Supporting Information

Hydro-Coupling of Isocyanates Promoted by 1,2-Bis(arylimino)acenaphthene Aluminum Hydrides

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Experimental section

General remarks. Compounds **3**-**10** are sensitive to air and moisture. Therefore, all manipulations were carried out in vacuo or under argon (nitrogen) using standard Schlenk technique or under nitrogen atmosphere in a glovebox. Toluene, diethyl ether, hexane and thf were dried over sodium/benzophenone and condensed under vacuum in the flasks just prior to use. The IR-spectra were recorded on a FSM-1201 spectrometer. The ESR spectra were recorded on Magnettech ESR5000 (9.48 GHz). The ESR signals of **3**-**10** were simulated using EasySpin (v. 5.2.28) software.[1] Compound **1** and **2** were prepared and isolated according to the literature procedure.[2] Elemental analysis was performed on a Vario EL Cube analyzer.

[(dpp-bian)Al(OC(H)N(Ph)C(NPh)O)$_2$] (3). To a solution of **1** (0.2 g, 0.37 mmol) in toluene (15 mL) PhNCO (0.17 g, 1.51 mmol) was added. The mixture was heated for 10 min at 80 °C. The resulting brown solution was concentrated and allowed to stand for 24 h at 25 °C. The yellow crystals of compound **3** (0.26 g, 63 %) were isolated. Anal. Calcd for $C_{71}H_{70}AlN_6O_4$ (1098.31): C, 77.64; H, 6.42; N, 7.65. Found: C, 77.60; H, 6.39; N, 7.63. ESR (toluene, 300 K): g = 2.0057, a_i (1 × ^{27}Al) = 0.488, a_i (2 × ^{14}N) = 0.457, a_i (2 × ^{1}H) = 0.132, a_i (2 × ^{1}H) = 0.091 mT. IR (mineral oil) v/cm^{-1}: 1690 (s, C=N), 1650 (s, C=N), 1626 w, 1592 m, 1548 m, 1407 w, 1319 m, 1258 m, 1187 m, 1169 w, 1151 w, 1109 w, 1075 m, 1057 w, 1035 w, 1008 w, 993 m, 950 w, 926 m, 892 m, 872 m, 843 w, 826 m, 803 m, 763 s, 730 s, 694 s, 672 w, 652 m, 621 w, 596 w, 585 w, 551 s, 520 w, 507 m, 489 m, 456 w.

[(Ar^{BIG}-bian)Al(OC(H)N(Ph)C(NPh)O)$_2$] (4). To a solution of **2** (0.25 g, 0.20 mmol) in thf (15 mL) PhNCO (0.09 g, 0.80 mmol) was added. The mixture was heated for 10 min at 80 °C. The resulting brown solution was allowed to stand for 48 h at 25 °C. The brown crystals of compound **3** (0.24 g, 70 %) were isolated. Anal. Calcd for $C_{116}H_{102}AlN_6O_{6.50}$ (1711.01): C, 81.05; H, 5.98; N, 4.89. Found: C, 81.03; H, 5.96; N, 4.88. ESR (2-MeTHF, 300 K): g = 2.0053, a_i (1 × ^{27}Al) = 0.484, a_i (2 × ^{14}N) = 0.458, a_i (2 × ^{1}H) = 0.138, a_i (2 × ^{1}H) = 0.082 mT. IR (mineral oil) v/cm^{-1}: 1683 s, 1646 s, 1619 m, 1592 s, 1545 s, 1492 w, 1405 w, 1302 s, 1256 m, 1213 w, 1189 m, 1164 w, 1075 m, 1028 m, 1006 w, 988 s, 950 w, 921 m, 921 m, 870 m, 843 w, 814 w, 790 w, 759 s, 745 m, 730 m, 696 s, 654 w, 634 w, 605 m, 569 m, 551 s, 505 m, 465 w, 453 w.

[(Ar^{BIG}-bian)Al(OC(H)N(Cy)C(NCy)O)$_2$] (5). To a solution of **2** (0.3 g, 0.24 mmol) in thf (15 mL) CyNCO (0.12 g, 1.0 mmol) was added. The mixture was heated

for 10 min at 80 °C. The resulting brown solution was allowed to stand for 48 h at 25 °C. The yellow crystals of compound **5** (0.33 g, 65 %) were isolated. Anal. Calcd for $C_{135}H_{164}AlN_6O_{11.25}$ (2077.69): C, 78.19; H, 7.97; N, 4.05. Found: C, 78.14; H, 7.93; N, 4.05. ESR (2-MeTHF, 309 K): g = 2.0055, a_i (1 × ^{27}Al) = 0.467, a_i (2 × ^{14}N) = 0.454, a_i (2 × ^{1}H) = 0.123, a_i (2 × ^{1}H) = 0.107 mT. IR (mineral oil) v/cm^{-1}: 1686 s, 1652 m, 1608 s, 1649 s, 1492 w, 1357 m, 1310 w, 1288 m, 1268 m, 1249 w, 1213 w, 1192 m, 1157 m, 1120 s, 1070 s, 1032 m, 1002 w, 951 w, 913 s, 870 m, 854 w, 816 m, 791 w, 764 m, 745 m, 704 s, 664 m, 635 w, 697 m, 571 m, 555 w, 540 m, 521 m, 472 m.

[(Ar^{BIG}-bian)Al(OC(H)N(3,5-Cl$_2$Ph)C(N(3,5-Cl$_2$Ph))O)$_2$] (6). To a solution of **2** (0.25 g, 0.20 mmol) in thf (15 mL) 3,5-Cl$_2$-PhNCO (0.15 g, 0.83 mmol) was added. The mixture was heated for 10 min at 80 °C. After cooling to room temperature, THF was removed from the reaction mixture almost completely, and toluene was added to obtain a 1: 3 solvent mixture. The resulting red solution was allowed to stand for 48 h at 10 °C. The red crystals of compound **6** (0.26 g, 60 %) were isolated. Anal. Calcd for $C_{127}H_{98}AlCl_8N_6O_4$ (2082.69): C, 73.24; H, 4.74; N, 4.04. Found: C, 73.21; H, 4.70; N, 4.03. ESR (THF, 300 K): g = 2.0054, a_i (1 × ^{27}Al) = 0.497, a_i (2 × ^{14}N) = 0.453, a_i (2 × ^{1}H) = 0.130, a_i (2 × ^{1}H) = 0.112 mT. IR (mineral oil) v/cm^{-1}: 1686 s, 1644 m, 1630 w, 1578 s, 1552 w, 1539 w, 1493 w, 1419 w, 1302 s, 1259 m, 1191 m, 1152 w, 1114 w, 1096 w, 1078 w, 1042 m, 991 w, 953 w, 906 s, 874 m, 842 w, 804 s, 767 s, 747 w, 731 w, 701 s, 681 w, 665 w, 634 w, 606 m, 568 m, 544 m, 513 w, 491 w, 463 w.

