Journal of Organometallic Chemistry 901 (2019) 120943

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Concise access to aluminum containing [3.3](2,6)pyridinophane and molecular bowl using 2,6-diamidopyridine modules

Chandrakala Negi [1], Deependra Bawari [1], Sandeep Kumar Thakur, Angshuman Roy Choudhury, Sanjay Singh*

Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali, Knowledge City, Sector 81, SAS Nagar, Mohali, 140306, Punjab, India

ARTICLE INFO

Article history:
Received 21 August 2019
Received in revised form
15 September 2019
Accepted 16 September 2019
Available online 17 September 2019

Keywords:
Pyridinophanes
Molecular bowl
Aluminum complexes
2,6-Disubstituted pyridine
Cyclophanes

ABSTRACT

By varying the relative stoichiometry of the building block bis(trimethylsilyl)−N,N′−2,6−diaminopyridine (bap) and $EtAlCl_2$ or $AlCl_3$, different molecular entities (mononuclear and dinuclear complexes, pyridinophane and molecular bowl) containing aluminum centres have been synthesized. Efforts to extend the approach to synthesize triazinophanes with bis(trimethylsilyl)-N,N′-2,4-diamino–6–(R)–triazines (R = Me, NH($SiMe_3$), Ph) in their reactions with $AlMe_3$ showed strong preference for the formation of dinuclear aluminum complexes over the analogous pyridinophane like structures. All the new compounds have been fully characterized using multinuclear NMR, HRMS and single crystal X-ray diffraction.

1. Introduction

Pyridinophanes, as the name suggests, are considered derivatives of cyclophanes when one or more of their benzene rings are replaced by pyridine [1]. Pyridinophanes and their derivatives are significant for their applications as pyridoxal models and for metal complexation [2]. Two types of pyridinophanes are common depending on the functionalized positions of the pyridine rings: one that contain the 3,5-disubstituted pyridine units and provides the building blocks for [n.n](3,5)pyridinophanes, the other type consists of 2,6-disubstituted pyridine units to assemble [n.n](2,6) pyridinophanes (Fig. 1) [1,3].

Based on our interest in pyridinophanes containing Lewis acidic elements from main group of the periodic table we have employed 2,6-N,N′-disubstituted pyridine units to this task to assemble [3.3](2,6)pyridinophanes. These disubsituted pyridine units of the type, $[RN(NR')_2]^{2-}$ (RN = pyridine) have proved to be promising due to the desired orientation of −NR′ group in their dianionic chelating amidinate like fragments, which makes them ideal for forming cyclic assemblies with suitable acceptors.

Prior to our reports, the successful attempts to incorporate aluminum in the macrocyclic environment [4-8] included the work of Uhl and co-workers using hydroalumination reaction of 1,4-di(tert-butylalkynyl)benzene with $HAlR_2$ (R = CMe_3, CH_2CMe_3) that led to aluminum bridged [3.3] and [3.3.3]cyclophanes (A, Fig. 2) [4,5]. Reddy et al. reported reactions of *N*-substituted amidines HN═C(R)−NH(R′) (R = Ph, 4-*t*Bu-Ph, Me; R′ = 2,6-$iPr_2C_6H_3$, Ph) with $AlMe_3$ and $AlMeCl_2$ to form tetrameric aluminum amidinates (B, Fig. 2) [6]. In these compounds, the amidinate ligand chelates to aluminum while bridging to another aluminum. Cowley and co-workers have synthesized a cage type compound, AlMe$[Al{-}Me_2\{N(H),N(H){-}C_5H_3N\}]_2$ by 3:2 reaction of $AlMe_3$ and 2,6-diaminopyridine (C, Fig. 2) [8].

Recently, we reported on a few aluminum containing pyridinophanes (C, D, Fig. 2) formed from the reaction between bis(trimethylsilyl)-N,N′-2,6-diaminopyridine (bap) with $AlMe_3$ and AlH_3 [9,10]. These examples include a bowl shaped pyridinophane, $[2,6\text{-}(Me_3SiN)_2C_5H_3N(AlMe_2)]_2[AlMe]$ (C), syn- and *anti* tetraazadialumino[3.3](2,6)pyridinophane, $[2,6\text{-}(Me_3SiN)_2C_5H_3NAlMe]_2$ (D), and a bicyclic pyridinophane, $[2,6\text{-}(Me_3SiN)_2C_5H_3N]_3Al_2$ (D). All these molecules involved donor-acceptor (Npy … Al) interaction between pyridine nitrogen with aluminum at the bridgeheads.

In extension of the previous work, herein we report on the

---

* Corresponding author.
E-mail address: sanjaysingh@iisermohali.ac.in (S. Singh).

[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.jorganchem.2019.120943
0022-328X/

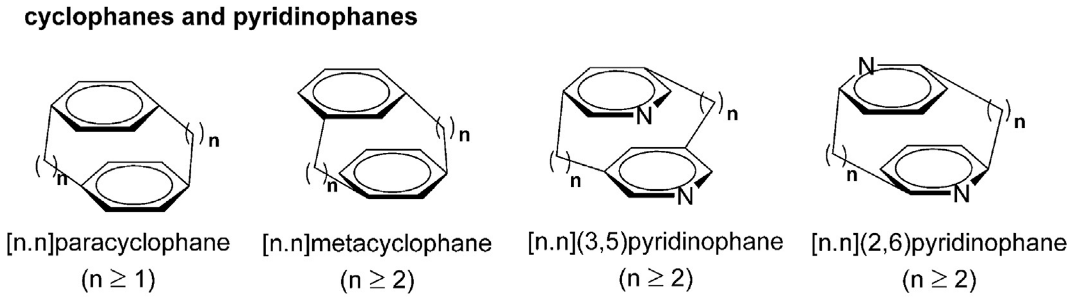


Fig. 1. Schematic representation of [n.n]paracyclophanes, [n.n]metacyclophanes, [n.n](3,5)pyridinophanes and [n.n](2,6)pyridinophanes.

