Supplemental Information:

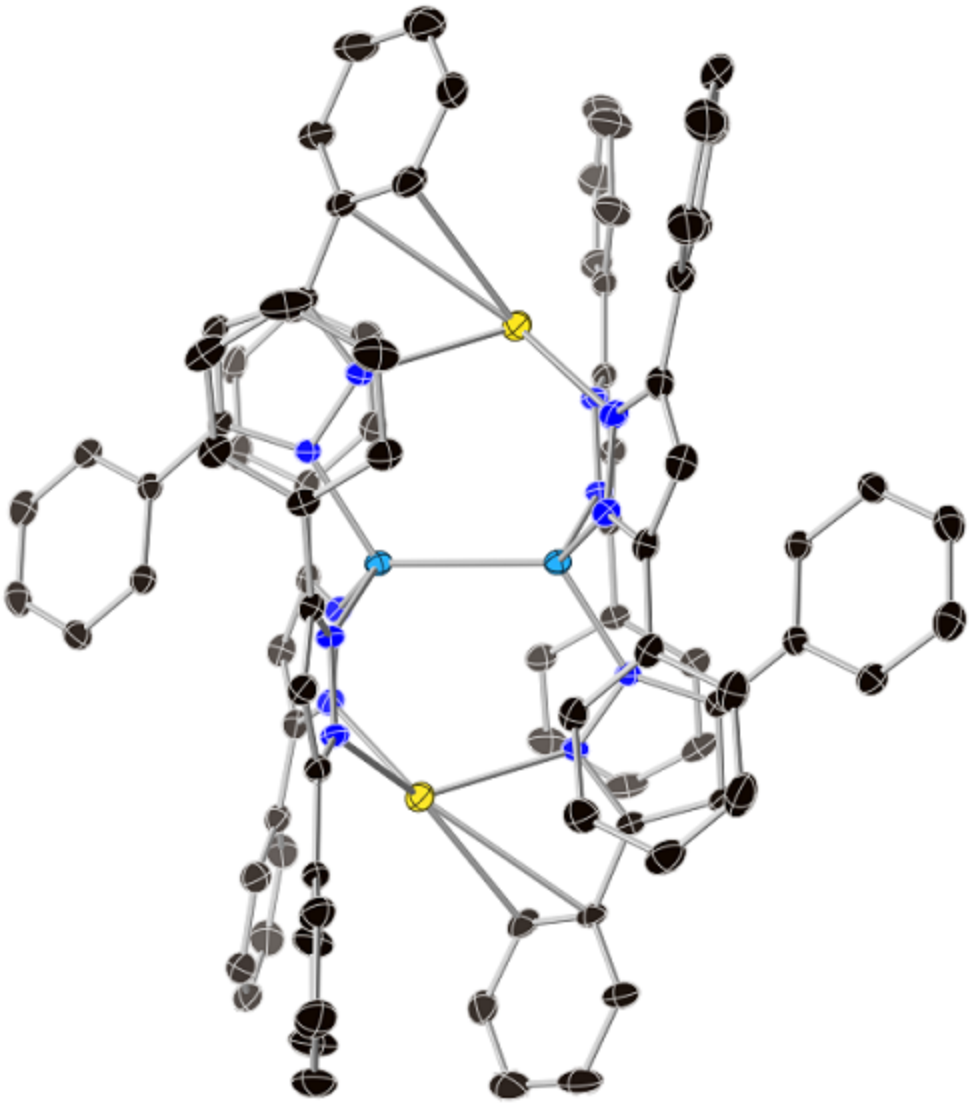
Experimental:

General Considerations: All reactions were performed in an inert atmosphere using standard Schlenk and dry box techniques. Toluene, diethyl ether, and tetrahydrofuran were purified by distillation from sodium benzophenone ketyl under a dinitrogen atmosphere. All purified solvents were stored in modified Schlenk vessels over 3 Å molecular sieves under a dinitrogen atmosphere. [Na(THF)][Ph_2pz][6d] and AlCl·$(OEt_2)_n$[14] were prepared according to literature procedures. ^{1}H and ^{13}C{^{1}H} NMR spectra were collected on a Bruker 500 MHz instrument. Elemental analysis was performed by Galbraith Laboratories.