[(dpp-bian)Al(OC(H)N(tBu))$_2$] (7). To a solution of **1** (0.2 g, 0.37 mmol) in Et$_2$O (15 mL) the excess of *t*BuNCO (0.14 g, 1.41 mmol) was added. The mixture was heated for 10 min at 80 °C. The resulting yellow solution was concentrated and allowed to stand for 3 h at 25 °C. The crystals of free dpp-bian were isolated. The solution was concentrated again and allowed to stand for 24 h at 25 °C. The yellow crystals of compound **7** (polymorphic form **7b**) (0.08 g, 28 %) were isolated. Crystals of **7a** were obtained by recrystallization of **7b** in hexane. Anal. Calcd for $C_{46}H_{60}AlN_4O_2$ (727.96): C, 75.89; H, 8.31; N, 4.04. Found: C, 75.88; H, 8.29; N, 4.04. ESR (toluene, 313 K): g = 2.0055, a_i (1 × ^{27}Al) = 0.462, a_i (2 × ^{14}N) = 0.451, a_i (4 × ^{1}H) = 0.120 mT. IR (mineral oil) v/cm^{-1}: 1593 s, 1579 w, 1548 s, 1327 m, 1263 s, 1236 w, 1208 m, 1187 w, 1154 w, 1109 w, 1087 w, 1056 w, 1035 w, 1003 m, 945 m, 888 m, 871 m, 820 s, 804 m, 773 w, 763 s, 720 w, 699 w, 670 w, 640 m, 625 w, 597 m, 582 w, 558 m, 537 w, 508 s, 457 w.

[(Ar^{BIG} -bian)Al(OC(H)N(tBu))$_2$] (8). To a solution of **2** (0.25 g, 0.20 mmol) in thf (15 mL) the excess of *t*BuNCO (0.08 g, 0.82 mmol) was added. The mixture was heated for 10 min at 80 °C. The solution was allowed to stand for 24 h at 25 °C. The formed yellow micro-crystalline precipitate of compound **8** (0.14 g, 54 %) was isolated. Anal. Calcd for $C_{88}H_{80}AlN_4O_2$ (1252.62): C, 84.38; H, 6.44; N, 4.47. Found: C, 84.35; H, 6.42; N, 4.46. ESR (THF, 313 K): g = 2.0056, a_i (1 × ^{27}Al) = 0.452, a_i (2 × ^{14}N) = 0.440, a_i (4 × ^{1}H) = 0.133 mT. IR (mineral oil) v/cm^{-1}: 1669 m, 1596 s, 1582 w, 1541 m, 1493 w, 1298 w, 1262 s, 1208 m, 1159 w, 1135 w, 1078 m, 1031 m, 1002 m, 946 w, 917 w, 870 m, 818 m, 766 m, 747 m, 702 s, 626 m, 605 s, 577 s, 544 m, 506 w, 458 s. X-ray quality crystals of compound **8** were obtained from toluene. The resulting crystals are cocrystallizates of compound **8** and a neutral Ar^{BIG}-bian ligand, which is probably caused by prolonged heating of the suspension of the complex in toluene, leading to its partial destruction.

[(dpp-bian)Al(N(Cy)$_2$CH)$_2$] (9). To a solution of **1** (0.2 g, 0.37 mmol) in toluene (15 mL) DCC (0.15 g, 0.75 mmol) was added. The mixture was heated for 10 min at 80 °C. The resulting brown micro-crystalline precipitate was recrystallized in thf, the solution was allowed to stand for 24 h at 25 °C. The brown crystals of compound **9** (0.23 g, 66 %) were isolated. Anal. Calcd for $C_{62}H_{86}AlN_6$ (942.34): C, 79.02; H, 9.20; N, 8.92. Found: C, 79.02; H, 9.19; N, 8.92. ESR (solid state, 300 K): g = 2.0058. IR (mineral oil) v/cm^{-1}: 1612 s, 1559 s, 1537 w, 1400 w, 1363 w, 1342 w, 1324 m, 1258 s, 1230 m, 1189 w, 1170 w, 1144 w, 1129 w, 1114 w, 1080 w, 1059 w, 1043 m, 1020 m, 955 m, 934 w, 900 w, 891 w, 867 m, 842 w, 820 m, 800 m, 764 s, 721 w, 704 w, 670 w, 657 w, 647 w, 595 w, 535 s, 485 s.

[(Ar^{BIG}-bian)Al(H)(N(Cy)$_2$CH)] (10). To a solution of **2** (0.25 g, 0.20 mmol) in thf (15 mL) the excess of DCC (0.08 g, 0.41 mmol) was added. The mixture was heated for 10 min at 80 °C. After replacement thf to toluene the resulting brown solution was allowed to stand for 24 h at 25 °C. The brown crystals of compound **10** (0.14 g, 55 %) were isolated. Anal. Calcd for $C_{91}H_{84}AlN_4$ (1260.68): C, 86.70; H, 6.72; N, 4.44. Found: C, 86.67; H, 6.68; N, 4.42. ESR (THF, 308 K): g = 2.0054, a_i (1 × ^{27}Al) = 0.479, a_i (2 × ^{14}N) = 0.422, a_i (1 × ^{1}H) = 1.098, a_i (4 × ^{1}H) = 0.104 mT. IR (mineral oil) v/cm^{-1}: 1810 s, 1599 m, 1561 m, 1537 m, 1493 w, 1337 w, 1293 w, 1267 m, 1240 w, 1220 m, 1186 w, 1166 w, 1122 m, 1080 s, 1031 s, 1003 w, 990 w, 962 w, 915 w, 889 w, 873 m, 838 w, 814 m, 794 w, 765 s, 744 m, 700 s, 651 m, 629 w, 605 s, 568 m, 548 m, 520 w, 504 w, 480 w, 458 w.

Single crystal X-ray diffraction studies. The X-ray diffraction data for complexes **3**-**10** were collected on an Oxford Xcalibur Eos diffractometer (Mo-K_α radiation, ω-scan technique, λ = 0.71073 Å). Data collection, cell refinement, data reduction and absorption corrections were carried out using CrysAlisPro.[3] Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The all compounds were solved by dual method[4] and were refined on F^2_{hkl} using SHELXTL package[5]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except H(79), H(93) in complex **5**, H(79A), H(93A) in **8**, H(27) in **9** and H(1), H(2) atoms in **10**, were placed in calculated positions and were refined using a riding model (U_{iso}(H) = 1.5U_{eq}(C) for CH_3-groups and U_{iso}(H) = 1.2U_{eq}(C) for other groups). In turn, the other hydrogen atoms were located from difference Fourier maps and were refinement without additional restraints.

Two pseudopolymorphic forms of complex **7** were obtained by the recrystallization from different organic solvents: hexane (**7a**) and Et_2O (**7b**). The main geometric characteristics in complexes **7a** and **7b** are in excellent agreement with each other (Table 1S). In the main text of the article, when describing the geometry of complex **7**, we use the geometry of pseudopolymorph **7a**. Information about solvent molecules in the crystal, disorders, constraints and restraints used to refine the structure, as well as other crystallographic information for complexes **3**-**10** is given in the summary Table 2S.

The main crystallographic data and structure refinement details for complexes **3**-**10** are presented in Table 3S. CCDC 2364136-2364144 contain the supplementary crystallographic data for this paper. These data can also be obtained free of charge by The Cambridge Crystallographic Data Centre: ccdc.cam.ac.uk/structures

Table 1S. Selected bond lengths [Å] and angles [°] for complexes **3-10**.

