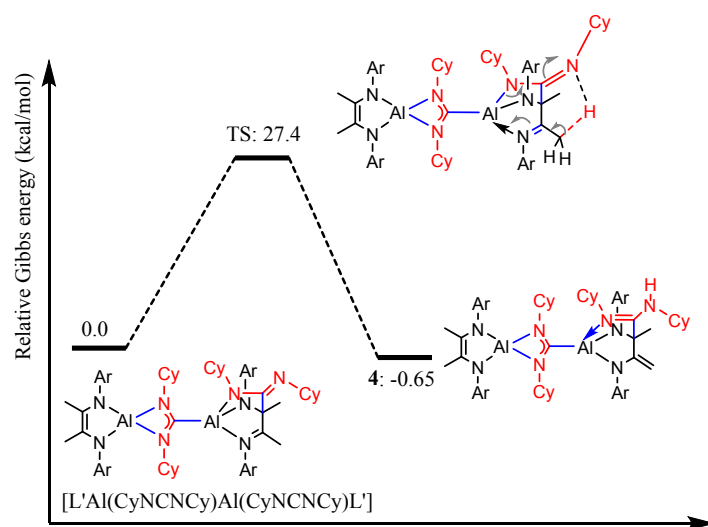


Fig. S17. Gibbs free energy profile of $[L^2-Al^{III}(CyNCNCy)_2-Al^{III}(L'(CyNCNCy))_2]^-$ with the [1,7]-hydride shift.

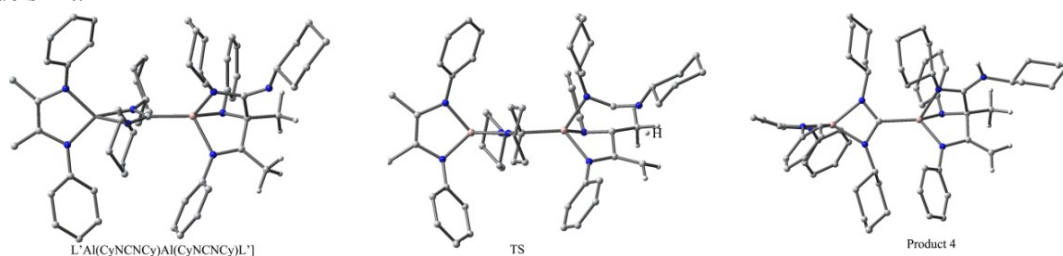


Fig. S18. The optimized structures with bond lengths (the hydrogen atoms omitted for clarity) of stationary points for $[LAl(CyNCNCy)Al(L(CyNCNCy))]$ with [1,7]-hydride shift, obtained with B3LYP/6-31G* method.

Table S6. The energies, enthalpies and free energies and corresponding relative values (au) for conversion of $[LAl(CyNCNCy)Al(L(CyNCNCy))]$ to 4, obtained with B3LYP/6-31G* method

species	E	H	G
$[LAl(CyNCNCy)Al(L(CyNCNCy))]$	-3177.745151	-3177.744207	-3177.917772
TS	-3177.703089	-3177.702144	-3177.873715
Product 4	-3177.747847	-3177.746902	-3177.918807

S4 Reference

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