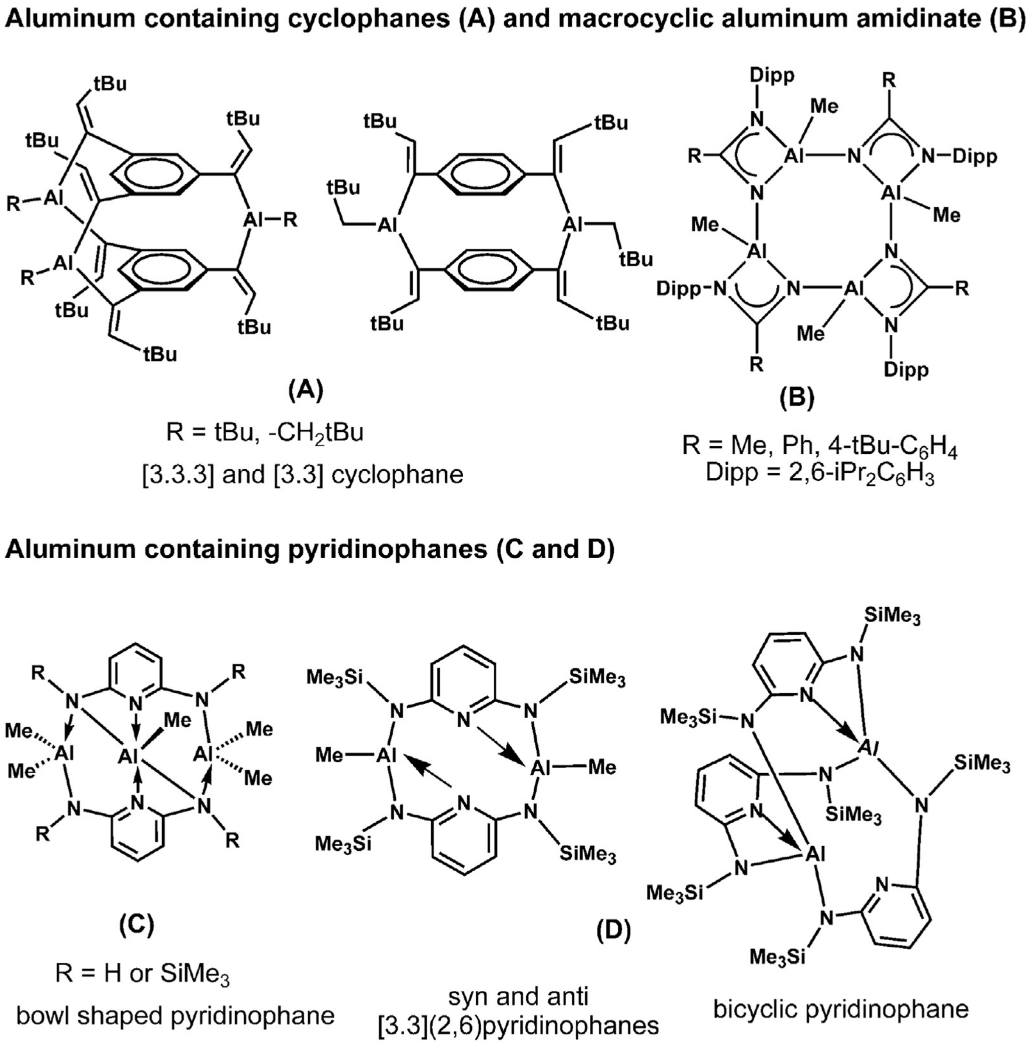


Fig. 2. Well characterized cyclophanes (A), macrocycles (B) and pyridinophanes (C and D) containing aluminum.

reactions between dilithium bis(trimethylsilyl)-N,N′-2,6-diamidopyridine (Li$_2$bap) with EtAlCl$_2$ and AlCl$_3$ that afforded the anti pyridinophane [{2,6–(Me$_3$SiN)$_2$C$_5$H$_3$N}AlEt]$_2$ (1) and the bowl shaped pyridinophane [2,6–(Me$_3$SiN)$_2$C$_5$H$_3$N(AlCl$_2$)]$_2$[AlCl] (2), respectively. The 1:1 reaction of bis(trimethylsilyl)-N,N′-2,6-diaminopyridine (bap) with EtAlCl$_2$ afforded the complex [{2–(Me$_3$SiN)–6–(Me$_3$SiNH)C$_5$H$_3$N}AlCl$_2$]$_2$ (3) whereas the 2:1 reaction of bap and EtAlCl$_2$ gave the complex [2–(Me$_3$SiN)–6–(Me$_3$SiNH)C$_5$H$_3$N]$_2$AlCl (4). The use of an external base Et$_3$N in the 3:1 reaction of bap and EtAlCl$_2$ afforded compound [2–(Me$_3$SiN)–6–(Me$_3$SiNH)C$_5$H$_3$N]$_3$Al (5). Efforts to extend the approach to synthesize triazinophanes with bis(trimethylsilyl)-N,N′-2,4-diamino–6–(R)–triazine in reactions with AlMe$_3$ showed strong preference for the formation of dinuclear complexes over the macrocycles to yield the products [2,4–(Me$_3$SiN)$_2$–6–(R)–C$_3$N$_3$](AlMe$_2$)$_2$ (R = Me (6), NHSiMe$_3$ (7) and Ph (8)).

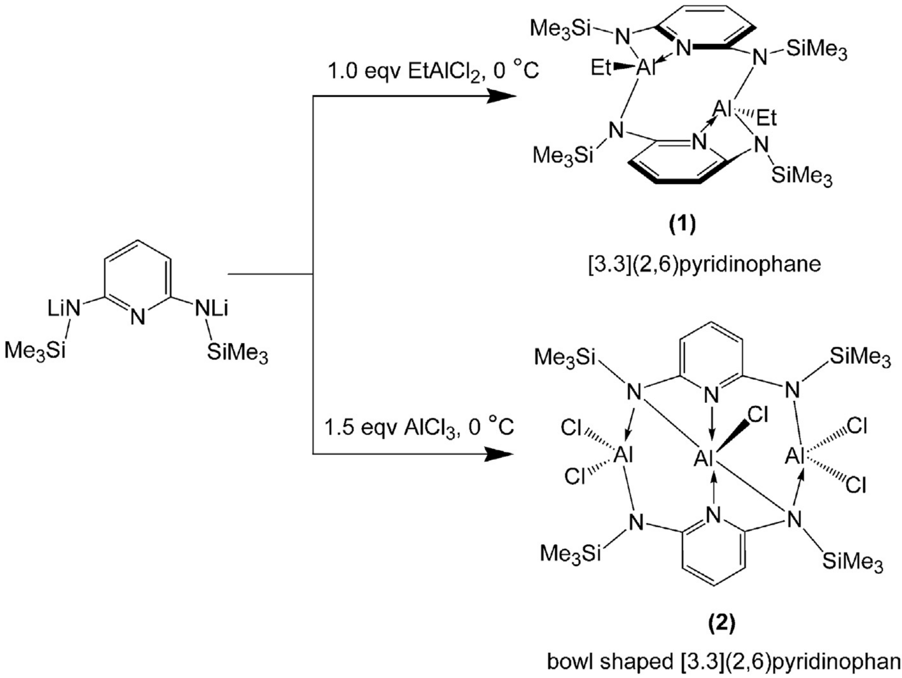
2. Results and discussion

The reaction between stoichiometric amount of dilithium bis(trimethylsilyl)-N,N′-2,6-diamidopyridine (Li_2bap) and $EtAlCl_2$ gave tetraazadialumino[3.3](2,6)pyridinophane, $[\{2,6-(Me_3SiN)_2C_5H_3N\}AlEt]_2$ (1) (Scheme 1). The presence of ethyl group on the aluminum centre in 1 was seen as a triplet (0.78 ppm, CH_3CH_2-) and a quartet (−0.21 ppm, CH_3CH_2-) in its ^1H NMR spectrum and the corresponding carbon signals respectively appeared at 8.6 and −2.1 ppm in its ^{13}C NMR spectrum. Two equal intensity signals in ^1H NMR (0.22 and 0.11 ppm) and ^{13}C NMR (2.3 and 0.5 ppm) spectra of 1 were attributed to four $SiMe_3$ groups. Surprisingly, only one signal at 3.15 ppm was observed in the ^{29}Si NMR spectrum of 1. The formation of 1 as the N−Al(Et)−N bridged dimer was confirmed in the HRMS measurement that showed signal at $m/z = 621.3503$ (calcd. 621.3509) for $[M+H]^+$.