Bond	**3**	**Bond**	**4**
Al(1)–N(1)	1.9846(12)	Al(1)–N(1)	2.006(4)
Al(1)–N(2)	1.9918(13)	Al(1)–N(2)	1.999(4)
N(1)–C(1)	1.3294(19)	N(1)–C(1)	1.336(5)
N(2)–C(2)	1.3308(18)	N(2)–C(2)	1.326(5)
C(1)–C(2)	1.431(2)	C(1)–C(2)	1.427(6)
Al(1)–O(1)	1.8580(11)	Al(1)–O(1)	1.897(3)
Al(1)–O(2)	1.9347(11)	Al(1)–O(2)	1.882(3)
Al(1)–O(3)	1.8529(11)	Al(1)–O(3)	1.915(3)
Al(1)–O(4)	1.9315(11)	Al(1)–O(4)	1.866(3)
C(37)–O(1)	1.2802(18)	C(79)–O(1)	1.250(5)
C(37)–N(3)	1.2785(19)	C(79)–N(3)	1.335(5)
C(37)–N(4)	1.456(2)	C(86)–N(3)	1.444(6)
C(44)–N(4)	1.334(2)	C(86)–N(4)	1.281(6)
C(44)–O(2)	1.2440(19)	C(86)–O(2)	1.303(5)
C(51)–O(3)	1.2849(18)	C(93)–O(3)	1.266(5)
C(51)–N(5)	1.275(2)	C(93)–N(5)	1.317(6)
C(51)–N(6)	1.454(2)	C(100)–N(5)	1.464(6)
C(58)–N(6)	1.332(2)	C(100)–N(6)	1.273(6)
C(58)–O(4)	1.2484(18)	C(100)–O(4)	1.311(5)
Angle	**3**	**Angle**	**4**
O(1)–Al(1)–O(3)	94.01(5)	O(1)–Al(1)–O(3)	175.87(16)
N(2)–Al(1)–N(1)	83.36(5)	N(2)–Al(1)–N(1)	83.22(15)
O(2)–Al(1)–O(4)	169.91(5)	O(2)–Al(1)–O(4)	92.18(14)
O(1)–Al(1)–O(2)	86.41(5)	O(1)–Al(1)–O(2)	86.43(15)
O(3)–Al(1)–O(4)	86.63(5)	O(3)–Al(1)–O(4)	87.16(14)

Bond	**5**	**Bond**	**6**
Al(1)–N(1)	2.014(2)	Al(1)–N(1)	1.992(2)
Al(1)–N(2)	2.008(2)	N(1)–C(1)	1.336(3)
N(1)–C(1)	1.335(4)	C(1)–C(1)’	1.437(5)
N(2)–C(2)	1.332(3)	Al(1)–O(1)	1.9051(17)
C(1)–C(2)	1.443(4)	Al(1)–O(2)	1.8849(18)
Al(1)–O(1)	1.913(2)	C(41)–O(1)	1.246(3)
Al(1)–O(2)	1.846(2)	C(41)–N(2)	1.334(3)
Al(1)–O(3)	1.911(2)	C(48)–N(2)	1.454(3)
Al(1)–O(4)	1.844(2)	C(48)–N(3)	1.276(3)

C(79)–O(1)	1.256(3)	C(48)–O(2)	1.289(3)
C(79)–N(3)	1.325(3)		
C(86)–N(3)	1.464(3)		
C(86)–N(4)	1.267(4)		
C(86)–O(2)	1.298(3)		
C(93)–O(3)	1.259(3)		
C(93)–N(5)	1.322(4)		
C(100)–N(5)	1.461(3)		
C(100)–N(6)	1.275(4)		
C(100)–O(4)	1.295(3)		
Angle	**5**	**Angle**	**6**
O(1)–Al(1)–O(3)	174.62(9)	O(1)–Al(1)–O(1)’	175.78(12)
N(2)–Al(1)–N(1)	82.74(9)	N(1)–Al(1)–N(1)’	84.68(12)
O(2)–Al(1)–O(4)	94.60(9)	O(2)–Al(1)–O(2)’	90.32(11)
O(1)–Al(1)–O(2)	87.38(8)	O(1)–Al(1)–O(2)	86.35(8)
O(3)–Al(1)–O(4)	87.15(9)		

Bond	**7a**	**Bond**	**7b**
Al(1)–N(1)	1.9985(17)	Al(1)–N(1)	1.9992(15)
Al(1)–N(2)	1.9977(17)	Al(1)–N(2)	1.9914(15)
N(1)–C(1)	1.328(2)	N(1)–C(1)	1.328(2)
N(2)–C(2)	1.326(2)	N(2)–C(2)	1.328(2)
C(1)–C(2)	1.434(3)	C(1)–C(2)	1.433(2)
Al(1)–O(1)	1.9062(15)	Al(1)–O(1)	1.9023(14)
Al(1)–O(2)	1.9045(15)	Al(1)–O(2)	1.9017(14)
Al(1)–N(3)	2.069(2)	Al(1)–N(3)	2.0559(18)
Al(1)–N(4)	2.073(2)	Al(1)–N(4)	2.0614(17)
O(1)–C(37)	1.297(3)	O(1)–C(37)	1.266(2)
N(3)–C(37)	1.286(3)	N(3)–C(37)	1.287(3)
O(2)–C(42)	1.317(3)	O(2)–C(42)	1.291(2)
N(4)–C(42)	1.286(3)	N(4)–C(42)	1.288(3)
Angle	**7a**	**Angle**	**7b**
O(1)–Al(1)–O(2)	157.97(7)	O(1)–Al(1)–O(2)	158.90(6)
N(1)–Al(1)–N(2)	82.74(7)	N(1)–Al(1)–N(2)	83.08(6)
N(3)–Al(1)–N(4)	90.21(9)	N(3)–Al(1)–N(4)	90.57(7)

Bond	**8**	**Bond**	**9**
Al(1)–N(1)	1.991(2)	Al(1)–N(1)	1.9979(13)
Al(1)–N(2)	2.008(2)	Al(1)–N(2)	1.9877(14)

N(1)–C(1)	1.335(3)	Al(1)–N(3)	1.8760(18)
N(2)–C(2)	1.340(3)	N(1)–C(1)	1.3335(18)
C(1)–C(2)	1.435(3)	C(1)–C(1)’	1.436(3)
Al(1)–O(1)	1.8838(17)	N(2)–C(20)	1.3122(17)
Al(1)–O(2)	1.9029(17)	N(3)–C(27)	1.377(3)
Al(1)–N(3)	2.078(2)	N(4)–C(27)	1.279(3)
Al(1)–N(4)	2.063(2)		
O(1)–C(79)	1.301(3)		
N(3)–C(79)	1.294(3)		
O(2)–C(84)	1.307(3)		
N(4)–C(84)	1.286(3)		
N(5)-C(89)	1.292(12)		
N(6)-C(90)	1.286(12)		
C(89)-C(90)	1.463(7)		
Angle	**8**	**Angle**	**9**
O(1)–Al(1)–O(2)	160.04(8)	N(1)–Al(1)–N(1)’	82.79(7)
N(1)–Al(1)–N(2)	83.34(8)	N(2)–Al(1)–N(2)’	66.90(8)
N(3)–Al(1)–N(4)	90.54(8)	N(2)–C(20)–N(2)’	113.2(2)

