Deprotonation and reductive addition reactions of hypervalent aluminium dihydride compounds containing substituted pyrrolyl ligands with phenols, ketones, and aldehydes†

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Received 23rd April 2009, Accepted 30th July 2009
First published as an Advance Article on the web 20th August 2009
DOI: 10.1039/b908164j

The reactivities of $[C_4H_2N(CH_2NMe_2)_2]AlH_2$ (**1**) with primary and secondary amines, phenols, ketones, and phenyl isothiocyanate were examined. Reactions of **1** with one or two equivalents of 2,6-dichloroaniline in methylene chloride generated $[C_4H_2N(CH_2NMe_2)_2]AlH(NHC_6H_3\text{-}2,6\text{-}Cl_2)$ (**2**) and $[C_4H_2N(CH_2NMe_2)_2]Al(NHC_6H_3\text{-}2,6\text{-}Cl_2)_2$ (**3**), respectively, following hydrogen elimination. Similarly, the reactions of **1** with one or two equivalents of carbazole afforded $[C_4H_2N(CH_2NMe_2)_2]AlH(NC_{12}H_8)$ (**4**) or $[C_4H_2N(CH_2NMe_2)_2]Al(NC_{12}H_8)_2$ (**5**) by deprotonating the acidic N–H of carbazole. Reacting **1** with one equivalent of 2,6-diisopropylphenol in diethyl ether formed an aluminium phenoxo compound $[C_4H_2N(CH_2NMe_2)_2]AlH(OC_6H_3\text{-}2,6\text{-}^iPr_2)$ (**6**), by deprotonation of phenol as well with the elimination of one equivalent hydrogen. Further reaction of **6** with one equivalent of 2,4,6-trimethylacetophenone in methylene chloride generated $[C_4H_2N(CH_2NMe_2)_2]Al(OC_6H_3\text{-}2,6\text{-}^iPr_2)[OC(=CH_2)(C_6H_2\text{-}2,4,6\text{-}Me_3)]$ (**7**) by deprotonating the methyl proton of the acetophenone. Similar deprotonation occurred when **1** reacted with two equivalents of 2,4,6-trimethylacetophenone in methylene chloride to generate $[C_4H_2N(CH_2NMe_2)_2]Al[OC(=CH_2)(C_6H_2\text{-}2,4,6\text{-}Me_3)]_2$ (**8**). Compounds $[C_4H_2N(CH_2NMe_2)_2]Al(OCHPh_2)_2$ (**9**), and $[C_4H_2N(CH_2NMe_2)_2]Al(SCHNPh)_2$ (**10**) could also be obtained by reacting **1** with two equivalents of benzophenone and phenyl isothiocyanate, respectively through hydroalumination. The ^1H NMR spectra of **10** showed broad signals for the CH_2N and NMe_2 groups, which represent dynamical fluctuations of the molecules in solution state. The estimated energy barrier ($\Delta G_c^{\ddagger}$) from the coalescence temperature for the fluctuation was estimated at 17.1 Kcal mol^{-1}. The solid-state structures of compounds **2**, **3**, **5**, **7**, **9**, and **10** have been determined.

Introduction

The reactivities of metal hydrides were widely studied and reviewed periodically.[1] For more than three decades transition-metal hydrides have held the limelight. This is understandable in view of the part played by M–H bonds in the organometallic chemistry of the transition metals, particularly in catalytic processes. Early transition metal hydride derivatives are thought to be responsible for a plethora of organic transformations, catalytic cycles and olefin polymerization intermediates, or deactivation products.[2] Among these metal hydrides, aluminium hydrides have been extensively used because of their versatility, high reactivity and inexpensiveness. Aluminium hydride compounds can undergo proton abstraction or nucleophilic reductive addition with organic molecules, as shown in Scheme 1. It shows that the hydride acts as a strong base and abstracts one proton from phenol[3] or amine[4] to yield an aluminium alkoxide or an amide compound. The reaction temperature, the stoichiometry of the reactants, and the steric demand of the substituents were found to play key roles in what degree of oligomerization was attained.[5] The reduction of carbonyl compounds by complex metal hydride reducing agents is one of the most important reactions of organic compounds. In this connection, the hydride can also act as a nucleophilic reagent attacking C=O,[6] an important significance of the high degree of π-facial diastereoselectivity. The hydride also takes part in initiating different hydroalumination reactions with CN,[7] NCE (where E = O, S),[8] and unsaturated alkenes and alkynes.[9] Power *et al.* have reported that the reaction of a bulky alkane $[Mes^*AlH_2]_2$ (Mes^* = 2,4,6-*t*-$Bu_3C_6H_2$) with nitriles RCN (R = Me, *t*-Bu, Mes) gives the *ortho*-metalated dimers, *cis*- and *trans*-$[AlC_6H_2\text{-}2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}CMe_2\text{-}CH_2\{\mu^2\text{-}N(H)CH_2R\}]_2$.[10] Different alumoxanes have also been previously reported,[11] mediated by controlled hydrolysis of aluminium alkyls or organoaluminium hydrides with water or reactive oxygen-containing species. Several hydroalumination reactions have been investigated before either involving trialkylaluminiums