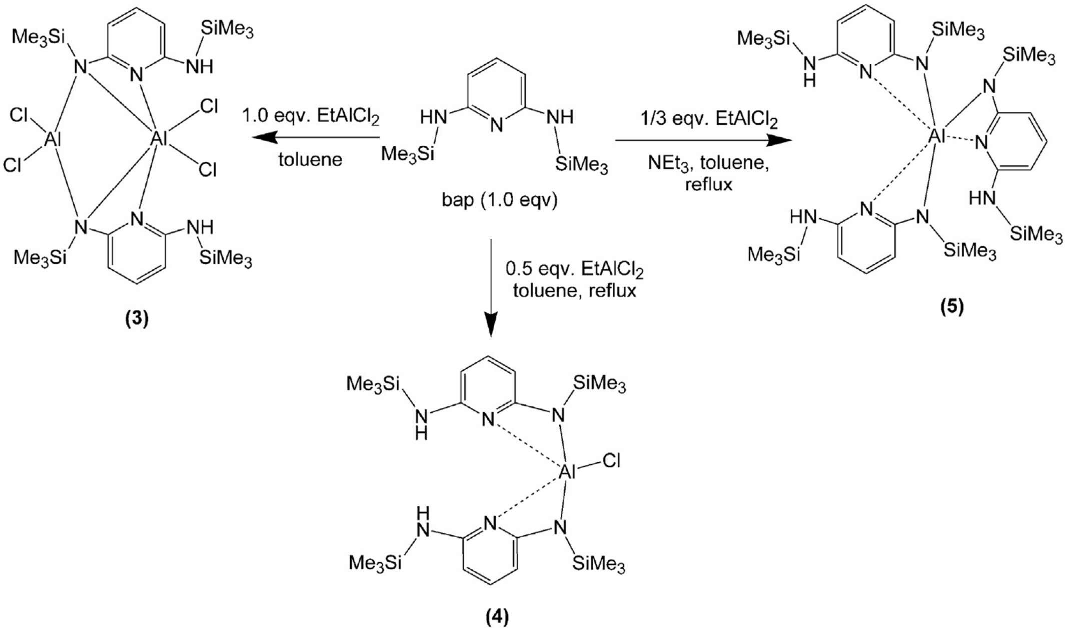
The 1:1 reaction of dilithium bis(trimethylsilyl)-N,N′-2,6-diamidopyridine (Li_2bap) and $AlCl_3$ at room temperature was expected to yield a pyridinophane like that of 1, instead a mixture of products formed that could not be separated. Attempts to simplify the reaction by varying the stoichiometry of reagents gave a pyridinophane based bowl shaped aluminum cage, $[2,6-(Me_3SiN)_2C_5H_3N(AlCl_2)]_2[AlCl]$ (2) (Scheme 1) in the 2:3 reaction of dilithium bis(trimethylsilyl)-N,N′-2,6-diamidopyridine (Li_2bap) and $AlCl_3$ at room temperature. The presence of a single resonance for $SiMe_3$ groups in the ^1H NMR (0.43 ppm) and ^{13}C NMR (2.4 ppm) spectra as well as a triplet (7.64 ppm, 2H) and a doublet (6.21 ppm, 4H) in the ^1H NMR spectrum of 2 indicated its symmetrical structure in solution. Surprisingly, no signal was observed in ^{29}Si NMR spectrum of 2. Further, the signal in the HRMS spectrum of 2 at $m/z = 758.0411$ (calcd. 758.0437), for $[M]^+$ corroborated to a trinuclear aluminum containing pyridinophane based bowl shaped structure similar to that previously observed in the reaction of $AlMe_3$ with bap (C, Fig. 2) [10]. In view of the X-ray structure of 2, see below, the magnetic equivalence of four $SiMe_3$ groups can be explained by considering that the central AlCl group switches intramolecularly between $NSiMe_3$ groups at the 2- and 6-position of the pyridyl unit in an overall rigid cage like structure of 2. This has been previously observed with a structurally similar AlMe analogue of 2 (C, Fig. 2) [10].

Emulating on the dependency of the product formation on the relative stoichiometry of the reagents in the formation of 2 and on our previous work [9,10], we varied the relative stoichiometry between bap and $EtAlCl_2$. Subsequently, we were successful in 1:1 and 2:1 stoichiometry reactions of bis(trimethylsilyl)-N,N′-2,6-diaminopyridine (bap) and $EtAlCl_2$ to isolate the complexes, $[\{2-(Me_3SiN)-6-(Me_3SiNH)C_5H_3N\}AlCl_2]_2$ (3) and $[2-(Me_3SiN)-6-(Me_3SiNH)C_5H_3N]_2AlCl$ (4) respectively (Scheme 2). The 3:1 reaction between bap and $EtAlCl_2$ gave a homoleptic complex $[2-(Me_3SiN)-6-(Me_3SiNH)C_5H_3N]_3Al$ (5) *via* ethane evolution and elimination of HCl in the presence of external base NEt_3 (Scheme 2). The IR spectra of these complexes showed −NH stretch at 3269 (for 3), 3372 and 3248 (for 4) and 3356 cm^{-1} (for 5). The ^1H NMR spectra of complexes 3−5 showed a triplet and two doublets for the pyridine hydrogens and their corresponding carbons were observed as five signals in their ^{13}C NMR spectra. This observation indicated towards chemically and magnetically non-equivalent environment around the pyridine rings. Consistent with these, the ^1H NMR spectra of 3 (0.51 and 0.07 ppm), 4 (0.28 and 0.04 ppm) and 5 (0.05 and 0.27 ppm) showed different signals for a pair of $SiMe_3$ groups as well. These observations were also consistent in the ^{13}C (only single resonance observed for 3 at −0.9 ppm), (0.7 & −0.2 ppm for 4 and 0.9 and −0.3 ppm for 5) and ^{29}Si (15.7 and 6.4 ppm for 3, 5.3 & −0.4 ppm for 4 and 3.2 & −3.2 ppm for 5) NMR spectra. The HRMS spectra of these complexes showed *m/z* values of 698.1058 (calcd. 698.1089 for 3), 566.2230 (calcd. 566.2208 for 4) and 783.3846 (calcd. 783.3872 for 5) corresponding to $[M]^+$.

The current protocol with pyridine rings that afforded the pyridinophane or the bowl shaped pyridinophane, was extended to triazine systems, bis(trimethylsilyl)-N,N′-2,4-diamino–6–(R)–triazine (bat) (R = Me, $NH(SiMe_3)$, Ph) in their reactions with $AlMe_3$. These attempts did not afford the expected triazinophanes and instead showed the preference for the formation of dinuclear $AlMe_2$ complexes, $[2,4-(Me_3SiN)_2-6-(R)-C_3N_3](AlMe_2)_2$ (R = Me (6), $NHSiMe_3$ (7), Ph (8)). Further optimization showed that



Scheme 1. Syntheses of aluminum based [3.3](2,6)pyridinophane, $[\{2,6-(Me_3SiN)_2C_5H_3N\}AlEt]_2$ (1) and pyridinophane based bowl shaped aluminum cage $[2,6-(Me_3SiN)_2C_5H_3N(AlCl_2)]_2[AlCl]$ (2).



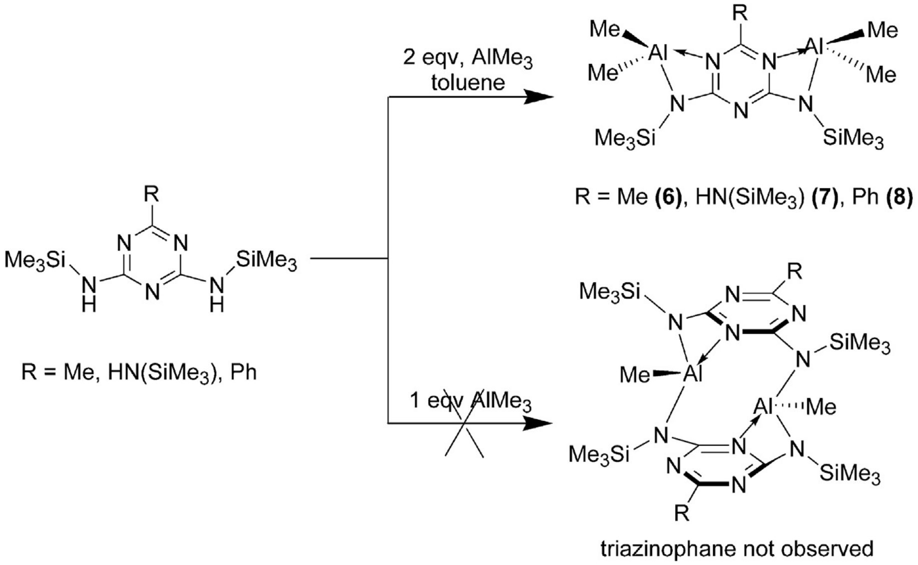
Scheme 2. Syntheses of aluminum complexes [{2-(Me_3SiN)-6-(Me_3SiNH)C_5H_3N}$AlCl_2$]$_2$ (3), [2–(Me_3SiN)–6–(Me_3SiNH)C_5H_3N]$_2$AlCl (4) and [2-(Me_3SiN)-6-(Me_3SiNH)C_5H_3N]$_3$Al (5).

complexes 6–8 can be best prepared in 1:2 reaction of bat with $AlMe_3$ at room temperature (Scheme 3). All of the products 6–8 formed under vigrous methane evolution leading to a slight turbid to transparent solution. Absence of the N–H signal (for 6 and 8) in the IR as well as in the ^{1}H NMR spectra confirmed the removal of both the -N*H*$SiMe_3$ protons. The intensity for 2x$AlMe_2$ signals for 6 as a singlet (12H at −0.69 ppm), two singlets for 7 (with 6H each at −0.63 & −0.68 ppm) and a singlet for 8 (12H at −0.61 ppm) were in accordance with the 1:2 ligand to $AlMe_2$ ratio confirming the formation of dinuclear $AlMe_2$ complexes. The Al*Me*$_2$ signal in the ^{13}C NMR spectra for complexes 6–8 appeared respectively at −10.7, −9.0 & −10.1 and −0.1 ppm. The ^{29}Si NMR spectra of these complexes showed signal at 3.1 (6), 8.6, 1.3, 0.6 (7) and 3.2 ppm (8). The HRMS spectra of 6–8 were also consistent with the dinuclear nature of these complexes due to signals at $m/z = 382.1971$ (calcd. 382.1984, $[M+H]^+$), 453.2155 (calcd. 453.2175, $[M-H]^+$) and 444.2126 (calcd. 444.2140, $[M+H]^+$), respectively.

