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Electronic Supplementary Information

for

Reactivity of cationic α-diimine cyclopentadienyl nickel complexes towards $AlEt_2Cl$: Synthesis, characterisation and ethylene polymerisation

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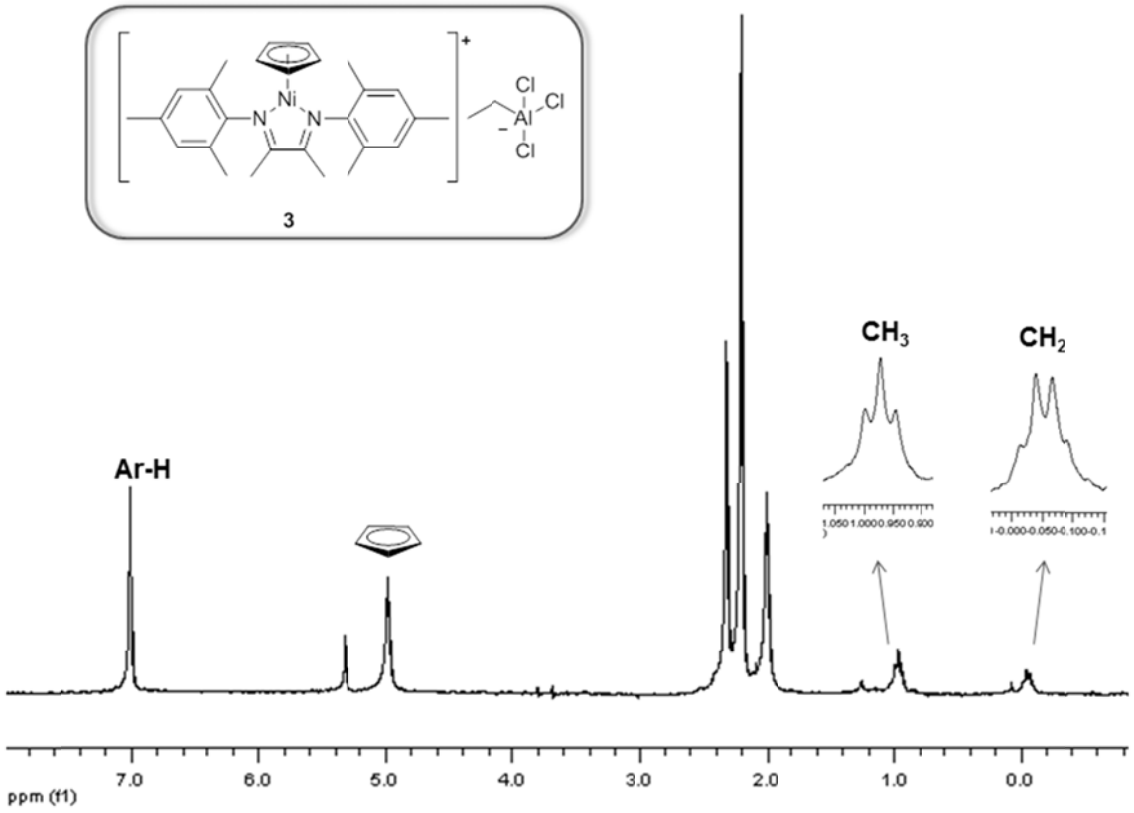


Figure S1. ^{1}H NMR spectrum (300 MHz) of [Ni(η^5-C_5H_5)(Mes-Me_2DAD)][$AlEtCl_3$] (**3**), in CD_2Cl_2, at room temperature.