Bond	**10**
Al(1)–N(1)	2.0405(18)
Al(1)–N(2)	1.9348(18)
N(1)–C(1)	1.340(3)
N(2)–C(2)	1.331(3)
C(1)–C(2)	1.435(3)
Al(1)–H(1)	1.53(3)
Al(1)–N(3)	1.9313(19)
Al(1)–N(4)	2.0533(19)
C(79)–N(3)	1.339(3)
C(79)–N(4)	1.303(3)
Angle	**10**
N(2)–Al(1)–N(1)	83.01(7)
N(3)–Al(1)–N(4)	66.88(8)
N(4)–C(79)–N(3)	112.6(2)

Table 2S. Solvent molecules and disorders in the crystal, constraints and restraints used to refine the structure, as well as other crystallographic information for complexes **3**-**10**

Complex	Solvent (per one molecule of the complex)	Disorders	Constraints and restraints used in the refinement	Comments
3	a toluene molecule	The aryl substituent at the N(1) atom and the Ph at the N(5) atom are disordered over two positions, while the solvate toluene molecule is disordered over three positions	EADP, SADI, DFIX, FLAT, ISOR, «AFIX 66»	–
4	2.5 THF molecules	Two Ph substituents (at the N(3) and N(5) atoms) and all solvent molecules are disordered over two positions	EADP, SADI, DFIX, ISOR, «AFIX 66»	For every two molecules of the complex in crystal there are five THF molecules, one of which is disordered near a special position
5	8 THF molecules	One cyclohexyl (at the N(4) atom) and one phenyl (in Ar^{BIG}-bian ligand) substituents are disordered over two positions. In addition, each of the eight solvent molecules are also disordered over two or three positions	EADP, SADI, DFIX, ISOR, «AFIX 66», SAME	–
6	three toluene molecules	Two Ph substituents in the Ar^{BIG}-bian ligand and two toluene molecules are disordered over two positions, while the third toluene molecule is disordered over four positions	EADP, SADI, DFIX, ISOR, «AFIX 66»	One of the toluene molecules is disordered near a special position
7a	–	The -CHN(*t*Bu) fragments of both forimidate ligands are disordered at two positions	EADP, SADI, DFIX, ISOR	**7a** is pseudopolymorphic form of the complex **7b** without any solvents in the crystal packing
7b	half a diethyl ether molecule	The -CHN(*t*Bu) fragments of both forimidate ligands are disordered at two positions. The diethyl ether molecule is disordered over four positions	EADP, SADI, DFIX, ISOR	**7b** is pseudopolymorphic form of the complex **7a** with solvent Et_2O molecule in the crystal packing. The diethyl ether molecule is disordered near a special position
8	one and a half molecules of toluene	The uncoordinated Ar^{BIG}-bian molecule and all toluene molecules in the crystal are disordered over two positions	EADP, SADI, DFIX, FLAT, ISOR, «AFIX 66»	The crystal is a cocrystal of complex **8** and a neutral Ar^{BIG}-bian ligand. For every two molecules of complex **8** in the crystal, there is one Ar^{BIG}-bian molecule and

				three toluene molecules, disordered near a special position.
9	–	one isopropyl group and one cyclohexyl substituent (at the N(2) atom) are disordered over two positions	EADP, SADI, ISOR	–
10	–	the hydride hydrogen atom is disordered with the chlorine atom with an approximate ratio of 0.91:0.09	–	Thus, the crystal studied is actually a cocrystal of complex **10** and complex [(Ar^{BIG}-bian)Al(Cl)($(NCy)_2CH$)]. The presence of chlorine atoms in compound **10** is probably due to its presence in the starting hydride **2**, the synthesis of which is a reaction of (Ar^{BIG}-bian)Na with H_2AlCl.[2]

Table 3S. Crystal data and structure refinement details for compounds **3-6**.

	3*(C_7H_8)	**4*2.5THF**	**5*8THF**	**6*3(C_7H_8)**
Empirical Formula	$C_{71}H_{70}AlN_6O_4$	$C_{116}H_{102}AlN_6O_{6.50}$	$C_{138}H_{170}AlN_6O_{12}$	$C_{127}H_{98}AlCl_8N_6O_4$
M	1098.31	1711.01	2131.77	2082.69
T/K	150(2)	100(2)	100(2)	100(2)
Crystal System	monoclinic	monoclinic	triclinic	triclinic
Space Group	*P2₁/c*	*P2₁/n*	*P-1*	*C2/c*
a/Å	10.68620(10)	13.9292(10)	17.4461(3)	15.5264(5)
b/Å	24.2190(3)	35.073(3)	18.1446(3)	32.4861(9)
c/Å	24.0009(3)	18.3381(13)	22.2454(4)	20.5560(7)
α/deg	90	90	77.716(2)	90
β/deg	101.2880(10)	93.597(6)	67.268(2)	92.086(3)
γ/deg	90	90	67.259(2)	90
V/Å^3	6091.49(12)	8941.1(11)	5973.3(2)	10361.4(6)
Z	4	4	2	4
d_{calc}/g cm^{-3}	1.198	1.271	1.185	1.335
μ/mm^{-1}	0.088	0.087	0.081	0.287
F(000)	2332	3620	2298	4332
Crystal Size/mm	0.46×0.43×0.21	0.58×0.08×0.07	0.53×0.33×0.29	0.56×0.23×0.10
θ range/deg	1.924–26.373	1.875–25.027	1.924–27.103	2.294–27.102
h, k, l	$-13 \le h \le 13$ $-30 \le k \le 30$ $-29 \le l \le 29$	$-16 \le h \le 16$ $-34 \le k \le 41$ $-21 \le l \le 21$	$-22 \le h \le 22$ $-23 \le k \le 23$ $-28 \le l \le 28$	$-19 \le h \le 19$ $-41 \le k \le 41$ $-26 \le l \le 26$
Reflections Collect. / unique	101640 / 12447	48777 / 15800	93829 / 26347	65053 / 11433
R_{int}	0.0410	0.1383	0.0954	0.0793
Data/Restr./Param.	12447 / 376 / 774	15800 / 321 / 1215	26347 / 824 / 1610	11433 / 251 / 688
S(F^2)	1.029	1.028	1.028	1.010
R_1 / *w*R_2 ($I>2\sigma(I)$)	0.0430 / 0.1011	0.0812 / 0.1404	0.0742 / 0.1772	0.0539 / 0.1168
R_1 / *w*R_2 (all data)	0.0633 / 0.1124	0.1988 / 0.1851	0.1488 / 0.2208	0.1028 / 0.1391
Larg. Diff. Peak and Hole/*e* Å^{-3}	0.349 / –0.338	0.319 / –0.324	0.712 / –0.531	0.468 / –0.657

Table 4S. Crystal data and structure refinement details for compounds **7-10**.