2.1. Solid-state structures of 1–5 and 8

The solid-state structure for compounds 1–5 and 8 were determined by single crystal X-ray diffraction method and their structures are shown in Figs. 3–8. Details of the crystallographic data for these compounds are provided in ESI (see Tables S1 and S2).

Pyridinophane 1 crystallized in the orthorhombic system with *Pbca* space group. The single crystal X-ray data for 1 showed its anti-conformer with respect to mutual orientation of two pyridine



Scheme 3. Syntheses of triazine-aluminum dinuclear complexes, [2,4-(Me_3SiN)$_2$–6–(R)–C_3N_3]($AlMe_2$)$_2$ (R = Me (6), $NHSiMe_3$ (7) and Ph (8)), the expected triazinophanes were not formed.

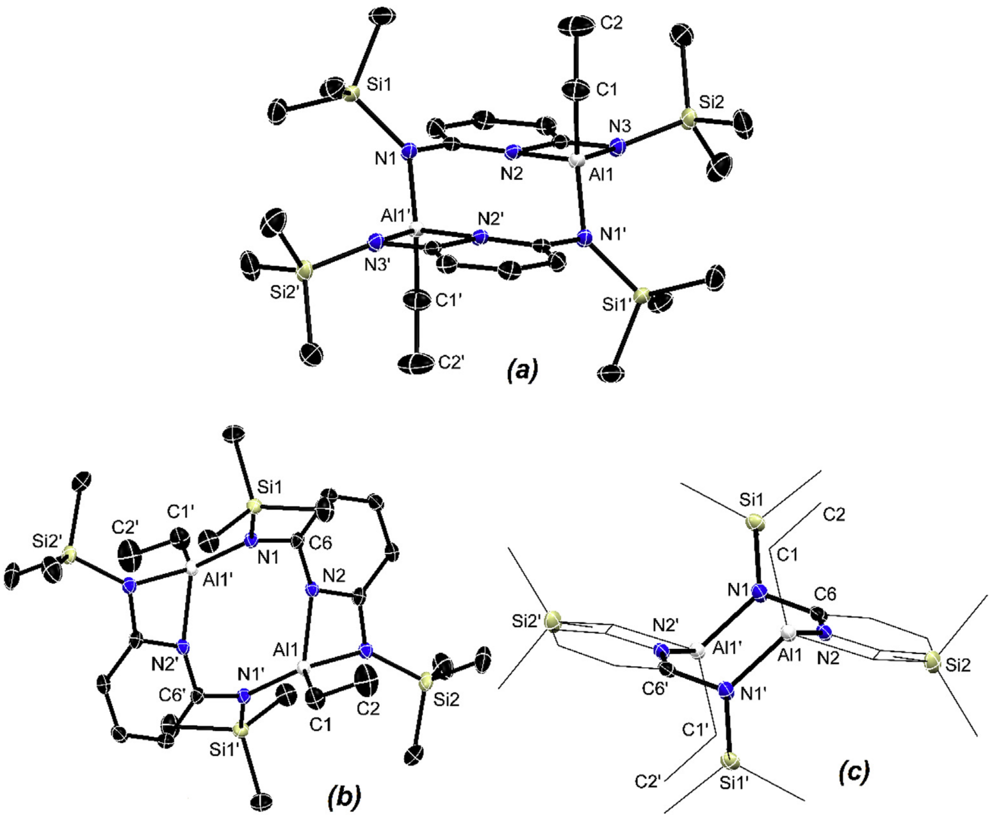


Fig. 3. Solid-state structure of tetraazadialumino[3.3](2,6)pyridinophane, $[\{2,6-(Me_3SiN)_2C_5H_3N\}AlEt]_2$ (1); (a) side view showing parallel orientation of pyridine rings & trans Al-ethyl groups and showing Npy … Al interaction; (b) top view of central 8 membered $[N_4Al_2C_2]$ ring; (c) the chair-chair conformation of the central $[N_4Al_2C_2]$ ring and anti arrangement of pyridine rings. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: N2–C6 1.354(2), N1–C6 1.394(2), Al1–N1′ 1.8504(14), Al1–N2 1.9560(14), Al1–N3 1.8943(14), Al1–C1 1.9522(19), C1–C2 1.495(3); N1′–Al1–C1 113.85(7), N2–Al1–C1 112.62(8), N3–Al1–C1 117.20(7), N1′–Al1–N2 116.75(6), N1′–Al1–N3 118.66(6), N2–Al1–N3 70.94(6).

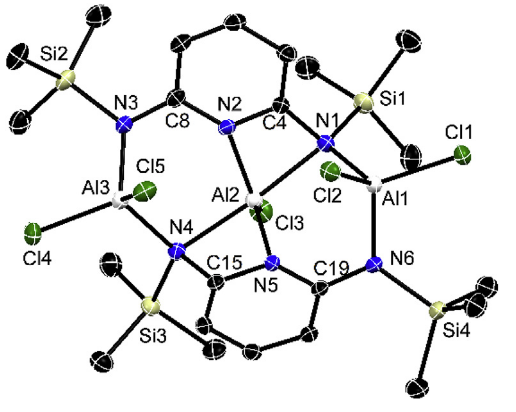


Fig. 4. Single crystal X-ray structure of pyridinophane based bowl shaped molecule, $[2,6-(Me_3SiN)_2C_5H_3N(AlCl_2)]_2[AlCl]$ (2). Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Al1–Cl1 2.1205(9), Al1–Cl2 2.1482(9), Al1–N1 1.933(2), Al1–N6 1.859(2), Al2–N1 2.142(2), Al2–N2 1.913(2), Al2–N4 2.173(2), Al2–N5 1.906(2), Al2–Cl3 2.1171(9), Cl4–Al3 2.1391(10), Cl5–Al3 2.1495(9), Al3–N3 1.855(2), Al3–N4 1.925(2), N1–C4 1.439(3), N2–C4 1.364(3), N2–C8 1.365(3), N3–C8 1.380(3), N4–C15 1.445(3), N5–C15 1.369(3), N5–C19 1.370(3), N6–C19 1.371(3); N1–Al1–N6 110.32(9), N4–Al3–N3 111.16(10), N1–Al2–N2 68.09(8), N5–Al2–N4 67.43(8), N1–Al2–N5 97.43(8), N2–Al2–N4 96.38(8), N1–Al2–N4 150.70(8), N2–Al2–N5 118.58(9), Cl2–Al1–Cl1 111.98(4), Cl5–Al3–Cl4 108.53(4), N5–Al2–Cl3 121.02(7), N1–Al2–Cl3 105.19(7), N2–Al2–Cl3 120.37(7), N4–Al2–Cl3 104.10(6).