AlCl·$(OEt_2)_n$: The synthesis of AlCl·$(OEt_2)_n$ prepared according to the published literature procedures.[14] Molten aluminum metal heated to approximately 1200 K in a graphite furnace was reacted with a slow, steady stream of gaseous hydrogen chloride through a mass flow controller over a 3 h period in a modified Schnöckel-type metal halide co-condensation reactor. The resultant gas-phase AlCl was co-condensed with a mixture of toluene:diethyl ether (3:1 v/v) onto the walls of the stainless steel reaction chamber cooled to 77 K with liquid nitrogen. The solvent matrix was thawed and the resultant yellow-brown solution was collected in a 200 mL Schlenk flask cooled to -78 °C using dry ice. The solution was stored in a -80 °C freezer prior to use.

[Al_2][Na(Ph_2pz)$_3$]$_2$·toluene (**1**·toluene): A 100 mL round-bottom Schlenk flask equipped with a magnetic stir bar was charged with [Na(THF)][Ph_2pz] (1.000 g, 3.181 mmol) and THF (10 mL). A 165 mM solution of AlCl (12.8 mL, 2.12 mmol) in 3:1 mixture of toluene:OEt_2 held at -78 °C was added quickly to the [Na(THF)][Ph_2pz] solution at room temperature and the resulting orange-brown mixture was stirred at room temperature for 16 h. The volatiles were removed under reduced pressure and the resulting

brown residue was extracted with toluene (10 mL) and filtered through a medium porosity glass frit with 2 cm of Celite. The filtrate was heated in an oil bath held at 60 °C for 7 days resulting in the formation of pale yellow crystals (0.085 g, 5.32 %). ^{1}H NMR (THF-d_8, 23 °C, δ) 6.93-7.82 (m, 65 H, aromatic C*H*), 6.34 (br s, 6 H, pyrazolate-4-C*H*), 2.31 (s, $C_6H_5CH_3$, 3 H); $^{13}C\{^{1}H\}$ NMR (THF-d_8, 23 °C, ppm) 155.5 (s, pyrazolate *C*-C_6H_5), 135.4 (s, *ipso*-*C* of C6H5), 129.7 (s, *ortho*-*C*H of toluene), 129.0 (s, *meta*-*C*H of toluene), 128.6 (s, *ortho*-*C*H of C_6H_5), 128.0 (s, *meta*-*C*H of C_6H_5), 127.2 (*para*-*C*H of C_6H_5), 126.1 (s, *para*-*C*H of C_6H_5), 105.3 (s, pyrazolate 4-*C*H), 21.5 (s, *C*H$_3$ of toluene). Anal Calcd. for $C_{97}H_{74}Al_2N_{12}Na_2$: C, 77.28; H, 4.95; N, 11.15. Found: C, 76.64; H, 4.91; N, 11.27.



Supplemental Figure 1. Perspective views of **1** showing Na:Ph and Ph:pz:Ph interactions

Table 1. Crystal data for complex **1**

Chemical formula	$C_{97}H_{74}Al_2N_{12}Na_2$
Formula weight	1507.62
Temperature	100(2) K
Wavelength	0.71073 Å

Crystal size	0.25 × 0.30 × 0.41 mm	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.8421(7) Å	α = 79.8104(10)°
	b = 12.1075(7) Å	β = 85.2777(10)°
	c = 15.5072(10) Å	γ = 80.2888(9)°
Volume	1971.9(2) $Å^3$	
Z	1	
Density (calculated)	1.270 Mg/cm^3	
Absorption coefficient	0.106 mm^{-1}	
F(000)	788	
Diffractometer	Bruker APEX-II CCD	
Radiation source	sealed tube, MoKα	
Theta range for data collection	1.91 to 30.00°	
Index ranges	$-15 \leq h \leq 15$, $-17 \leq k \leq 17$, $-21 \leq l \leq 21$	
Reflections collected	32694	
Independent reflections	11388 [R(int) = 0.0167]	
Coverage of independent reflections	99.10%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9740 and 0.9060	
Structure solution technique	direct methods	
Structure solution program	ShelXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	ShelXL-2012 (Sheldrick, 2012)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	11388 / 62 / 581	
Goodness-of-fit on F^2	1	
Δ/σ_{max}	0.001	
Final R indices	9858 data; I>2σ(I)	$R_1 = 0.0375$, $wR_2 = 0.0754$

	all data	$R_1 = 0.0447$, $wR_2 = 0.0791$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0100P)^2+1.3130P]$, $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.372 and -0.321 eÅ^{-3}	
R.M.S. deviation from mean	0.044 eÅ^{-3}	