	7a	**7b*0.5(Et$_2$O)**	**2(8)*(Ar^{BIG}-bian)*3(C$_7$H$_8$)**	**9**	**0.91(10)* 0.09(C$_{91}$H$_{83}$AlClN$_4$)**
Empirical Formula	$C_{46}H_{60}AlN_4O_2$	$C_{48}H_{65}AlN_4O_{2.50}$	$C_{275}H_{244}Al_2N_{10}O_4$	$C_{62}H_{86}AlN_6$	$C_{91}H_{83.91}AlCl_{0.09}N_4$
M	727.96	765.02	3806.75	942.34	1263.78
T/K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal System	triclinic	monoclinic	triclinic	orthorhombic	monoclinic
Space Group	*P-1*	*I2/a*	*P-1*	*Pnma*	*P2$_1$/n*
a/Å	10.1372(2)	19.8354(4)	12.8415(2)	17.0207(7)	13.4157(3)
b/Å	10.9091(3)	10.1426(2)	13.0763(2)	20.0834(8)	19.8661(4)
c/Å	22.0327(6)	44.3154(8)	35.5128(6)	15.5972(7)	26.8279(6)
α/deg	90.294(2)	90	94.674(2)	90	90
β/deg	101.579(2)	97.485(2)	91.642(2)	90	103.845(2)
γ/deg	116.479(2)	90	118.087(2)	90	90
V/Å^3	2124.08(10)	8839.5(3)	5228.26(17)	5331.6(4)	6942.3(3)
Z	2	8	1	4	4
d_{calc}/g cm^{-3}	1.138	1.150	1.209	1.174	1.209
μ/mm^{-1}	0.088	0.089	0.078	0.084	0.085
F(000)	786	3312	2022	2052	2690
Crystal Size/mm	0.46×0.36×0.19	0.47×0.35×0.27	0.35×0.22×0.05	0.40×0.31×0.22	0.27×0.21×0.18
θ range/deg	2.207–30.034	2.061–30.508	2.065–26.020	2.028–30.507	1.869–25.027
h, k, l	$-14 \le h \le 14$ $-15 \le k \le 15$ $-31 \le l \le 31$	$-28 \le h \le 28$ $-14 \le k \le 14$ $-63 \le l \le 62$	$-15 \le h \le 15$ $-16 \le k \le 16$ $-43 \le l \le 43$	$-24 \le h \le 24$ $-28 \le k \le 22$ $-22 \le l \le 22$	$-15 \le h \le 15$ $-23 \le k \le 23$ $-31 \le l \le 31$
Reflections Collect. / unique	40367 / 12438	87011 / 13497	219031 / 20573	64257 / 8351	75318 / 12252
R_{int}	0.0679	0.0762	0.0808	0.1010	0.0569
Data/Restr./Param.	12438 / 186 / 537	13497 / 254 / 604	20573 / 593 / 1631	8351 / 0 / 338	12252 / 0 / 885
S(F^2)	1.037	1.012	1.100	1.021	1.039
R_1 / wR_2 (I>2σ(I))	0.0666 / 0.1319	0.0598 / 0.1240	0.0629 / 0.1299	0.0579 / 0.1388	0.0491 / 0.1030
R_1 / wR_2 (all data)	0.1280 / 0.1566	0.1168 / 0.1481	0.1002 / 0.1460	0.0921 / 0.1628	0.0814 / 0.1165
Larg. Diff. Peak and Hole/*e* Å^{-3}	0.388 / –0.376	0.429 / –0.386	0.796 / –0.367	0.436 / –0.510	0.272 / –0.399

Table 5S. SHAPE analysis for complexes **3**-**8**.

Complex	**JPPY-6**	**TPR-6**	**OC-6**	**PPY-6**	**HP-6**
3	29.860	12.523	0.564	26.008	31.913
4	29.520	13.305	0.434	26.113	31.677
5	29.790	12.654	0.480	26.469	31.681
6	29.311	13.168	0.498	25.940	31.195
7 (7a)	28.585	12.189	2.978	24.389	27.178
7 (7b)	28.015	11.827	3.250	23.602	27.662
8	28.287	12.090	3.131	23.881	27.535
JPPY-6: Johnson pentagonal pyramid J2 TPR-6: Trigonal prism OC-6: Octahedron PPY-6: Pentagonal pyramid HP-6: Hexagon[6]					

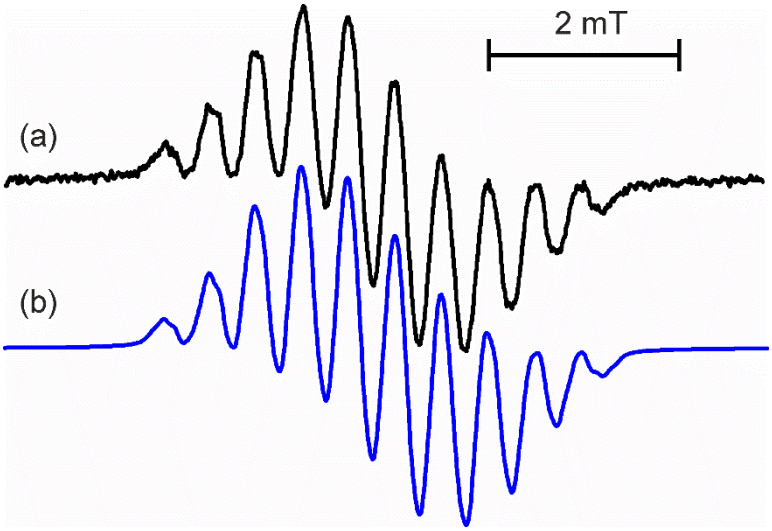

Figure S1. ESR spectrum of compound **3** (toluene, 300 K): (a) experimental; (b) simulated, g = 2.0057, a_i ($1 \times {}^{27}Al$) = 0.488, a_i ($2 \times {}^{14}N$) = 0.457, a_i ($2 \times {}^{1}H$) = 0.132, a_i ($2 \times {}^{1}H$) = 0.091 mT.

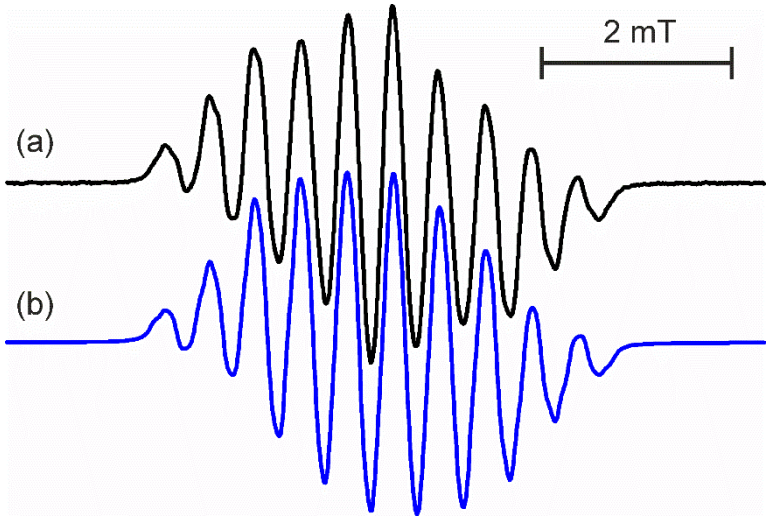

Figure S2. ESR spectrum of compound **4** (2-MeTHF, 300 K): (a) experimental; (b) simulated, g = 2.0053, a_i ($1 \times {}^{27}Al$) = 0.484, a_i ($2 \times {}^{14}N$) = 0.458, a_i ($2 \times {}^{1}H$) = 0.138, a_i ($2 \times {}^{1}H$) = 0.082 mT.