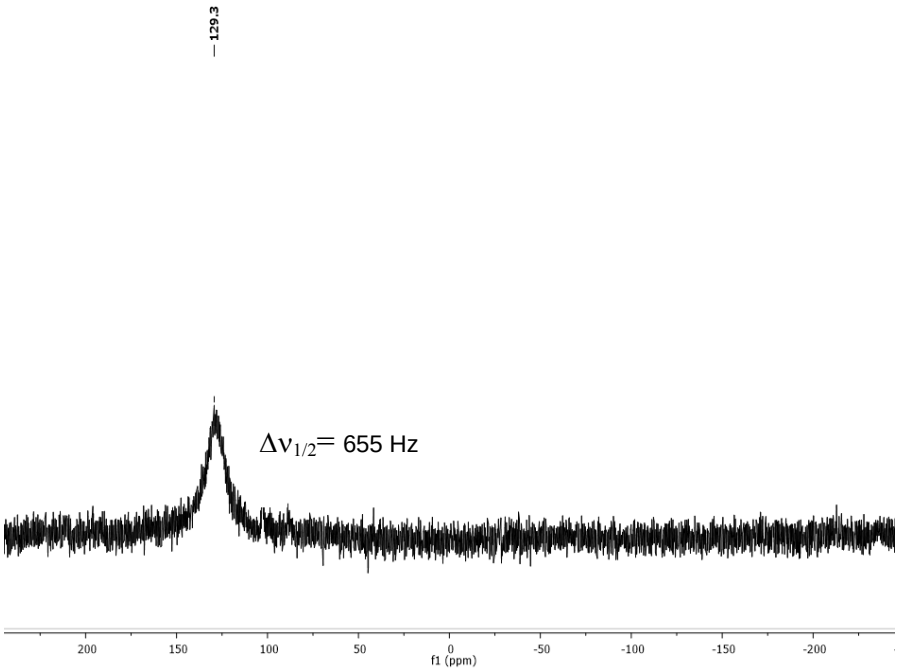


Figure S2. $^{27}Al\{^{1}H\}$ NMR (78 MHz) spectrum of $[Ni(\eta^5\text{-}C_5H_5)(Mes\text{-}Me_2DAD)][AlEtCl_3]$ (**3**), in CD_2Cl_2, at room temperature.

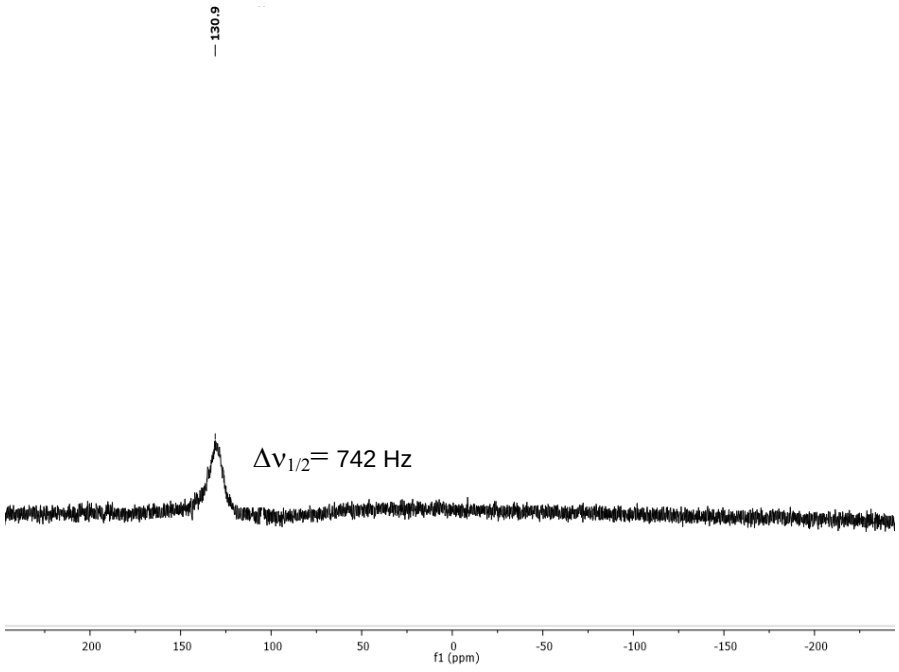


Figure S3. $^{27}Al\{^{1}H\}$ NMR spectrum (78 MHz) of $[Ni(\eta^5\text{-}C_5H_5)(Mes\text{-}BIAN)][AlEtCl_3]$ (**4**), in CD_2Cl_2, at room temperature.