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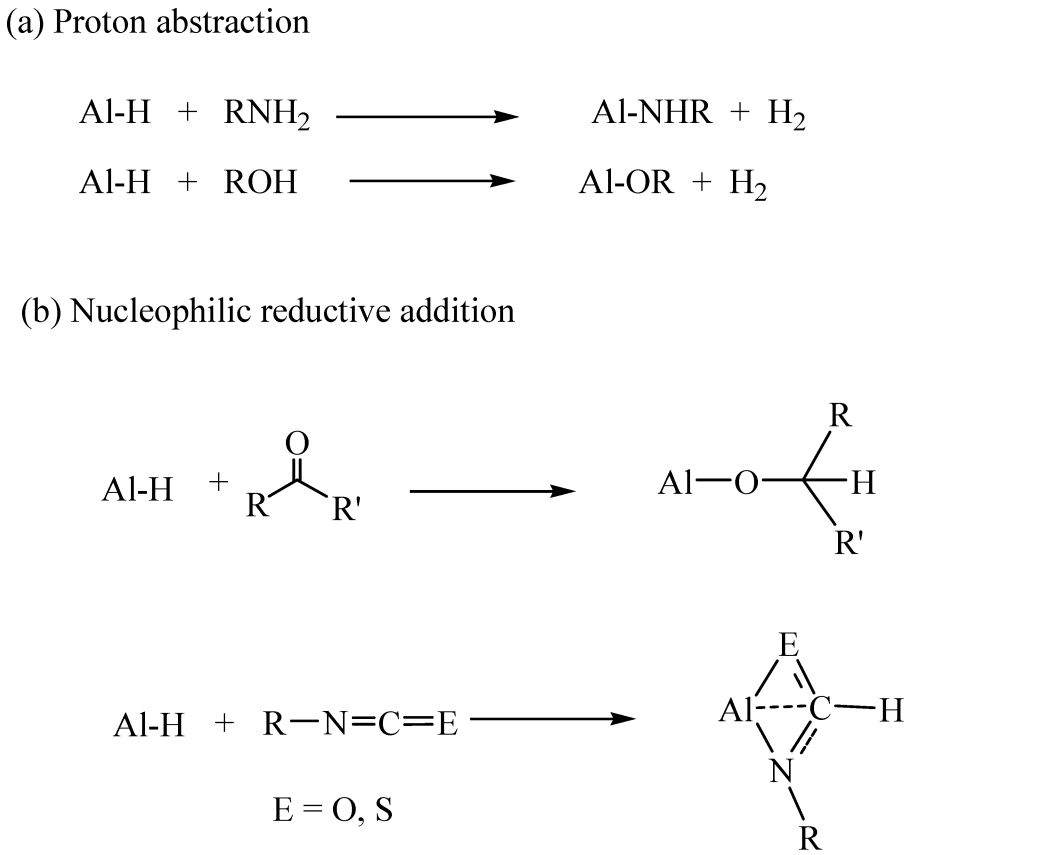
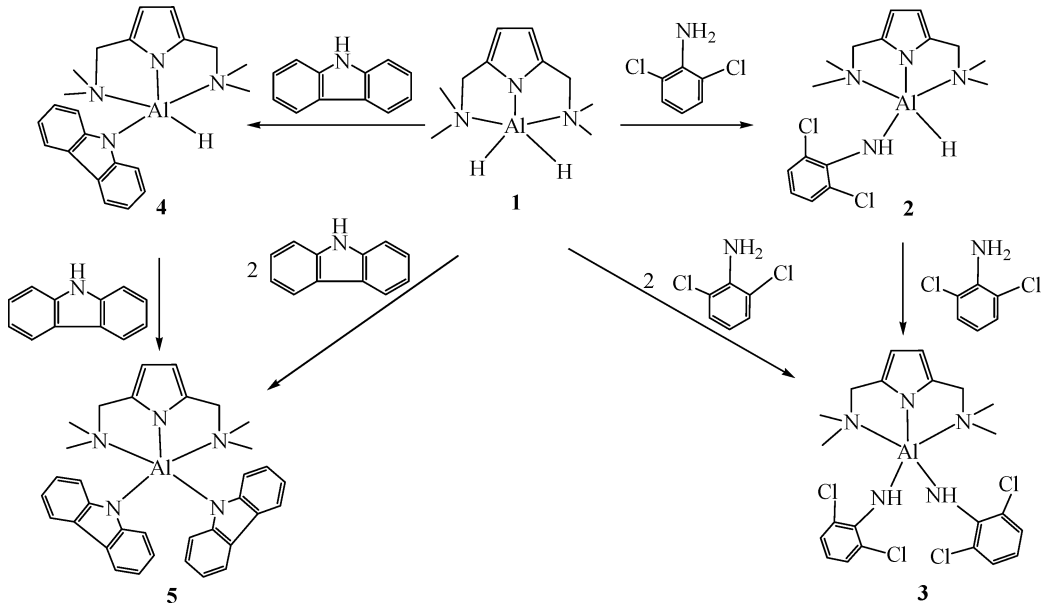
† CCDC reference numbers 721352 (**2**), 721534 (**3**), 721356 (**5**), 721355 (**7**), 721354 (**9**), and 721353 (**10**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b908164j