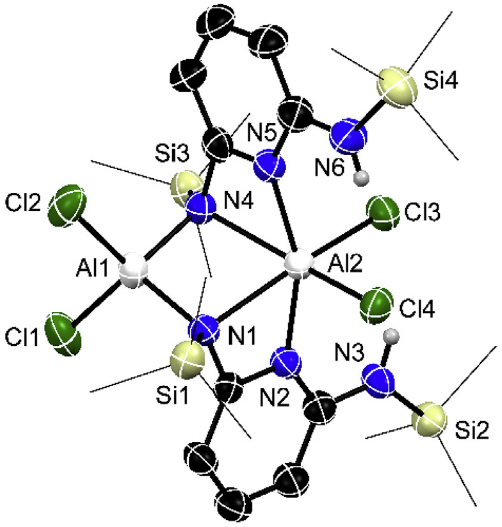


Fig. 5. Single crystal X-ray structure of $[\{2-(Me_3SiN)-6-(Me_3SiNH)C_5H_3N\}AlCl_2]_2$ (3). Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Al1–Cl1 2.1183(18), Al1–Cl2 2.1336(18), Al2–Cl3 2.2305(18), Al2–Cl4 2.2262(17), Al1–N1 1.885(4), Al1–N4 1.894(4), Al2–N1 2.223(4), Al2–N2 1.982(4), Al2–N4 2.281(4), Al2–N5 1.976(4); Cl1–Al1–Cl2 109.64(8), N1–Al1–Cl1 111.85(13), N4–Al1–Cl1 114.13(13), N1–Al1–Cl2 113.05(12), N4–Al1–Cl2 110.53(13), Cl3–Al2–Cl4 98.16(7), N1–Al2–N2 65.69(14), N4–Al2–N5 64.32(14), N1–Al2–N4 78.00(13), N1–Al1–N4 97.23(16), N1–Al2–N5 97.76(14), N2–Al2–N4 96.00(14), N2–Al2–N5 157.39(16).

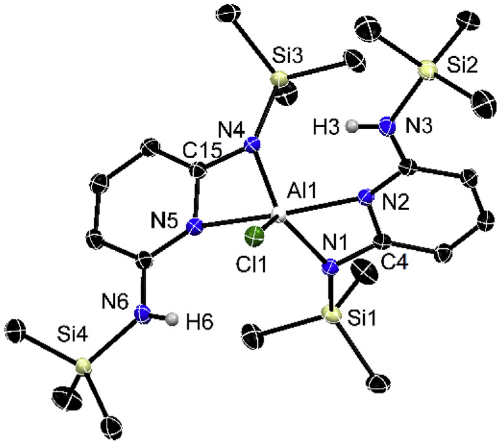


Fig. 6. Single crystal X-ray structure of $[2-(Me_3SiN)-6-(Me_3SiNH)C_5H_3N]_2AlCl$ (4). Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Al1−Cl1 2.1996(5), Al1−N1 1.9115(11), Al1−N2 2.0255(11), Al1−N4 1.9108(11), Al1−N5 2.0155(11), N4−C15 1.3826(16), N5−C15 1.3771(16), N2−C4 1.3751(16), N1−C4 1.3752(16); N1−Al1−Cl1 124.87(4), N2−Al1−Cl1 94.83(3), N1−Al1−N2 69.26(5), N1−Al1−N4 114.88(5), N1−Al1−N5 103.64(5), N2−Al1−N5 170.06(5), N4−Al1−N5 69.68(4), N2−C4−N1 109.02(10), N5−C15−N4 108.86(11).

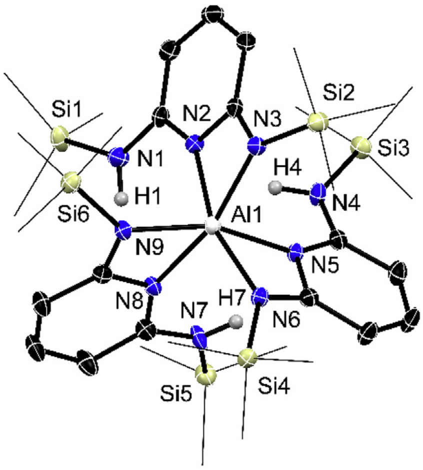


Fig. 7. Single crystal X-ray structure of $[2-(Me_3SiN)-6-(Me_3SiNH)C_5H_3N]_3Al$ (5). Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms (except N−H) have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Al1−N2 2.0563(18), Al1−N3 1.9734(18), Al1−N5 2.0544(19), Al1−N6 1.9602(18), Al1−N8 2.0636(18), Al1−N9 1.957(2); N2−Al1−N8 94.63(7), N5−Al1−N2 94.91(8), N5−Al1−N8 93.40(7), N3−Al1−N2 66.84(7), N9−Al1−N8 67.33(7), N6−Al1−N5 67.47(8), N3−Al1−N5 91.10(8), N6−Al1−N8 95.03(7), N9−Al1−N2 94.42(8), N6−Al1−N3 103.48(8), N9−Al1−N6 105.08(8), N9−Al1−N3 109.67(8), N3−Al1−N8 161.26(8).

rings. The anti-conformer of 1 is composed of a $[N_4Al_2C_2]$ eight membered ring that acquire chair-chair conformation similar to that for cyclooctane chair-chair conformation as well as that seen in tetraazadialumino[3.3](2,6)pyridinophane [9]. The ethyl groups on the N−Al(*Et*)−N bridges are mutually trans (Fig. 3). As a result of Npy … Al (donor-acceptor) interaction, aluminum atoms are tertacoordinated and two planar four member $[N_2AlC]$ rings are formed. The separation between transannular Al atoms (3.725 Å) and distance between the centroids of the pyridine rings in 1 (6.043 Å) compare well with the structurally related tetraazadialumino[3.3](2,6)pyridinophane (3.732 and 6.060 Å) (D Fig. 1) [9].

Compound 2 crystallized in the monoclinic system with $P2_1/c$ space group. The solid state structure of 2 confirmed its cyclic nature and showed a bowl shaped molecule containing three Al centres where two $(bapAlCl_2)$ units are connected to each other *via* a diagonal −Al(Cl)− bridge forming an overall pyridinophane based bowl shaped structure (Fig. 4). Among three Al centres, two are tetracoordinated and form part of the main cyclic backbone whereas the third Al centre, located at the centre of the molecule, is pentacoordinated. Each of the tetracoordinated Al centres have two Cl atoms; one Cl atom is oriented towards the cavity whereas the other Cl is projecting away from the cavity. The N−Al distances around tetracoordinated Al centres in 2 (N1−Al1 and N6−Al1) are 1.933(2) and 1.859(2) Å and can be attributed to coordinate N→Al and covalent N−Al bonds respectively, whereas the pentacoordinated Al2 centre showed Al−N distances in the range 1.906(2)-2.173(2) Å.

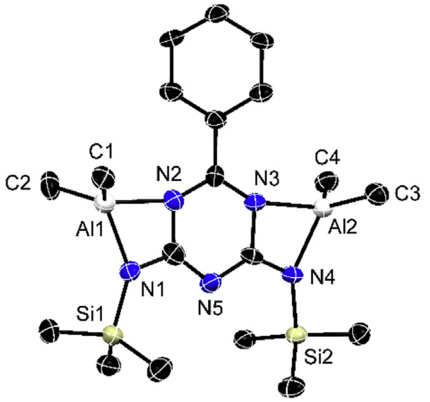


Fig. 8. Single crystal X-ray structure of $[2,4-((CH_3)_3SiN)2-6-(Ph)-C_3N_3](AlMe_2)_2$ (8). Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Al1−N1 1.918(3), Al1−N2 1.991(2), Al2−N3 1.977(2), Al2−N4 1.922(2), Al1−C1 1.946(3), Al1−C2 1.947(3), Al2−C3 1.951(3), Al2−C4 1.955(3), N1−Si1 1.754(2), N4−Si2 1.745(2); N1−Al1−N2 69.03(9), N3−Al2−N4 69.78(9), C1−Al1−C2 121.82(15), C3−Al2−C4 121.54(13), C1−Al1−N1 111.68(13), C2−Al1−N1 117.00(14), C1−Al1−N2 111.63(12), C2−Al1−N2 114.04(12), C3−Al2−N3 115.67(11), C4−Al2−N3 109.51(12), C4−Al2−N4 115.24(12).