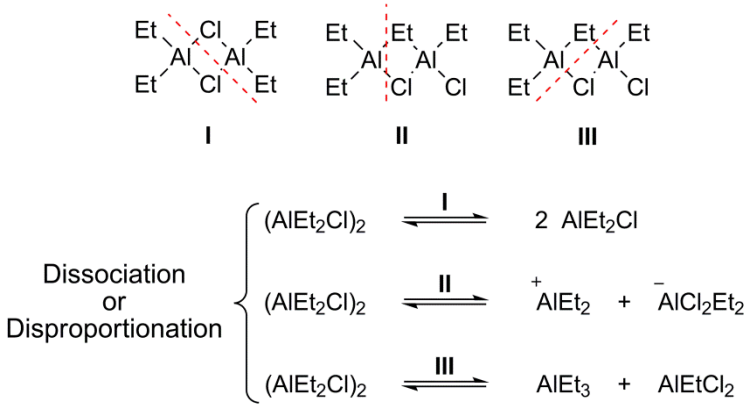
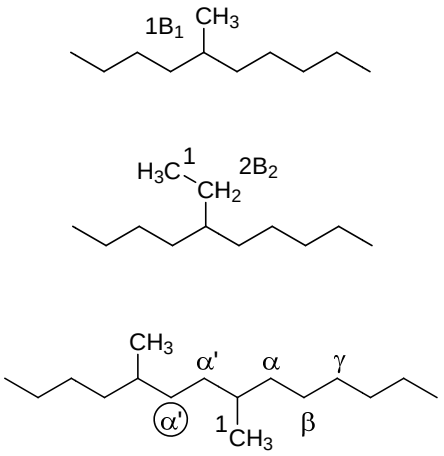


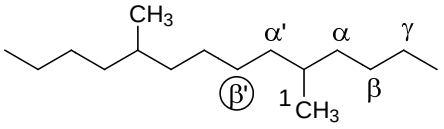
Figure S4. Dissociation or disproportionation modes for $AlEt_2Cl$:[1] (a) symmetric bridge cleavage; (b) asymmetric bridge cleavage of mixed chloro-alkyl-bridged dimers; and (c) asymmetric cleavage of the mixed chloro-ethyl-bridged dimers.

[1] M. F. Self, W. T. Pennington, J. A. Laske and G. H. Robinson, *Organometallics*, 1991, **10**, 36.

Assignment of the PE Branches by $^{13}C\{^1H\}$ NMR Spectroscopy



Circled carbon is 1,4-α'B_1
Methyl carbon is 1,4-1B_1



Circled carbon is 1,6-β'B_1
Methyl carbon is 1,6-1B_1

Peak no.	δ (ppm)	Assignment
1	11.16	$1B_2$
2	14.06	$1B_4$; $1B_5$; $1B_n$; 1,4-$1B_n$
3	14.59	$1B_3$
4	19.93	$1B_1$; 1,5-B_1; 1,6-B_1
5		1,4-B_1
6	22.30	$2B_3$
7	22.87	$2B_5$; $2B_n$; 1,4-$2B_n$
8	23.27	$2B_4$
9	24.67	1,5-β'B_1
10	26.67	$2B_2$
11	27.28	βB_2; βB_4; βB_5; βB_n;
12	27.44	βB_1; 1,4-βB_1; 1,5-βB_1;
13	27.82	1,6-β'B_1
14		$3B_4$
15	29.58	$4B_n$; 1,4-$4B_n$
16	30.00	$\delta B_{1\text{-}n}$
17	30.38	γB_1; 1,4-γB_1; 1,5-γB_1;
18	30.48	γB_2; γB_3; γB_4; γB_5
19	31.70	1,4-α'B_n
20	32.17	$3B_n$; 1,4-$3B_n$
21	32.67	$3B_5$
22	33.22	brB_1; 1,5-brB_1
23	33.58	1,4-brB_1
24		αB_2
25	34.02	$4B_4$
26	34.51	αB_3; αB_4; $5B_5$; αB_5
27	34.80	1,4-α'B_1
28	36.90	$3B_3$
29	37.52	αB_1
30		brB_3; 1,5-α'B_1
31	38.15	brB_4
32		1,4-brB_n
33	39.63	brB_2