Scheme 1 (a) Proton abstraction (b) Nucleophilic reductive addition (c) Reactions of Al–H with organic molecules containing C=O groups.

or dialkylaluminium hydrides with dialkylaluminium acetylides[12] or using bis-alkynyl alcohols having an adjacent stereogenic center which provides access to stereo-defined *tert*-alcohols.[13] The reactivity of two sterically bulky amidines, ArNC(R)N(H)Ar [Ar = 2,6-diisopropylphenyl; R = H (HFiso); *t*Bu, (HPiso)] towards aluminium have examined before[14] and the structural motif generated by the prepared complexes are rationalized in terms of the steric bulk of the amidinate ligands and electronic properties of metal. Recently, Gladfelter *et al*, reported volatile aluminium dihydrides, $H_2Al[N(CH_2CH_2NMe_2)_2]$ and $H_2Al[N(CH_2CH_2NMe_2)_2]AlH_3$,[15] stabilized with a tridentate nitrogen ligand, $[N(CH_2CH_2NMe_2)_2]^-$, having stability for use in chemical vapor deposition and related applications. The relative basicity of hydride to the acidity of organic molecules determines the types of reactions. For example, the reactions of aluminium hydrides with ketones (Scheme 1c) proceed either *via* proton abstractions or *via* nucleophilic reductive addition depending on the relative acidity of the reactants and the availability of the ketone proton sources. We have been interested in hydroalumination reactions and have been pursuing this topic in our present article. Herein, the reactions of monomeric aluminium dihydride compounds containing substituted tridentate pyrrolyl ligands with primary and secondary amines, phenols, ketones and phenyl isothiocyanate have been discussed. Proton abstraction and reductive addition products were both observed while the aluminium dihydrides react with ketones. All the products were investigated in detail by multinuclear NMR spectroscopy (^1H, ^{13}C) and six compounds were also characterized by single-crystal X-ray diffraction.



Scheme 2 Deprotonation reactions of aluminium dihydride with primary and secondary amines.