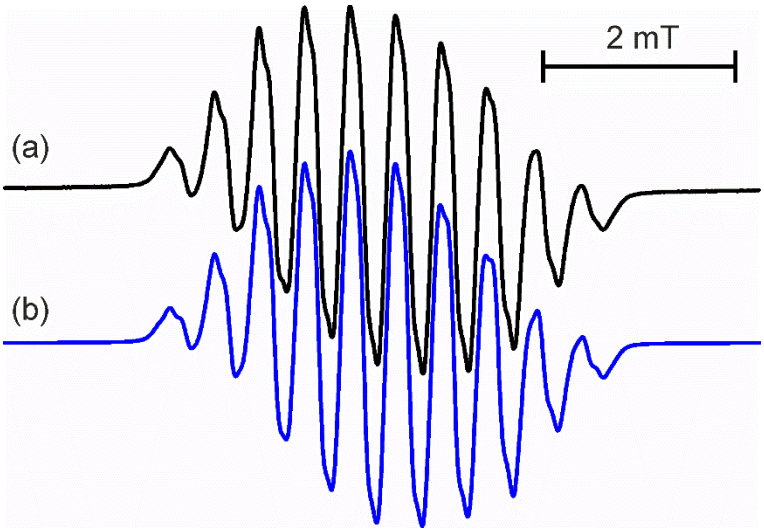

Figure S3. ESR spectrum of compound **5** (2-MeTHF, 309 K): (a) experimental; (b) simulated, g = 2.0055, a_i (1 × ^{27}Al) = 0.467, a_i (2 × ^{14}N) = 0.454, a_i (2 × ^{1}H) = 0.123, a_i (2 × ^{1}H) = 0.107 mT.

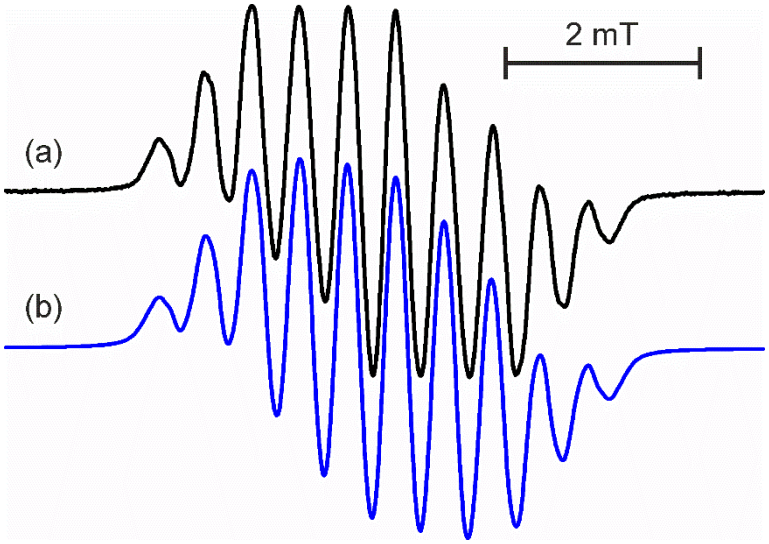

Figure S4. ESR spectrum of compound **6** (THF, 300 K): (a) experimental; (b) simulated, g = 2.0054, a_i (1 × ^{27}Al) = 0.497, a_i (2 × ^{14}N) = 0.453, a_i (2 × ^{1}H) = 0.130, a_i (2 × ^{1}H) = 0.112 mT.

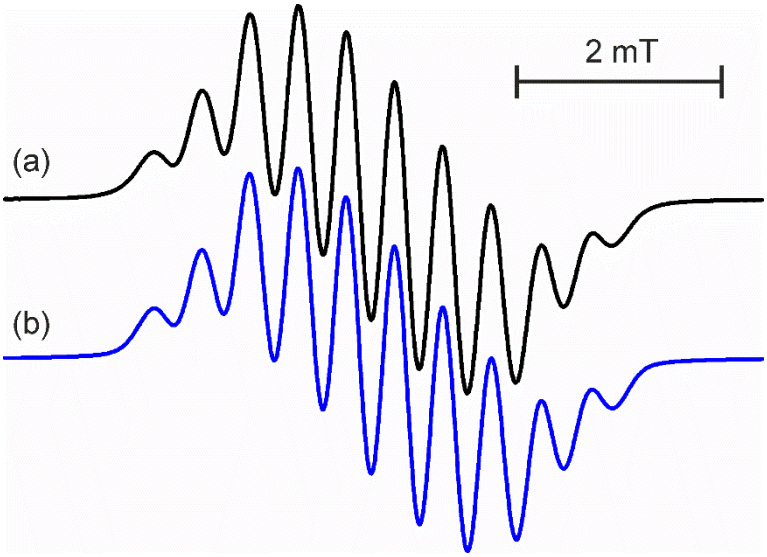

Figure S5. ESR spectrum of compound **7** (toluene, 313 K): (a) experimental; (b) simulated, g = 2.0055, a_i (1 × ^{27}Al) = 0.462, a_i (2 × ^{14}N) = 0.451, a_i (4 × ^{1}H) = 0.120 mT.

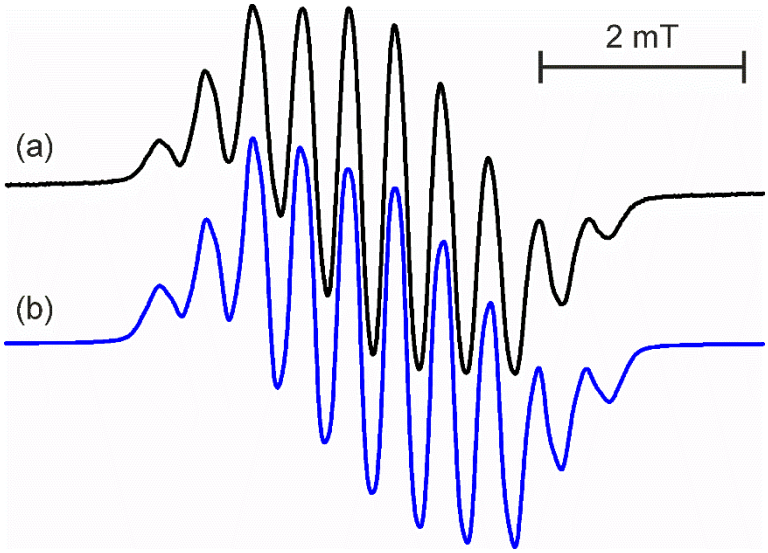

Figure S6. ESR spectrum of compound **8** (THF, 313 K): (a) experimental; (b) simulated, g = 2.0056, a_i (1 × ^{27}Al) = 0.452, a_i (2 × ^{14}N) = 0.440, a_i (4 × ^{1}H) = 0.133 mT.