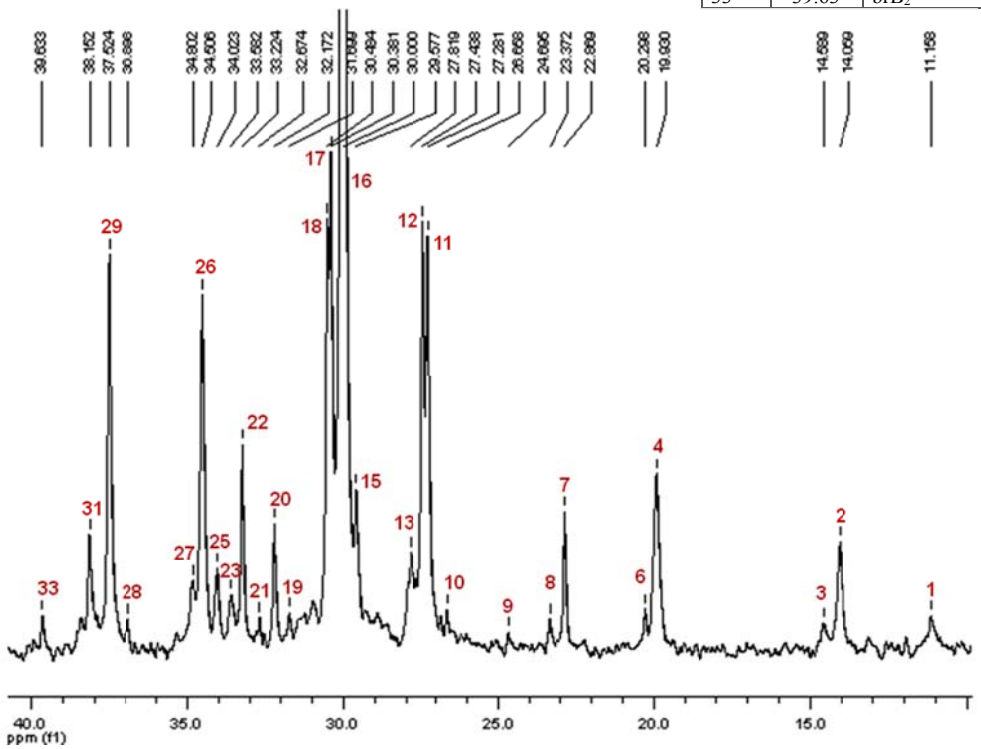


Figure S5. $^{13}C\{^1H\}$ NMR spectrum (75 MHz, 1,2,4-trichlorobenzene/C_6D_6 (75:25 v/v), 110 ºC) of the polyethylene of entry 6 (see Table 3 of the article), showing the observed chemical shifts and the assignment of each type of branches.

The assignment of the resonances of Fig. S3, which allows the quantification of the different branches, such as methyl (N_M), ethyl (N_E), propyl (N_P), butyl (N_B), amyl (N_A), and longer ($n \geq 6$, N_L) branches, was performed according to the literature.[2–4] In fact, for the polyethylene sample of entry 6 (see Table 3 in the main article text), the resonances at δ 19.93, 24.67, 27.82, 33.58 and 34.80 ppm (peaks 4, 9, 13, 23 and 27 in Fig. S4) correspond to methyl branches (N_M); δ 26.67 and 39.63 (peaks 10 and 33) to ethyl branches (N_E); δ 36.90 (peak 28) to a propyl branch (N_P); δ 23.27 and 34.02 (peaks 8 and 25) to butyl branches (N_B), δ 32.67 (peak 21) to an amyl branch (N_A); and δ 29.58, 31.70 and 32.17 (peaks 15, 19 and 20) to longer branches. The relative integration of these resonances allows the determination of the branching distribution. For this sample, it was possible to determine that, in 1000 carbon atoms, *ca.* 26 are methyl branches, 3 are ethyl, 6 are propyl, 11 are butyl, 4 are amyl, and 17 are longer branches. Therefore, it is possible to observe that the majority of the branches present in the polymer are methyl groups, following the order:

$$\text{methyl} > \text{long} > \text{butyl} > \text{propyl} > \text{amyl} \approx \text{ethyl}$$

For the polyethylene sample of entry 6, the branching number (N) is 67, as determined from ^{1}H NMR spectroscopy,[5] whereas for entries 1 and 5 the branching degrees are 18 and 30, respectively (Table 3 of the article). In the case of entry 1, only *ca.* 13 methyl (δ 19.93 ppm) and 5 butyl (δ 34.1 ppm) branches are present in the polymer, while in entry 5 there are 18 methyl (δ 19.94 ppm) branches, 3 butyl (δ 34.03 ppm), 5 amyl (δ 32.72 ppm), and 4 longer (δ 32.17 ppm) branches.

[2] (a) G. B. Galland, R. F. Souza, R. S. Mauler, F. F. Nunes, *Macromolecules*, 1999, **32**, 1620; (b) L. C. Simon, J. B. P. Soares, R. F. Souza, *AIChE J.*, 2000, **46**, 1324.
[3] D. E. Axelson, G. C. Levy and L. Mandelkern, *Macromolecules*, 1979, **12**, 41
[4] F. A. Bovey, F. C. Schilling, F. L. McCrackin and H. L. Wagner, *Macromolecules*, 1976, **9**, 77.
[5] A. C. Gottfried and M. Brookhart, *Macromolecules*, 2003, **36**, 3085.