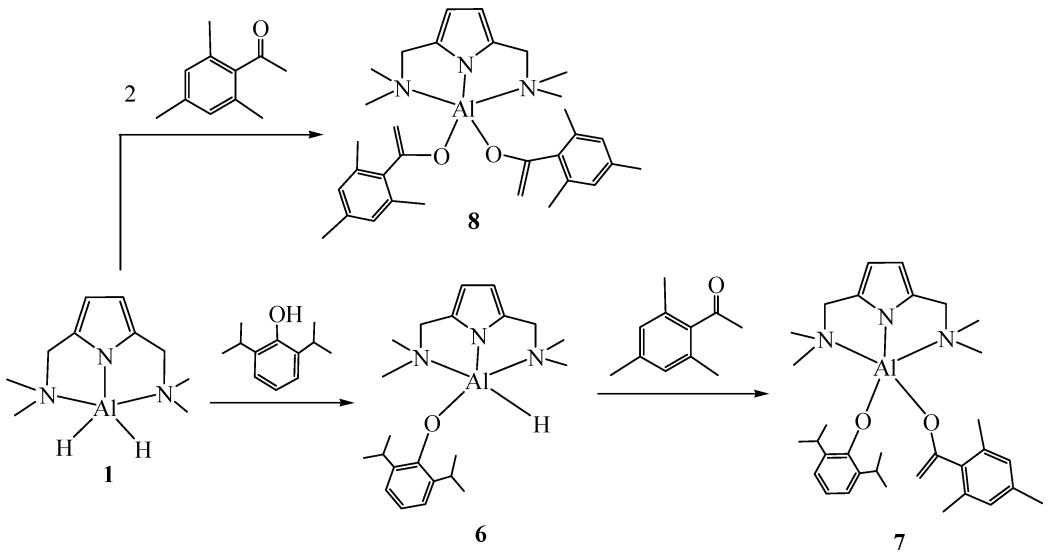
Results and discussion

Syntheses and characterization

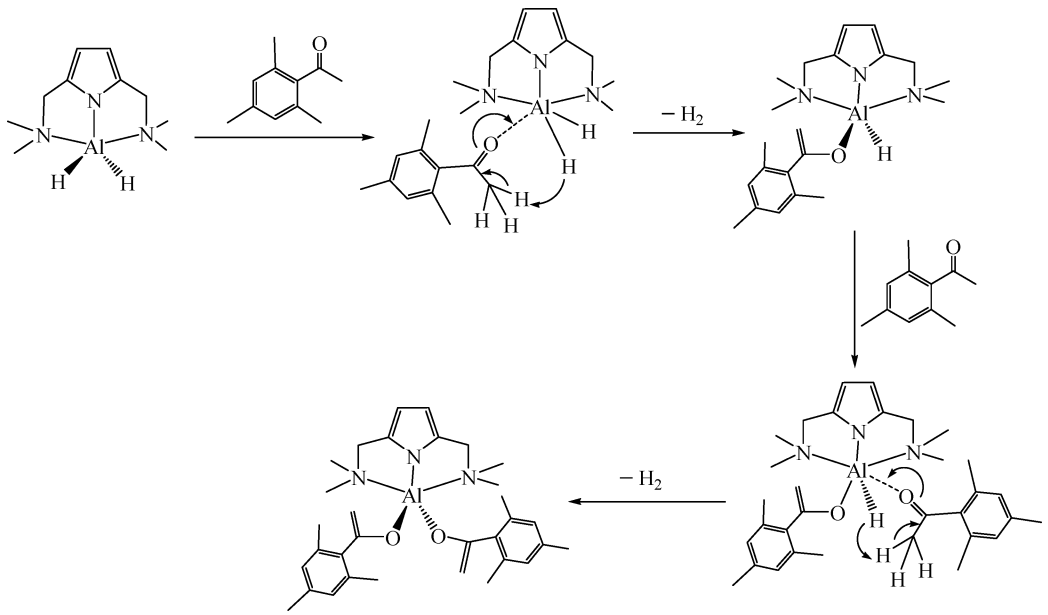
The reactions of $[C_4H_2N(CH_2NMe_2)_2]AlH_2$ (**1**) with primary and secondary amines, phenols, ketones, and phenyl isothiocyanate are described. Due to the strong basic characteristics, the aluminium dihydride compound **1** shows a strong reactivity towards functional organic molecules. Reaction of **1** with one equivalent of 2,6-dichloroaniline in methylene chloride generated an aluminium hydride compound $[C_4H_2N(CH_2NMe_2)_2]AlH(NHC_6H_3$-2,6-$Cl_2)$ (**2**) *via* hydrogen elimination (Scheme 2). Similarly, $[C_4H_2N(CH_2NMe_2)_2]AlD(NHC_6H_3$-2,6-$Cl_2)$ (**2-D**) can be obtained from the reaction of **1-D** with one equivalent of 2,6-dichloroaniline. The ^{1}H NMR spectrum of **2** shows one resonance for the NMe_2 fragments and two doublets for the CH_2N fragments. The IR spectrum shows the Al–H absorption at 1851 cm^{-1} and the corresponding Al–D absorption for compound **2-D** at 1344 cm^{-1} (calculation at 1333 cm^{-1}). While with the reaction between two equivalents of 2,6-dichloroaniline and **1**, an aluminium diamide compound $[C_4H_2N(CH_2NMe_2)_2]Al(NHC_6H_3$-2,6-$Cl_2)_2$ (**3**) can be isolated. Compound **3** exhibits a planar symmetry with the ^{1}H NMR spectra of CH_2N and NMe_2 fragments appeared as two singlets at δ 3.83 and 2.44, respectively.