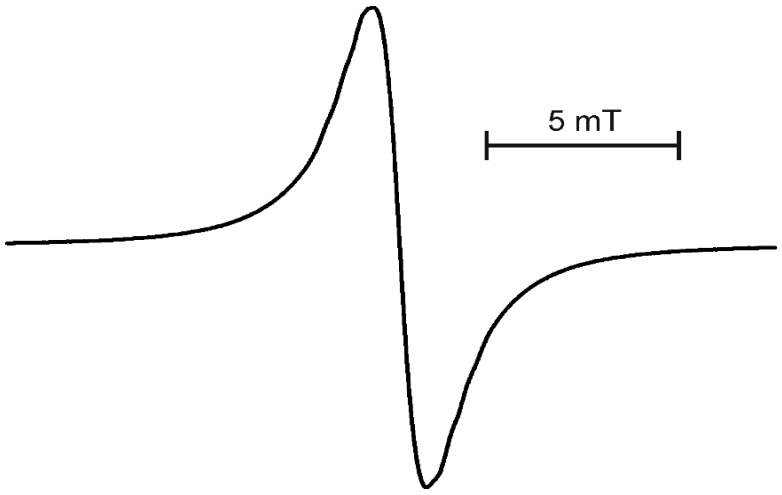

Figure S7. ESR spectrum of compound **9** in the solid state (300 K), g = 2.0058.

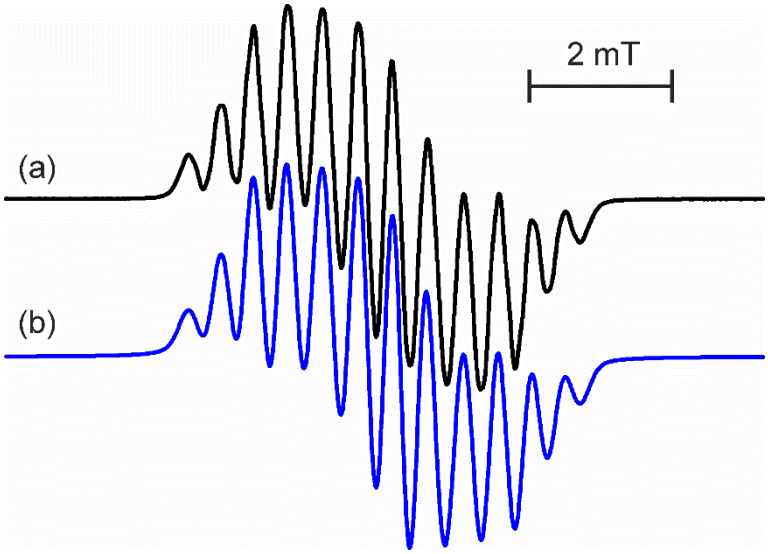

Figure S8. ESR spectrum of compound **10** (THF, 308 K): (a) experimental; (b) simulated, g = 2.0054, a_i (1 × ^{27}Al) = 0.479, a_i (2 × ^{14}N) = 0.422, a_i (1 × ^{1}H) = 1.098, a_i (4 × ^{1}H) = 0.104 mT.

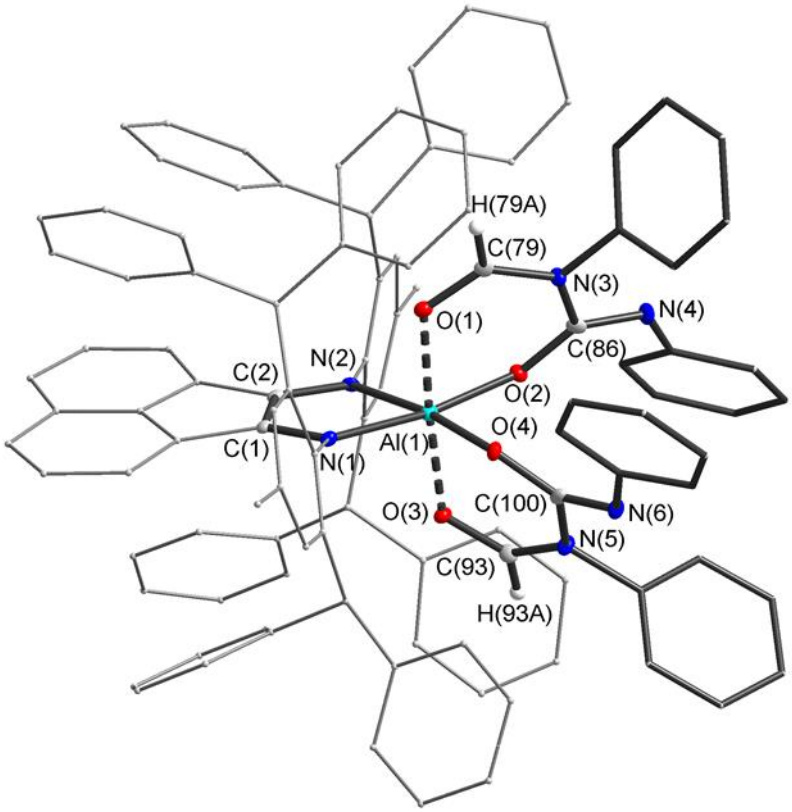

Figure S9. Molecular structure of **4**. Thermal ellipsoids at 30 % probability.

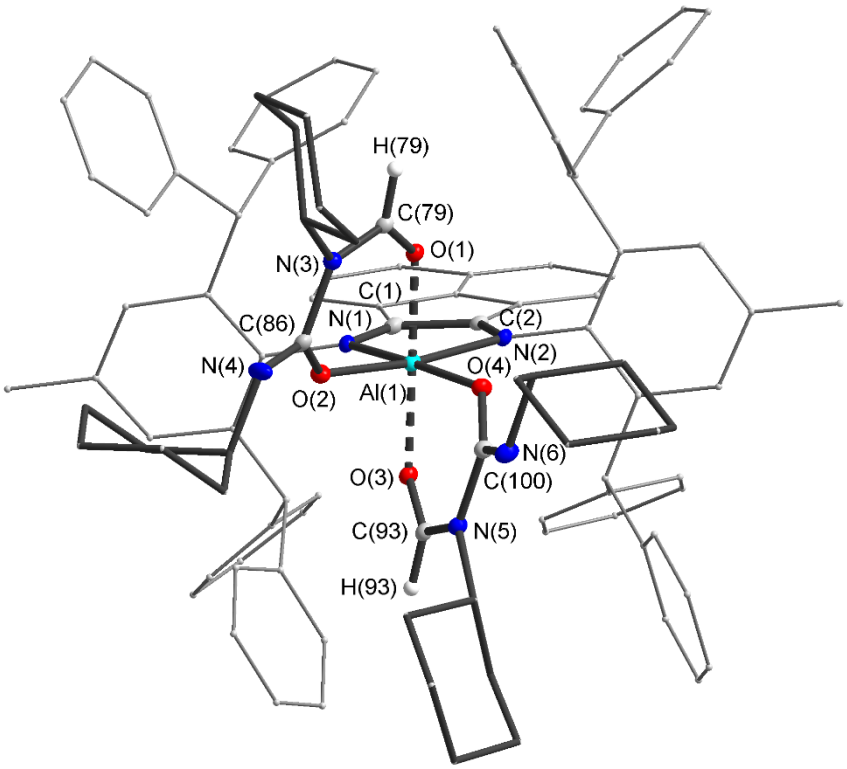

Figure S10. Molecular structure of **5**. Thermal ellipsoids at 30 % probability.