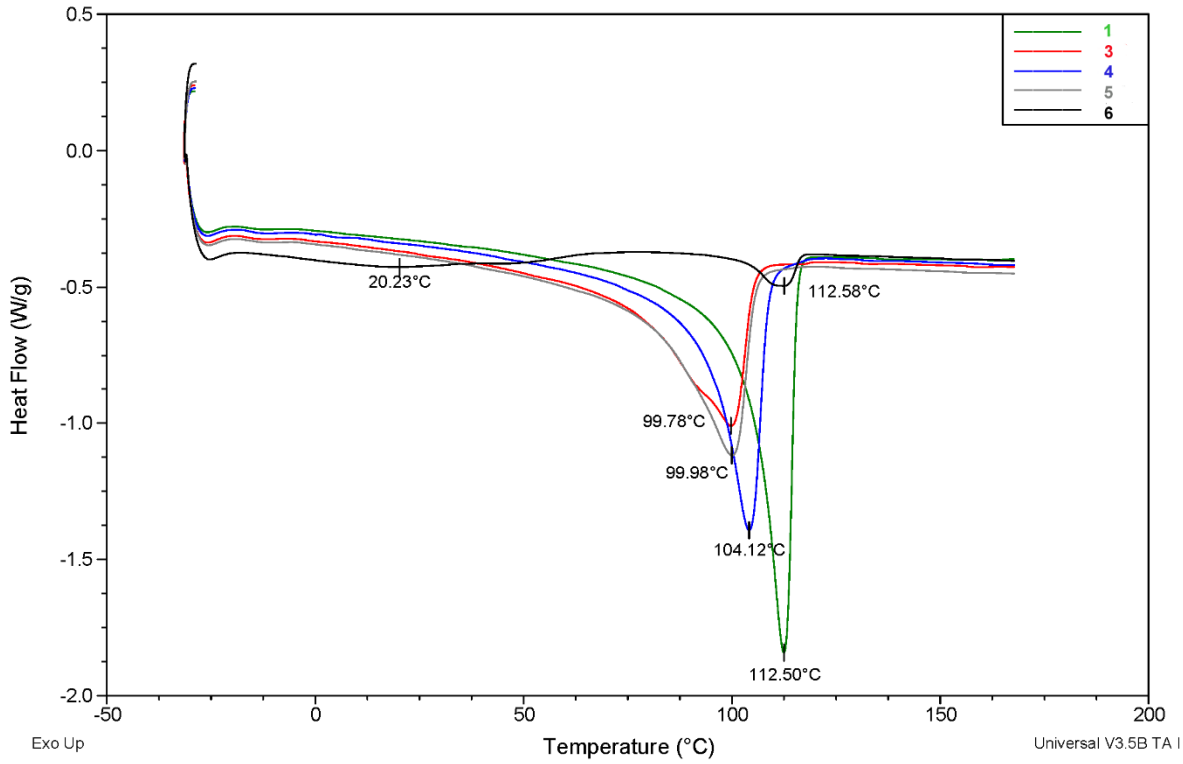


Fig. S6 DSC thermograms of the polyethylenes prepared using systems **3**/DEAC (Table 3 of the main article text, entries 1 and 3-5) and **5**/DEAC (entry 6, Table 3, main article text), showing the melting point for each sample.

Table S1. Selected bond distances (Å), angles (º) and other relevant structural parameters for [Ni(η^5-C_5H_5)(Mes-DAD)][$AlEtCl_3$] (**3**).