Table 2. Bond distances (Å) for complex **1**

Al1-N1	1.9088(9)	Na1-C21	3.0430(11)
Al1-N4	1.9430(9)	N1-C1	1.3688(13)
Al1-Na1	3.4437(5)	N2-C2	1.3440(13)
Na1-N5	2.3390(10)	C1-C3	1.3893(14)
Na1-C22	2.7585(12)	C2-C3	1.4005(14)
Na1-C2	3.0760(11)	C2-Na1	3.0760(11)
N1-N2	1.3736(11)	C11-C12	1.3998(14)
N2-Na1	2.3538(10)	C12-C13	1.3947(14)
C1-C11	1.4749(14)	C13-C14	1.3872(16)
C2-C21	1.4748(14)	C14-C15	1.3912(17)
C11-C16	1.4015(14)	C15-C16	1.3912(15)
C21-C26	1.3971(16)	C21-C22	1.4004(16)
C21-Na1	3.0429(11)	C22-C23	1.3955(16)
C22-Na1	2.7585(12)	N4-C4	1.3705(13)
C23-C24	1.386(2)	N5-C5	1.3442(13)
C24-C25	1.387(2)	C4-C41	1.4855(14)
C25-C26	1.3908(17)	C5-C51	1.4746(14)
N4-N5	1.3807(11)	C41-C42	1.3961(15)
C4-C6	1.3811(14)	C42-C43	1.3932(16)
C5-C6	1.4049(14)	C43-C44	1.3888(19)
C41-C46	1.3970(15)	C44-C45	1.3869(19)
C51-C52	1.3982(16)	C45-C46	1.3921(16)

C52-C53	1.3922(17)	C51-C56	1.3986(16)
C53-C54	1.384(2)	N7-N8	1.3676(12)
C54-C55	1.387(2)	N8-C8	1.3438(13)
C55-C56	1.3937(16)	C7-C71	1.4740(15)
N7-C7	1.3682(13)	C8-C81	1.4747(15)
C7-C9	1.3914(14)	C71-C72	1.4007(15)
C8-C9	1.4010(16)	C72-C73	1.3927(16)
C71-C76	1.4010(15)	C73-C74	1.3914(17)
C81-C82	1.3982(17)	C74-C75	1.3882(19)
C82-C83	1.3922(17)	C75-C76	1.3924(18)
C83-C84	1.392(2)	C81-C86	1.3990(15)
C84-C85	1.381(2)	C1A-C2A	1.508(5)
C85-C86	1.3920(18)	C2A-C7A	1.374(5)
C2A-C3A	1.399(4)	C3A-C4A	1.394(5)
Al1-N7	1.9192(9)	C4A-C5A	1.366(6)
Al1-Al1	2.5794(6)	C5A-C6A	1.392(5)
Na1-N8	2.3246(10)	C6A-C7A	1.394(5)
Na1-N2	2.3538(10)		

Table 3. Bond angles (°) for complex **1**

N1-Al1-N7	100.68(4)	N1-Al1-Al1	121.73(3)
N7-Al1-N4	112.10(4)	N4-Al1-Al1	107.79(3)
N7-Al1-Al1	111.23(3)	N7-Al1-Na1	68.57(3)
N1-Al1-Na1	157.73(3)	Al1-Al1-Na1	80.524(15)
N4-Al1-Na1	65.92(3)	N8-Na1-N2	110.71(4)
N8-Na1-N5	85.60(3)	N8-Na1-C22	117.17(4)
N5-Na1-N2	113.22(3)	N2-Na1-C22	70.10(3)
N5-Na1-C22	155.02(4)	N5-Na1-C21	135.01(3)
N8-Na1-C21	138.26(4)	C22-Na1-C21	27.37(3)
N2-Na1-C21	51.67(3)	N5-Na1-C2	123.48(3)
N8-Na1-C2	129.70(3)	C22-Na1-C2	50.52(3)
N2-Na1-C2	24.32(3)	N8-Na1-Al1	52.11(2)