Compound 3 crystallized in the monoclinic system with $P2_1/n$ space group. The solid state structure of $[\{2-(Me_3SiN)-6-(Me_3SiNH)C_5H_3N\}AlCl_2]_2$ (3) (Fig. 5) contain two aluminum centres, one of the aluminum centre Al1 is bonded to two chlorides and two amido groups (Al1−N1 1.883(3) and Al1−N4 1.895(3) Å) in a distorted tetrahedral geometry whereas the second aluminum centre Al2 is hexacoordinated forming a distorted octahedral geometry and is bonded to two chlorides, two pyridine N and two amido N. The core structure of 3 is based on a four membered $[Al_2N_2]$ ring with an Al⋯Al separation of 2.996(3) Å.

Compound 4 crystallized in the monoclinic system with $P2_1/c$ space group. The solid state structure of $[2-(Me_3SiN)-6-(Me_3SiNH)C_5H_3N]_2AlCl$ (4) confirmed its composition predicted based on observation from NMR and HRMS measurements. The structure of 4 is composed of a pentacoordinated mononuclear Al centre in a distorted square pyramidal geometry where the pyridine N and an amido sites of each bap ligands bind to it to form two $[N_2CAl]$ rings while two $NHSiMe_3$ groups do not coordinate to aluminum (Fig. 6).

Compound 5 crystallized in the triclinic system with $P\overline{1}$ space group. The composition of 5 was confirmed as the mononuclear homoleptic tris-bap complex, $[2-(Me_3SiN)-6-(Me_3SiNH)C_5H_3N]_3Al$ in line with the observations from HRMS measurements. The Al centre in 5 is hexacoordinated by binding to one amido and one pyridine nitrogen from each of the three bap units (Fig. 7).

Repeated efforts to grow single crystals of complexes 6 and 7 were unsuccessful. Compound 8 crystallized in the triclinic system with $P\bar{1}$ space group. The single crystal X-ray structure of complex 8 showed the expected binuclear [2,4-$(Me_3SiN)_2$–6–(Ph)–C_3N_3]$(AlMe_2)_2$ complex where the Al centres adopt distorted tetrahedral geometry and are connected with two methyl groups and two nitrogen atoms of triazine ring (Fig. 8). This structure consists of two four membered [N_2CAl] chelate rings where the triazine ring nitrogen and amido sites of bat bind to the aluminum centres. In complex 8, the observed Al—C bond lengths are uniform (1.946(3) and 1.947(3) Å).

3. Conclusions

In conclusion, we have synthesized and characterized aluminum containing pyridinophane, a bowl shaped pyridinophane and a few Al complexes. The reactions between $EtAlCl_2$ and dilithium bis(trimethylsilyl)—N,N′—2,6—diamidopyridine resulted in the formation of small sized aluminum containing [3.3](2,6)pyridinophane. The use of bis(trimethylsilyl)—N,N′—2,6—diaminopyridine (bap) with $EtAlCl_2$ gave mono- and dinuclear aluminum complexes. The reaction of dilithium bis(trimethylsilyl)—N,N′—2,6—diamidopyridine with $AlCl_3$ gave a bowl shaped pyridinophane. Efforts to extend the approach to synthesize similar structures with triazine based systems bis(-trimethylsilyl)-N,N′-2,4-diamino–6–(R)–triazine (R = Me, $NH(SiMe_3)$, Ph) with $AlMe_3$ afforded the dinuclear complexes. The results, taken together, demonstrate that synthesis of macrocycles containing main group elements are conceivable if the reaction strategy and conditions are carefully selected to join the components that constitute the macrocycles. Currently, we are engaged in extending our efforts to synthesize new examples of [n,n]pyridinophanes (where $n > 3$) with bigger cavity sizes by using 2,6—dialkylaminopyridines instead of 2,6—diaminopyridine used thus far to obtain [3.3]pyridinophanes.

4. Experimental procedures

4.1. General considerations

All manipulations were performed under nitrogen/argon atmosphere using Schlenk line or glove box techniques. All glassware were dried at 150 °C in an oven for at least 12 h and assembled hot and cooled in vacuo prior to use. Solvents were purified by MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Sigma-Aldrich and used without further purification. The starting materials bis(trimethylsilyl)-N,N′-2,6-diaminopyridine (bap), dilithium bis(trimethylsilyl)-N,N′-2,6-diamidopyridine and bis(trimethylsilyl)-N,N′-2,4-diamino–6–(R)–triazine (R = Me, $NHSiMe_3$ and Ph) were prepared using reported procedures [11–13]. The ^1H, ^{13}C and ^{29}Si NMR spectra were recorded with a Bruker 400 MHz spectrometer with TMS as external references. Chemical shifts were reported in ppm. High resolution mass spectra were recorded on a Waters SYNAPT G2-S instrument. IR spectra of the complexes were recorded in the range 4000—400 cm^{-1} using a PerkinElmer Lambda 35-spectrophotometer. The absorptions of the characteristic functional groups were only assigned and other absorptions (moderate to very strong) were only listed. Melting points were obtained in sealed capillaries on a Büchi B—540 melting point instrument.

Synthesis of [{2,6—$(Me_3SiN)_2C_5H_3N$}AlEt]$_2$ (1): To a solution of dilithium bis(trimethylsilyl)-N,N′-2,6-diamidopyridine (3.8 mmol, 1.0 g) in hexane (30 mL), $EtAlCl_2$ (3.8 mmol, 2.1 mL, 25w% in toluene) was added slowly at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for further 12 h. The mixture was then filtered to remove LiCl and the volume of the filtrate was reduced to 10 mL and stored at −20 °C to afford transparent crystals of 1. Yield: 0.40 g (34%). Mp. 196—199 °C. IR (nujol) ν: 2954, 2924, 2855, 1584, 1549, 1456, 1378, 1341, 1262, 1249, 1162, 1103, 1074, 842, 734, 686, 656, 616, 518, 496 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.34$ (t, 2H, *p*–ArH, $^3J_{H\text{-}H} = 8$ Hz), 6.0 (broad, 4H, *m*–ArH), 0.78 (t, 6H, $-CH_2\text{-}CH_3$, $^3J_{H\text{-}H} = 8$ Hz), 0.22 (s, 18H, $SiMe_3$), 0.11 (s, 18H, $SiMe_3$), −0.21 (q, 4H, $\text{-}CH_2\text{-}CH_3$, $^3J_{H\text{-}H} = 8$ Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 166.2$ (Py-C2), 143.4 (Py-C4), 129.0 (Py-C6), 108.2, 101.4 (Py-C3, Py-C5) [14], 8.6 ($-CH_2-CH_3$), 2.3 ($SiMe_3$), 0.5 ($SiMe_3$), −2.1 ($\text{-}CH_2\text{-}CH_3$) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$): $\delta = 3.2$ ($SiMe_3$) ppm. HRMS (AP^+): *m/z* calcd for $C_{26}H_{59}Al_2N_6Si_4$: (621.3509) $[M+H]^+$; found: (621.3503).

Synthesis of [2,6—$(Me_3SiN)_2C_5H_3N(AlCl_2)$]$_2$[AlCl] (2): A solution of dilithium bis(trimethylsilyl)-N,N′-2,6-diamidopyridine (3.8 mmol, 1.0 g) in toluene (30 mL) was added slowly to a solution of $AlCl_3$ (5.7 mmol, 0.76 g) in toluene (30 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for further 12 h. The mixture was then filtered to remove LiCl and the volume of the filtrate was reduced to 10 mL and stored at −20 °C to afford transparent crystals of 2. Yield: 0.35 g (24%). Mp. 276—280 °C (decomposition). IR (nujol) ν: 2956, 2924, 2855, 1646, 1607, 1547, 1457, 1378, 1259, 1173, 1088, 1044, 1028, 846, 801 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.64$ (t, 2H, *p*–ArH, $^3J_{H\text{-}H} = 8$ Hz), 6.62 (d, 4H, *m*–ArH), 0.43 (s, 36H, $SiMe_3$), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 160.9$ (Py-C2, Py-C6), 144.4 (Py-C4), 113.0 (Py-C3, Py-C5) [14], 2.4 ($SiMe_3$) ppm. HRMS (AP^+): *m/z* calcd for $C_{22}H_{42}Al_3Cl_5N_6Si_4$: (758.0437) $[M]^+$; found: (758.0411).