	molecule 1	molecule 2
Bond distances (Å)		
Ni1-C1	2.096(13)	
Ni1-C2	2.101(14)	
Ni1-C3	2.129(15)	
Ni1-C4	2.028(16)	
Ni1-C5	2.105(14)	
Ni1-N1	1.874(11)	
Ni1-N2	1.848(11)	
C1-C2	1.44(2)	
C2-C3	1.47(2)	
C3-C4	1.40(2)	
C4-C5	1.42(2)	
C5-C1	1.38(2)	
Ni2-C31		2.124(16)
Ni2-C32		2.042(16)
Ni2-C33		2.143(17)
Ni2-C34		2.065(14)
Ni2-C35		2.071(14)
Ni2-N3		1.849(10)
Ni2-N4		1.858(11)
C31-C32		1.42(3)
C32-C33		1.37(3)
C33-C34		1.37(2)
C34-C35		1.39(2)
C35-C31		1.41(2)
Ni-$Cp_{centroid}$	1.707(8)	1.721(9)
Al1-Cl1	2.124(7)	
Al1-Cl2	2.141(8)	
Al1-Cl3	2.166(6)	
Al1-C28	1.92(2)	
Al1-Cl4		2.165(6)
Al1-Cl5		2.153(6)
Al1-Cl6		2.167(7)
Al1-C58		1.946(15)
Distance A[a]	0.07(2) (C4)	0.05(3) (C32)
Bond Angles (º)		
N1-Ni1-N2	83.9(5)	
N3-Ni2-N4		82.8(5)
N1-Ni1-$Cp_{c.}$	139.6(6)	
N2-Ni1-$Cp_{c.}$	136.4(6)	
N3-Ni2-$Cp_{c.}$		139.6(7)
N4-Ni2-$Cp_{c.}$		137.6(7)
Dihedral χ[b]	92.1(6)	91.4(7)

[a] Shortest distance between a carbon atom of the Cp ring (in brackets) and the plane(Ni1-N1-N2). [b] Dihedral χ= angle between the plane (N1-Ni1-N2) and the average plane of the Cp ring.

Table S2. Top view of complex **3** (molecules A and B) and a schematic representation of the corresponding delocalised Cp rings. The N-Ni-N planes are indicated by dashed lines (distances in Å).

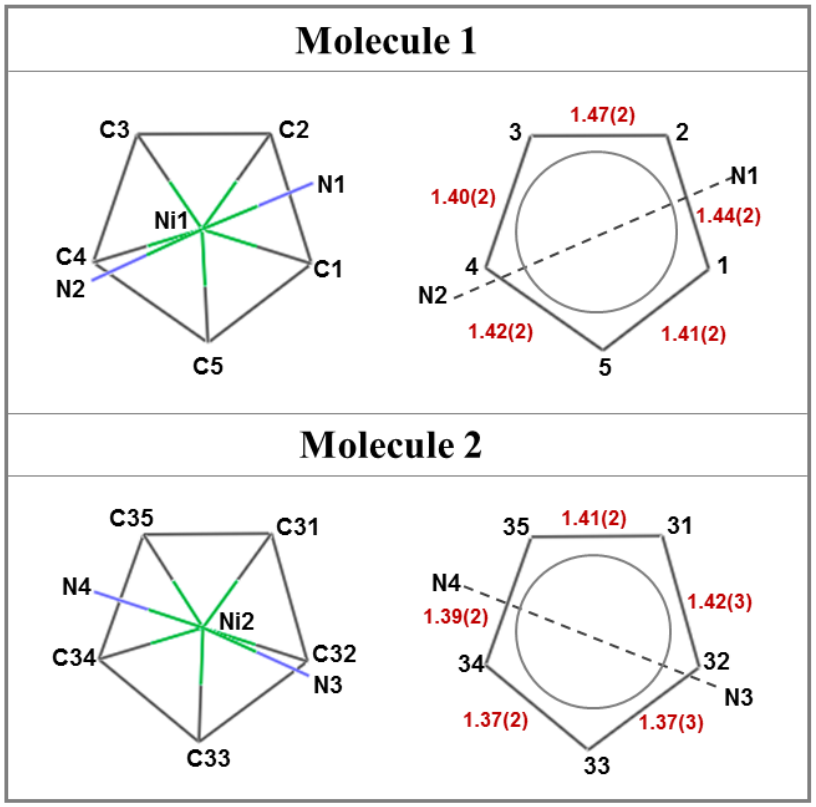


Table S3. Selected bond distances (Å) and angles (º) for complex **5**.