C21-Na1-C2	27.89(3)	N2-Na1-Al1	83.14(2)
N5-Na1-Al1	56.66(2)	C21-Na1-Al1	134.80(2)
C22-Na1-Al1	145.27(3)	C1-N1-N2	109.34(8)
C2-Na1-Al1	107.06(2)	N2-N1-Al1	113.33(6)
C1-N1-Al1	136.78(7)	C2-N2-Na1	109.53(7)
C2-N2-N1	106.74(8)	N1-C1-C3	108.19(9)
N1-N2-Na1	138.15(6)	C3-C1-C11	127.47(9)
N1-C1-C11	124.30(9)	N2-C2-C21	119.21(9)
N2-C2-C3	110.67(9)	N2-C2-Na1	46.16(5)
C3-C2-C21	129.98(9)	C21-C2-Na1	74.81(6)
C3-C2-Na1	150.76(7)	C12-C11-C16	118.26(10)
C1-C3-C2	105.06(9)	C16-C11-C1	118.57(9)
C12-C11-C1	123.16(9)	C14-C13-C12	120.35(11)
C13-C12-C11	120.70(10)	C16-C15-C14	120.21(11)
C13-C14-C15	119.58(10)	C26-C21-C22	118.66(10)
C15-C16-C11	120.88(11)	C22-C21-C2	121.31(10)
C26-C21-C2	119.95(10)	C22-C21-Na1	64.93(6)
C26-C21-Na1	128.10(8)	C23-C22-C21	120.44(12)
C2-C21-Na1	77.30(6)	C21-C22-Na1	87.70(6)
C23-C22-Na1	116.08(8)	C24-C23-C22	120.12(13)
C23-C24-C25	119.86(12)	C24-C25-C26	120.26(13)
C25-C26-C21	120.61(12)	C4-N4-N5	108.67(8)
C4-N4-Al1	127.60(7)	N5-N4-Al1	121.38(6)
C5-N5-N4	106.82(8)	C5-N5-Na1	132.13(7)
N4-N5-Na1	115.66(6)	N4-C4-C6	108.96(9)
N4-C4-C41	124.19(9)	C6-C4-C41	126.84(9)
N5-C5-C6	110.66(9)	N5-C5-C51	120.98(9)
C6-C5-C51	128.36(10)	C4-C6-C5	104.87(9)
C42-C41-C46	119.38(10)	C42-C41-C4	120.94(10)
C46-C41-C4	119.57(9)	C43-C42-C41	120.23(11)
C44-C43-C42	119.95(11)	C45-C44-C43	120.16(11)
C44-C45-C46	120.10(11)	C45-C46-C41	120.15(11)
C52-C51-C56	118.08(10)	C52-C51-C5	121.56(10)
C56-C51-C5	120.36(10)	C53-C52-C51	121.11(12)

C54-C53-C52	120.13(13)	C53-C54-C55	119.55(12)
C54-C55-C56	120.48(12)	C55-C56-C51	120.63(12)
N8-N7-C7	109.32(8)	N8-N7-Al1	110.95(6)
C7-N7-Al1	139.38(7)	C8-N8-N7	107.17(9)
C8-N8-Na1	125.60(7)	N7-N8-Na1	122.75(6)
N7-C7-C9	108.09(9)	N7-C7-C71	122.23(9)
C9-C7-C71	129.67(10)	N8-C8-C9	110.31(9)
N8-C8-C81	118.04(10)	C9-C8-C81	131.64(10)
C7-C9-C8	105.11(9)	C72-C71-C76	118.54(10)
C72-C71-C7	121.41(10)	C76-C71-C7	120.02(10)
C73-C72-C71	120.81(11)	C74-C73-C72	119.96(12)
C75-C74-C73	119.69(12)	C74-C75-C76	120.50(11)
C75-C76-C71	120.35(11)	C82-C81-C86	118.94(11)
C82-C81-C8	119.42(10)	C86-C81-C8	121.64(11)
C83-C82-C81	120.72(12)	C84-C83-C82	119.60(13)
C85-C84-C83	120.14(12)	C84-C85-C86	120.52(12)
C85-C86-C81	120.05(13)	C7A-C2A-C3A	118.1(3)
C4A-C5A-C6A	119.3(4)	C3A-C2A-C1A	121.5(3)
C2A-C7A-C6A	121.7(4)	C5A-C4A-C3A	121.0(3)
N1-Al1-N4	103.00(4)	C5A-C6A-C7A	119.6(4)