Synthesis of [{2—(Me_3SiN)—6—$(Me_3SiNH)C_5H_3N$}$AlCl_2$]$_2$ (3): $EtAlCl_2$ (3.9 mmol, 2.2 mL, 25w% in toluene) was added slowly to a stirred solution of bis(trimethylsilyl)-N,N′-2,6-diaminopyridine (3.9 mmol, 1.0 g) in toluene (40 mL) at 0 °C. The reaction mixture was allowed to come to room temperature and stirred for 12 h. All the volatiles were removed under vacuum to give a greenish solid that afforded transparent crystals of 3 on crystallization from DCM at −30 °C. Yield: 0.7 g (51%). Mp: 199—203 °C. IR (nujol) ν: 3269 (N—H), 2953, 2923, 2853, 1616, 1565, 1490, 1460, 1378, 1256, 1239, 1173, 1042, 846, 779, 643, 629, 522, 479, 436 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): $\delta = 8.00$ (s, 2H, —NH), 6.98 (t, 2H, *p*-ArH, $^3J_{H\text{-}H} = 8$ Hz), 6.31 (d, 2H, *m*-ArH, $^3J_{H\text{-}H} = 8$ Hz), 6.01 (d, 2H, *m*-ArH, $^3J_{H\text{-}H} = 8$ Hz), 0.51 (s, 18H, $SiMe_3$), 0.07 (s, 18H, $SiMe_3$) ppm. ^{13}C NMR (100 MHz, C_6D_6): $\delta = 158.3$, 158.1 (Py-C2, Py-C6), 143.0 (Py-C4), 108.7 (Py-C3), 106.5 (Py-C5) [15], −0.9 ($SiMe_3$) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6): $\delta = 15.7$, 6.4 ($SiMe_3$) ppm. HRMS (AP^+): *m/z* calcd for $C_{22}H_{44}Al_2Cl_4N_6Si_4$: (698.1089) $[M]^+$; found: (698.1058).

Synthesis of [2—(Me_3SiN)—6—$(Me_3SiNH)C_5H_3N$]$_2$AlCl (4): $EtAlCl_2$ (1.9 mmol, 1.1 mL, 25w% in toluene) was added slowly to a stirred solution of bis(trimethylsilyl)-N,N′-2,6-diaminopyridine (3.9 mmol, 1.0 g) in toluene (40 mL) at 0 °C. The reaction mixture was allowed to come to room temperature followed by 15 h of reflux. All the volatiles were removed under vacuum to give a white solid that afforded transparent crystals of 4 on crystallizing from hexane at −30 °C. Yield: 0.65 g (58%). Mp: 146—150 °C. IR (nujol) ν: 3372 (N—H), 3248 (N—H), 2925, 2855, 1599, 1572, 1459, 1377, 1336, 1296, 1256, 1160, 1097, 1075, 1047, 846, 781, 723, 693, 639, 599, 517, 463 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.24$ (t, 2H, *p*-ArH, $^3J_{H\text{-}H} = 8$ Hz), 5.85 (d, 2H, *m*-ArH, $^3J_{H\text{-}H} = 8$ Hz), 5.71 (d, 2H, *m*-ArH, $^3J_{H\text{-}H} = 8$ Hz), 4.40 (s, 2H, NH), 0.28 (s, 18H, $SiMe_3$), 0.04 (s, 18H, $SiMe_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165$ (Py-C2), 154.9 (Py-C6), 142.8 (Py-C4), 98.2 (Py-C3), 96.6 (Py-C5) [15], 0.7 ($SiMe_3$), −0.2 ($SiMe_3$) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$): $\delta = 5.3$, −0.4 ($SiMe_3$) ppm. HRMS (AP^+): *m/z* calcd for $C_{22}H_{44}AlN_6Si_4$: (566.2208) $[M]^+$; found: (566.2230).

Synthesis of [2—(Me_3SiN)—6—$(Me_3SiNH)C_5H_3N$]$_3$Al (5): To a solution of bis(trimethylsilyl)-N,N′-2,6-diaminopyridine (3.9 mmol, 1.0 g) and excess NEt_3 (1.5 mL) in toluene (30 mL), $EtAlCl_2$ (1.3 mmol, 0.7 mL, 25w% in toluene) was added slowly at 0 °C. The reaction mixture was allowed to warm to room temperature followed by further 12 h of reflux. All the volatiles were removed under vacuum and transparent crystals of 5 were obtained from pentane at −20 °C. Yield: 0.5 g (48%). Mp. 134−137 °C. IR (nujol) ν: 3356 (N−H), 2954, 2924, 2854, 1599, 1564, 1464, 1377, 1326, 1296, 1258, 1246, 1159, 1093, 1071, 884, 722, 632, 594, 490, 426 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.13$ (t, 3H, *p*–ArH, $^3J_{H\text{-}H} = 8$ Hz), 5.83 (d, 3H, *m*–ArH, $^3J_{H\text{-}H} = 8$ Hz), 5.49 (d, 3H, *m*–ArH, $^3J_{H\text{-}H} = 8$ Hz), 0.05 (s, 27H, $SiMe_3$), 0.00 (s, 27H, $SiMe_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165.6$ (Py-C2), 155.2 (Py-C6), 141.0 (Py-C4), 99.00 (Py-C3), 93.4(Py-C5) [15], 0.9 (Si*Me*$_3$), −0.3 (Si*Me*$_3$) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$): $\delta = 3.2$, −3.2 (*Si*Me$_3$) ppm. HRMS (AP^+): *m/z* calcd for $C_{33}H_{66}AlN_9Si_6$: (783.3872) $[M]^+$; found: (783.3846).

Synthesis of [2,4−(Me_3SiN)$_2$–6–(Me)−C_3N_3]($AlMe_2$)$_2$ (6): $AlMe_3$ (7.4 mmol, 3.7 mL, 2.0 M in toluene) was added slowly to a stirred solution of bis(trimethylsilyl)-N,N′-2,4-diamino–6–(Me)–triazine (3.7 mmol, 1 g) in toluene (10 mL) at 0 °C. The reaction mixture was allowed to come to room temperature and stirred for 3 h. On evaporating all volatiles 6 was obtained as a white solid in sufficient purity. Yield: 1.28 g (91%). Mp: 161−164 °C. IR (nujol) ν: 2956, 2921, 2855, 1603, 1494, 1459, 1378, 1355, 1251, 1193, 1150, 893, 876, 845, 756, 717, 690, 593, 427 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.07$ (s, 3H, Ar-Me), 0.22 (s, 18H, $SiMe_3$), −0.69 (s, 12H, AlMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 166.7$ & 165.7 (triazine ring C) [16], 20.9 (triazine-6-Me), −0.1 (Si*Me*$_3$), −10.7 (Al*Me*) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$): $\delta = 3.1$ (*Si*Me$_3$) ppm. HRMS (AP^+): *m/z* calcd for $C_{14}H_{34}Al_2N_5Si_2$: (382.1984) $[M+H]^+$; found: (382.1951).

Synthesis of [2,4−(Me_3SiN)$_2$–6–(Me_3SiNH)−C_3N_3]($AlMe_2$)$_2$ (7): $AlMe_3$ (5.8 mmol, 2.9 mL, 2.0 M in toluene) was added slowly to a stirred solution of bis(trimethylsilyl)-N,N′-2,4-diamino–6–(Me_3SiNH)–triazine (2.9 mmol, 1 g) in toluene (10 mL) at 0 °C. The reaction mixture was allowed to come to room temperature and stirred for 3 h. On evaporating all volatiles, a sticky material was obtained that gave a white powder after washing with hexane in sufficient purity. Yield: 1.25 g (94%). Mp: 185−190 °C. IR (nujol) ν: 2956, 2926, 2856, 1590, 1551, 1466, 1389, 1155, 1097, 1024, 843, 804, 723, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.99$ (s, 1H, NH), 0.34 (s, 9H, $SiMe_3$), 0.21 & 0.20 (overlapped s, 18H, $SiMe_3$), −0.63 (s, 6H, AlMe), −0.68 (s, 6H, AlMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 168.0$ (triazine-C6), 163.1, 161.8 (triazine-C2 or triazine-C4) [13], 0.8 (Si*Me*$_3$), 0.4 (Si*Me*$_3$), 0.1 (Si*Me*$_3$), −9.0 (Al*Me*), −10.1 (Al*Me*) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$): $\delta = 8.6$, 1.3, 0.6 (*Si*Me$_3$) ppm. HRMS (AP^+): *m/z* calcd for $C_{16}H_{39}Al_2N_6Si_3$: (453.2175) $[M-H]^+$; found: (453.2155).