Bond distances (Å)				*Angles (º)*	
Ni1-Cl1	2.4363(18)	Ni1-N1	2.088(5)	N1-Ni1-N2	81.3(2)
Ni1-Cl2	2.4220(18)	Ni1-N2	2.087(5)	N3-Ni2-N4	80.9(2)
Ni1-Cl3	2.4520(17)	Ni2-N3	2.100(5)	N5-Ni3-N6	80.8(2)
Ni1-Cl4	2.4211(18)	Ni2-N4	2.099(5)	Cl2-Ni1-Cl4	160.02(6)
Ni2-Cl1	2.4772(18)	Ni3-N5	2.085(5)	Cl1-Ni2-Cl3	86.18(6)
Ni2-Cl2	2.3916(18)	Ni3-N6	2.093(5)	Cl2-Ni2-Cl5	160.18(7)
Ni2-Cl3	2.4389(17)	Al1-Cl6	2.337(6)	Cl1-Ni3-Cl3	86.83(7)
Ni2-Cl5	2.4035(18)	Al1-Cl7	2.141(4)	Cl4-Ni3-Cl5	160.97(6)
Ni3-Cl1	2.4380(17)	Al1-Cl8	2.274(5)	Cl1-Ni3-Cl3	86.79(6)
Ni3-Cl3	2.4489(18)	Al1-Cl9	2.216(8)		
Ni3-Cl4	2.4115(18)	Al1-Cl9a	2.088(10)		
Ni3-Cl5	2.4207(18)				

Table S4. Selected bond distances (Å) angles (º) for complex **6**.

Bond distances (Å)			*Angles (º)*		
	molecule A	molecule B		molecule A	molecule B
Ni1-Cl1	2.284(3)	2.286(3)	N1-Ni1-N2	79.5(3)	78.7(3)
Ni1-N1	2.059(7)	2.083(7)	N3-Ni1-N4	79.8(3)	78.1(3)
Ni1-N2	2.141(7)	2.092(7)	N1-Ni1-N3	98.6(3)	100.4(3)
Ni1-N3	2.137(7)	2.128(7)	N2-Ni1-N4	99.9(3)	100.3(3)
Ni1-N4	2.080(7)	2.093(7)	Cl1-Ni1-N1	103.89(19)	101.6(2)
Al1-Cl2	2.138(4)	2.115(4)	Cl1-Ni1-N2	93.8(2)	92.5(2)
Al1-Cl3	2.108(4)	2.108(5)	Cl1-Ni1-N3	91.42(19)	94.0(2)
Al1-Cl4	2.134(4)	2.125(4)	Cl1-Ni1-N4	100.00(19)	100.1(2)
Al1-Cl5	2.097(4)	2.150(5)	Cl2-Al1-Cl3	111.23(17)	111.9(2)
			Cl3-Al1-Cl4	108.27(18)	109.2(2)
			Cl4-Al1-Cl5	112.04(18)	108.35(19)
			Cl5-Al1-Cl2	109.98(18)	107.7(2)
τ parameter [6]	0.311	0.252			

[6] K.-N. Yeh and R. H. Barker, *Inorg. Chem.* 1967, **6**, 830.

Table S5. Crystallographic data and details about refinement for the structures of **3**, **5** and **6**.

	3	**5**	**6**
Formula	$C_{34.25}H_{41.50}AlCl_{4.75}N_2Ni$	$C_{90}H_{84}AlCl_9N_6Ni_3$	$C_{123}H_{118}Al_2Cl_{16}N_8Ni_2$
M	735.25	1771.79	2446.83
λ (Å)	0.67710	0.71073	0.71073
T (K)	150(2)	150(2)	150(2)
crystal system	Monoclinic	Triclinic	Monoclinic
space group	$P\,2_1$	P-1	$P\,2_1$
a (Å)	12.6520(1)	14.507(3)	16.975(8)
b (Å)	23.8430(1)	16.966(3)	15.547(6)
c (Å)	12.7390(2)	19.647(4)	24.680(12)
α (°)	90	112.115(9)	90
β (°)	100.8580(10)	101.465(10)	101.91(3)
γ (°)	90	100.432(11)	90
V (Å^3)	3774.07(7)	4212.4(14)	6373(5)
Z	4	2	2
ρ_{calc} (g.cm^{-3})	1.294	1.397	1.275
μ (mm^{-1})	0.758	1.009	0.693
Crystal dimensions	0.10×0.10×0.20	0.12×0.09×0.01	0.10×0.20×0.26
Crystal colour	Brown	black	black
Crystal description	Block	plate	plate
θ_{max} (°)	20.892	25.20	26.05
total data	22526	68728	51553
unique data	9232	8407	11426
R_{int}	0.0495	0.1159	0.1089
R [I>2σ(I)]	0.0635	0.0621	0.0775
R_w	0.1655	0.1550	0.1814
Goodness of fit	1.033	0.978	0.920
ρ_{min}	-0.422	-1.382	-0.698
ρ_{max}	1.093	1.108	0.504