Similarly, the reactions of **1** with one or two equivalents of carbazole generated $[C_4H_2N(CH_2NMe_2)_2]AlH(NC_{12}H_8)$ (**4**) and $[C_4H_2N(CH_2NMe_2)_2]Al(NC_{12}H_8)_2$ (**5**), respectively (Scheme 2). The ^{1}H NMR spectra of **4** and **5** both show two singlets (δ 1.87 and 2.58 for **4**; δ 1.55 and 2.35 for **5**) for the NMe_2 fragments and two doublets (δ 3.70 and 3.79 for **4**; δ 3.65 and 4.47 for **5**) for the CH_2N fragments. The IR spectrum of **4** in solid KBr shows an absorption at 1830 cm^{-1} for the Al–H stretching.

The aluminium dihydride compound **1** shows strong basicity which results in the deprotonation of phenol and the β-proton of ketones. Reaction of **1** with one equivalent of 2,6-diisopropylphenol in diethyl ether afforded an aluminium phenoxide compound $[C_4H_2N(CH_2NMe_2)_2]AlH(OC_6H_3$-2,6-$^i Pr_2)$ (**6**) *via* the elimination of one equivalent of hydrogen (Scheme 3). The ^{1}H NMR spectrum of **6** exhibits one singlet for the NMe_2 fragments at δ 2.42 and two doublets for CH_2N at δ 3.63 and 3.75. The IR spectrum of **6** also shows an absorption at 1853 cm^{-1} due to the Al–H stretching frequency. The Al–H of **6** can further deprotonate the β-proton of ketones to form an aluminium enolate compound. Reacting **6** with one equivalent of 2,4,6-trimethylacetophenone in methylene chloride generated $[C_4H_2N(CH_2NMe_2)_2]Al(OC_6H_3$-2,6-$^i Pr_2)[OC(=CH_2)(C_6H_2$-2,4,6-$Me_3)]$ (**7**) in 84% yield (Scheme 3). The ^{1}H NMR signals for **7** shows one resonance at δ 2.38 and two doublets at δ 3.57 and 3.64 for NMe_2 fragments and CH_2N fragments, respectively. The signals for the methylene protons of the enolate Al-O-C(=CH_2)-Ar show two singlets at δ 4.08 and 4.38 with no $^2J_{HH}$ geminal coupling found. The result differs from previous literature where the two methylene protons are coupled to each other.[16] Compound **1** can also deprotonate the β-proton of ketones. Reaction of **1** with two equivalents of 2,4,6-trimethylacetophenone in methylene chloride generated $[C_4H_2N(CH_2NMe_2)_2]Al[OC(=CH_2)(C_6H_2$-2,4,6-$Me_3)]_2$ (**8**). Again, the ^{1}H NMR signals for the methylene protons of the enolate CH_2=COAr showed two singlets at δ 3.99 and 4.46 with no $^2J_{HH}$ coupling found. A Gated-Decoupled ^{13}C NMR spectrum of **8** shows two doublets of the methylene carbon due to its coupling with two different geometrical methylene protons and a 2-D ^{1}H–^{13}C HSQC spectrum also proved the correlation of methylene carbon (δ 91.4) with two singlets of the methylene protons (δ 3.99 and 4.46). A reasonable mechanism for the deprotonation reaction is shown in Scheme 4. The reaction of **1** with 2,4,6-trimethylacetophenone can be monitored by ^{1}H NMR spectra showing the deprotonation occurs along with the elimination of hydrogen which has been observed at δ 4.64. Similar observations could be established concerning the use of **1-D** where HD signals appeared at δ 4.64 as a triplet with the J_{HD} coupling constant of 42.6 Hz.



Scheme 3 Deprotonation of aluminium dihydride with phenol and ketone.



Scheme 4 The possible reaction mechanism for the deprotonation reactions of **1** with 2′,4′,6′-trimethylacetophenone.