Synthesis of [2,4−(Me_3SiN)$_2$–6–(Ph)–C_3N_3]($AlMe_2$)$_2$ (8): $AlMe_3$ (6.0 mmol, 3.0 mL, 2.0 M in toluene) was added slowly to a stirred solution of bis(trimethylsilyl)-N,N′-2,4-diamino–6–(Ph)–triazine (3.0 mmol, 1 g) in toluene (10 mL) at 0 °C. The reaction mixture was allowed to come to room temperature and stirred for 3 h. On evaporating all volatiles an orange solid was obtained which on crystallization with pentane at −30 °C afforded colorless crystals of 8. Yield: 1.22 g (92%). Mp. 212−215 °C. IR (nujol) ν: 2926, 2853, 1601, 1567, 1540, 1459, 1374, 1251, 1220, 1193, 1047, 1024, 954, 847, 781, 693, 592, 431 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.75$, (d, 2H, ArH, $^3J_{H\text{-}H} = 8$ Hz), 7.51−7.56 (m, 3H, ArH), 0.27 (s, 18H, $SiMe_3$), −0.61 (s, 12H, AlMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 167.0$ (triazine-C6), 163.3 (triazine-C2, triazine-C4), 133.6 (Ph-*Cipso*), 131.1 (Ph-*Cpara*), 129.7, 129.0 (Ph-*Cmeta*), 128.1, 127.0 (Ph-*Cortho*) [17], −0.1 (Si*Me*$_3$), −10.2 (Al*Me*) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$): $\delta = 3.2$ (*Si*Me$_3$) ppm. HRMS (AP^+): *m/z* calcd for $C_{19}H_{36}Al_2N_5Si_2$: (444.2140) $[M+H]^+$; found: (444.2105).

Acknowledgements

This research was supported by grants from the Department of Science and Technology (DST) New Delhi [DST/SERB (EMR/2016/003911)]. C.N. acknowledges IISER Mohali for a fellowship. We are grateful to IISER Mohali for central NMR, HRMS and SCXRD facility and the Department of Chemical Sciences at IISER Mohali for SCXRD facility.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.120943.

References

[1] a) G.P. Shkil, R.S. Sagitnllin, Chem. Heterocycl. Comp. 34 (1998) 507−528;
b) P.G. Ghasemabadi, T. Yao, G.J. Bodwell, Chem. Soc. Rev. 44 (2015) 6494−6518;
c) Z. Hassan, E. Spuling, D.M. Knoll, J. Lahann, S. Bräse, Chem. Soc. Rev. 47 (2018) 6947−6963.

[2] a) A.R. Sabio, C.S. Bonnet, M.M. Iglesias, D.E. Gómez, É. Tóth, A. de Blas, T.R. Blas, C.P. Iglesias, Inorg. Chem. 51 (2012) 10893−10903;
b) F. Tang, N.P. Rath, L.M. Mirica, Chem. Commun. 51 (2015) 3113−3116;
c) G. Castro, R. Bastida, A. Macías, P.P. Lourido, C.P. Iglesias, L. Valencia, Inorg. Chem. 54 (2015) 1671−1683;
d) H. Kuzuhara, N. Watanabe, M. Ando, J. Chem. Soc., Chem. Commun. (1987) 95−96;
e) K. Fuchigami, N.P. Rath, L.M. Mirica, Inorg. Chem. 56 (2017) 9404−9408;
f) H. Kuzuhara, M. Iwata, S. Emoto, J. Am. Chem. Soc. 99 (1977) 4173−4175.

[3] a) H. Kawai, T. Suzuki, M. Ohkita, T. Tsuji, Angew. Chem. Int. Ed. 37 (1998) 817−819;
b) W. Jenny, H. Holzrichter, Chimia 21 (1967) 509−510;
c) H.J.J.B. Martel, S. McMahon, M. Rasmussen, Aust. J. Chem. 32 (1979) 1241−1250;
d) N.B. Pahor, M. Calligaris, L. Randaccio, J. Chem. Soc. Perkin Trans. II (1978) 38−42;
e) T. Kawashima, S. Kurioka, Y. Tohda, M. Argia, Y. Mori, S. Misumi, Chem. Lett. 14 (1985) 1289−1292;
f) D.J. Cram, H. Steinbrg, J. Am. Chem. Soc. 73 (1951) 5691−5704.

[4] W. Uhl, A. Hepp, M. Matar, A. Vinogradov, Eur. J. Inorg. Chem. (2007) 4133−4137.

[5] W. Uhl, M. Claesener, A. Hepp, B. Jasper, A. Vinogradov, L. van Wüllen, T.K.J. Köster, Dalton Trans. (2009) 10550−10562.

[6] K. Maheswari, N.D. Reddy, Organometallics 31 (2012) 197−206.

[7] Aluminum bridged macrocyclic systems: a) S.L. Aeilts, M.P. Coles, D.C. Swenson, R.F. Jordan, Organometallics 17 (1998) 3265−3270;
b) Y.A. Wasslen, A. Kurek, P.A. Johnson, T.C. Pigeon, W.H. Monillas, G.P.A. Yap, S.T. Barry, Dalton Trans. 39 (2010) 9046−9054.

[8] P. Shukla, J.C. Gordon, A.H. Cowley, J.N. Jones, Inorg. Chim. Acta 358 (2005) 4407−4411.

[9] D. Bawari, C. Negi, K. Jaiswal, B. Prashanth, A.R. Choudhury, S. Singh, Chem. Commun. 54 (2018) 8857−8860.

[10] D. Bawari, C. Negi, V.K. Porwal, S. Ravi, K.R. Shamasundar, S. Singh, Dalton Trans. 48 (2019) 7442−7450.

[11] L. Beer, J.F. Britten, J.L. Brusso, A.W. Cordes, R.C. Haddon, M.E. Itkis, D.S. MacGregor, R.T. Oakley, R.W. Reed, C.M. Robertson, J. Am. Chem. Soc. 125 (2003) 14394−14403.

[12] G.G. Skvortsov, G.K. Fukin, S.Y. Ketkov, A.V. Cherkasov, K.A. Lyssenko, A.A. Trifonov, Eur. J. Inorg. Chem. (2013) 4173−4183.

[13] B. Parker, D.Y. Son, Inorg. Chem. Commun. 5 (2002) 516−518.

[14] a) N. Farfán, H. Höpfl, V. Barba, Ma. E. Ochoa, R. Santillan, E. Gómez, A. Gutiérrez, J. Organomet. Chem. 581 (1999) 70−81;
b) B. Wrackmeyer, G. Kehr, H. Zhou, S. Ali, Magn. Reson. Chem. 34 (1996) 921−928.

[15] a) A.K. El-Qisairi, H.A. Qaseer, M.H. Zaghal, S. Magaireh, R. Saymeh, Y.A. Yousef, Jordan J. Chem. 2 (2007) 255−264;
b) C. Schröder-Holzhacker, B. Stöger, E. Pittenauer, G. Allmaier, L.F. Veiros, K. Kirchner, Monatshefte Chem. 147 (2016) 1539−1545.

[16] a) N.M. Aghatabay, Y. Mahmiani, H. Cevik, F. Gucin, B. Dulger, Struct. Chem. 19 (2008) 833−842;
b) M. Mastalir, B. Stöger, E. Pittenauer, G. Allmaier, K. Kirchner, Org. Lett. 18 (2016) 3186−3189.

[17] N.M. Aghatabay, A. Bas, A. Kircali, G. Sen, M.B. Yazicioglu, F. Gucin, B. Dulger, Eur. J. Med. Chem. 44 (2009) 4681−4689.