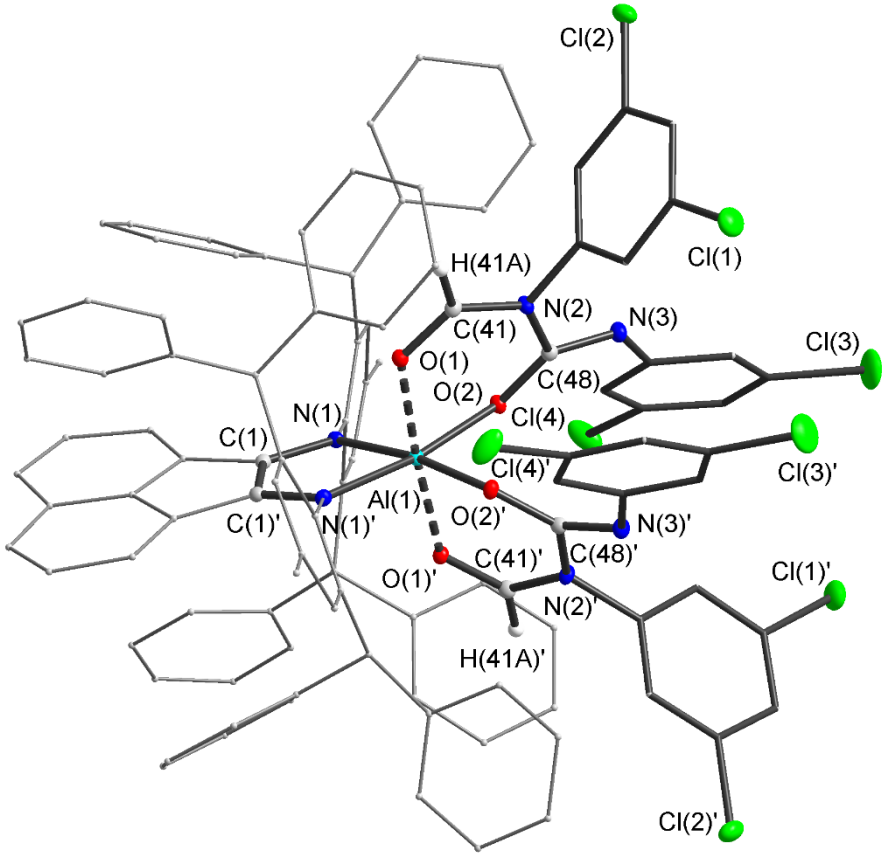

Figure S11. Molecular structure of **6**. Thermal ellipsoids at 30 % probability. Symmetry transformations used to generate equivalent atoms (atom'): –x+1, y, –z+1/2.

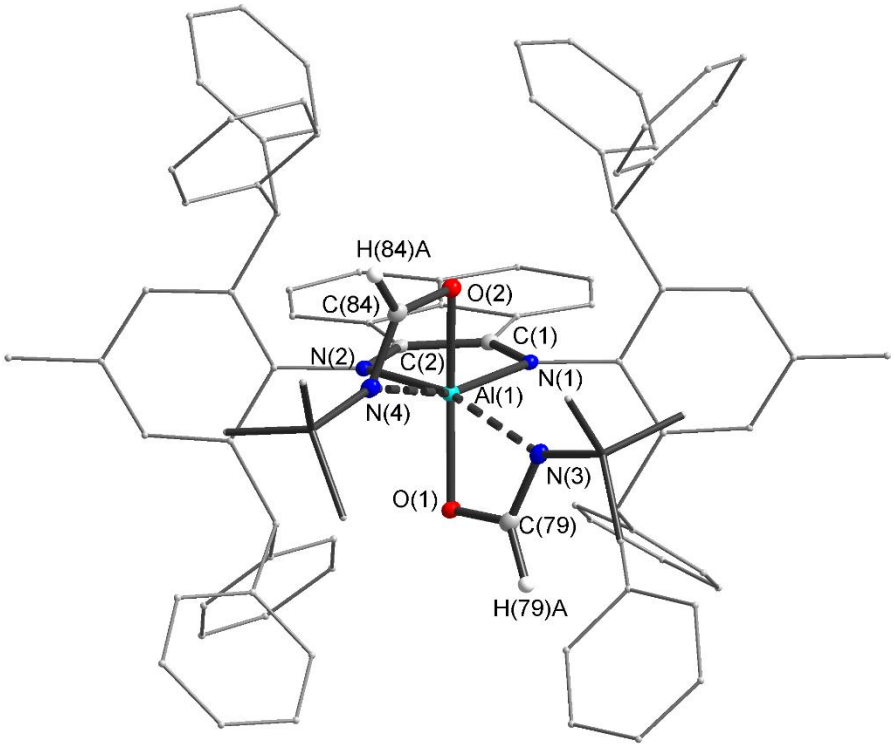

Figure S12. Molecular structure of **8**: Thermal ellipsoids at 30 % probability.

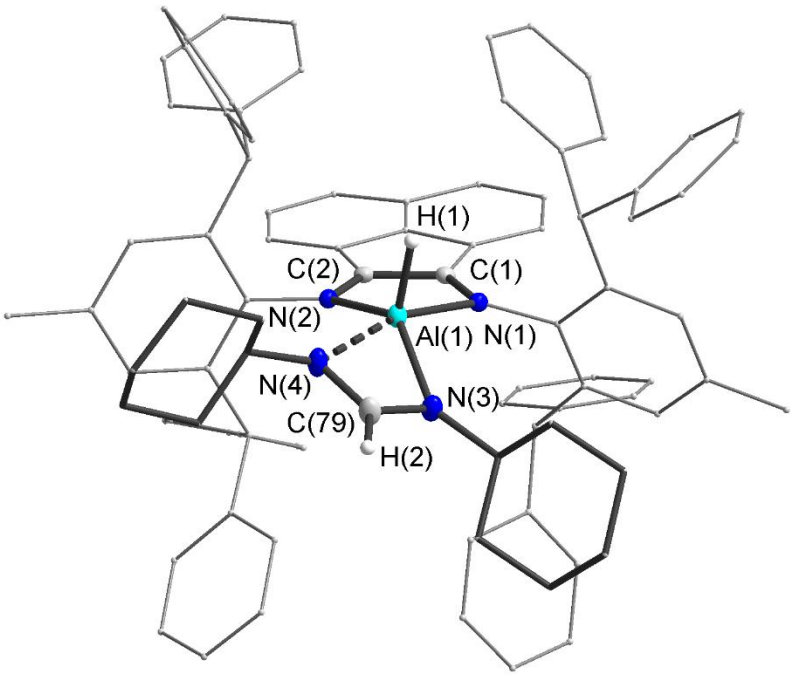

Figure S13. Molecular structure of **10**: Thermal ellipsoids at 30 % probability.

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