Aluminium dihydride compound, **1** undergoes hydroalumination reactions (reductive addition) with benzophenone and PhNCS resulting in aluminium alkoxides and thiocarbamate compounds (Scheme 5). While compound **1** reacting with two equivalents of benzophenone, compound $[C_4H_2N(CH_2NMe_2)_2]Al(OCHPh_2)_2$ (**9**) was obtained through hydroalumination and the ^1H and ^{13}C NMR spectra are also matched with the structure assignments. Reaction of **1** with two equivalents of phenyl isothiocyanate in diethyl ether generates $[C_4H_2N(CH_2NMe_2)_2]Al(SCHNPh)_2$ (**10**) in 61% yield. The ^1H NMR spectrum of **10** showed broad signals for both CH_2N and NMe_2 representing a dynamical fluctuation for **10** in solution. Variable temperature ^1H NMR spectra were therefore recorded from 230 to 330 K and shown in Fig. 1. At the slow limit of the fluctuation (250 K), there are two singlets for the NC*H*S fragments at δ 9.13 and 9.46, four doublets for the coordinated and un-coordinated C*H*$_2$N fragments at δ 2.09, 2.90, 3.60, and 4.14, and two singlets for the coordinated NMe_2 at δ 2.54 and 2.83 and one singlet for the un-coordinated NMe_2 at δ 1.61. On raising the temperature, signals broadened and coalescence occurred at *ca.* 295 K, eventually becoming two singlets for the CH_2N and NMe_2 at the fast limit. The estimated energy barrier[17] from the coalescence temperature for the fluctuation $\Delta G_c^{\ddagger}$ is *ca.* 17.1 kcal mol^{-1}. A possible fluxional mechanism is shown in Scheme 6. Due to the steric congestion of **10**, the two NMe_2 fragments are coordinated to the aluminium center in an on–off mode followed by a rotation along the aluminium pyrrolyl nitrogen bond. A fluxional mechanism through the NCS fragments is ruled out due to the formation energy concern. An energy profile of the fluxional *via* calculation is shown in Fig. 2. With regard to

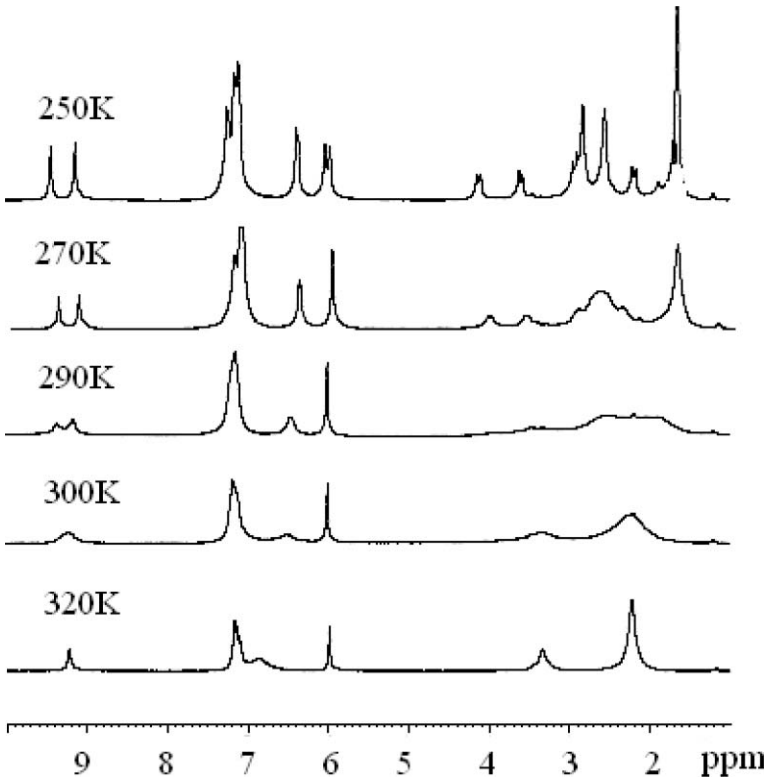


Fig. 1 Variable temperature NMR spectra of compound **10** in $CDCl_3$ using a 300 MHz NMR spectrometer showing the temperature range from 250 to 320 K.

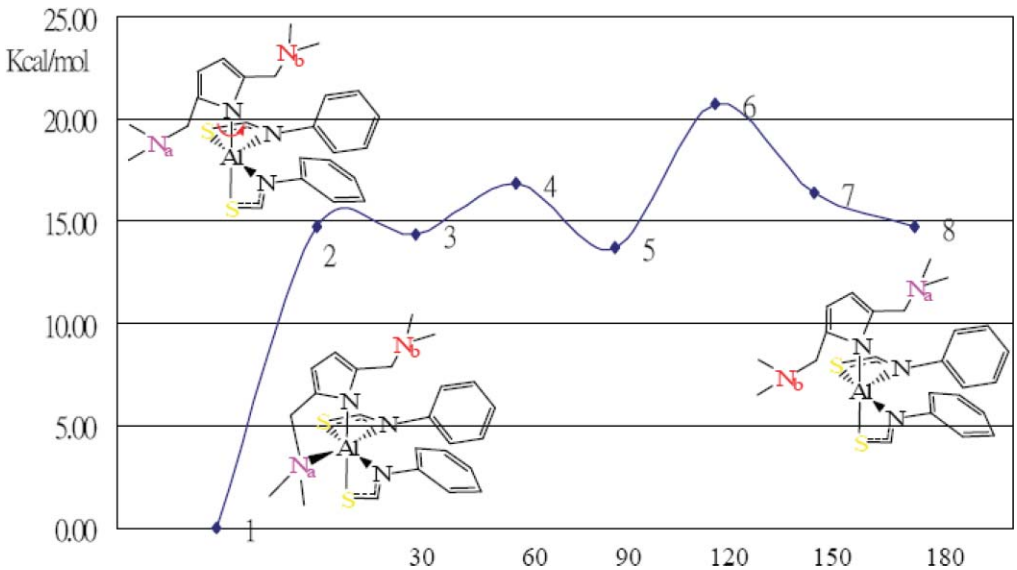
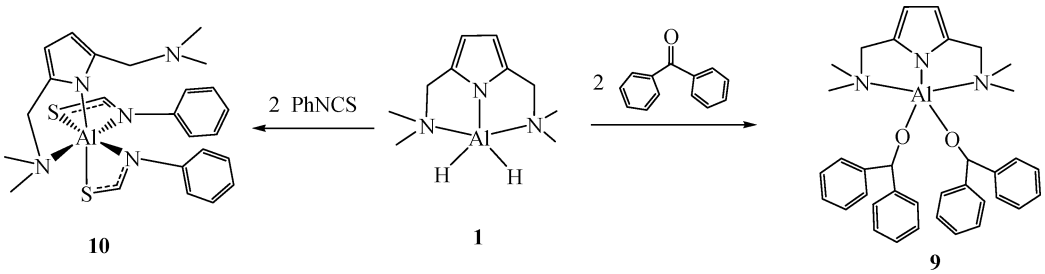


Fig. 2 The energy profile for compound **10** at different geometries *via* calculation. Geometry 1 was adopted directly from the X-ray single crystal structure; 2, the NMe_2 fragments away from the aluminium center; 3–8, rotation along the aluminium–N (pyrrolyl) bond.

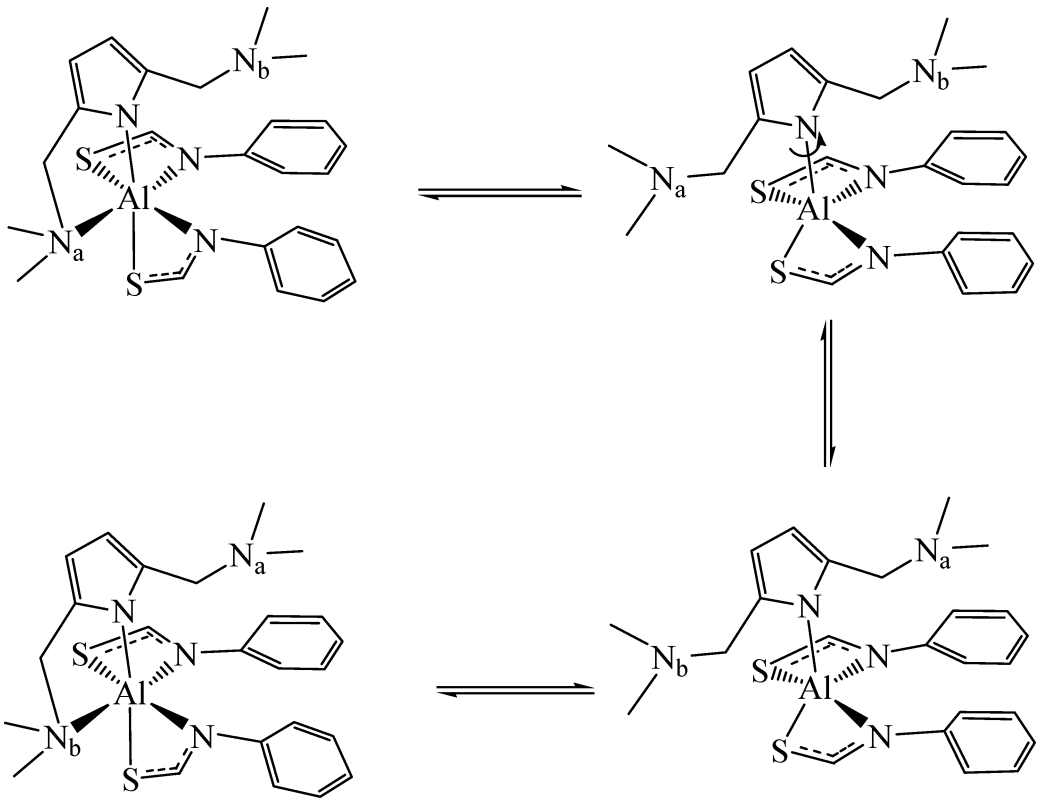
the diagram, the geometry 1 is adopted directly from an X-ray single crystal structure and is considered a stable conformation. This is also consistent with the calculated results. The Al–N_aMe_2 bond dissociation energy is 14.7 kcal mol^{-1} (geometry 2) and the rotation of the Al–N (pyrrolyl) bond needs an additional 6 kcal mol^{-1} (geometries 3–7) making the total fluxional energy 20.7 kcal mol^{-1}.

Description of molecular structures of compounds 2, 3, 5, 7, 9, and 10

The solid-state structures of compounds **2**, **3**, **5**, **7**, **9**, and **10** have been determined and molecular structures are shown in Fig. 3–8. The summary of crystal data collection along with the refinement parameters and selected bond lengths and angles are



Scheme 5 Hydroalumination reactions of aluminium dihydride with ketone, and PhNCS.



Scheme 6

listed in Table 1 and 2, respectively. Two independent molecules are found in one unit cell for compound **3**; however, their structures are similar and only one molecule has been discussed here. The crystal **5** contains a methylene chloride molecule in the lattice which has been omitted in the molecular diagram. In summary, a schematic drawing of the crystal structures of **2**, **3**, **5**, **7** and **9** have been represented in Fig. 9. Compounds **2**, **3**, **5**, **7**, and **9**, all adopt a distorted trigonal bipyramidal geometry with the two NMe_2 fragments occupying the axial positions. The sterically hindered **2** exhibits an asymmetrical geometry into which two NMe_2 fragments pointed away from the bulkier arylamide group where as the NMe_2 fragments in **3**, **5**, **7**, and **9** show equally arranged conformation in the structures (see Fig. 9). All the structures have similar Al–N(pyrrolyl) and Al–N(dimethylamino) bond lengths, which are in the range of 1.8308(12)–1.8453(13) Å and 2.1872(17)–2.4171(18) Å, respectively and agreed with the previously reported literature.[18,19] The bulkiness of aryloxide and arylamide ligands have little effect in consideration of the bond lengths. Again, the bite angles of dimethylamino and pyrrolyl groups to the aluminium center (74.42(7)–79.44(7)°) remain in a similar range.

The molecular structure of **10** possesses a pseudo-octahedral geometry with the three axes occupying by N(pyrrolyl)–S(PhNCS), N(NMe_2)–N(PhNCS), and N(PhNCS)–S(PhNCS) to form the angles of 164.33(5)°, 158.62(6)°, and 161.52(5)°, respectively. The bonding modes of isothiocyanate to the aluminium atom have been reported in the literature.[20] The tridentate pyrrolyl ligand only coordinates to the aluminium center through pyrrolyl nitrogen and one NMe_2 fragment leaving another NMe_2 fragment dangling outside the coordination sphere. This arrangement also causes a dynamical fluxionality.

Summary

The reactivities of $[C_4H_2N(CH_2NMe_2)_2]AlH_2$ (**1**) with primary and secondary amines, phenols, ketones, and phenyl isothiocyanate were investigated and generalized different modes of deprotonation and hydroalumination reactions along with NMR

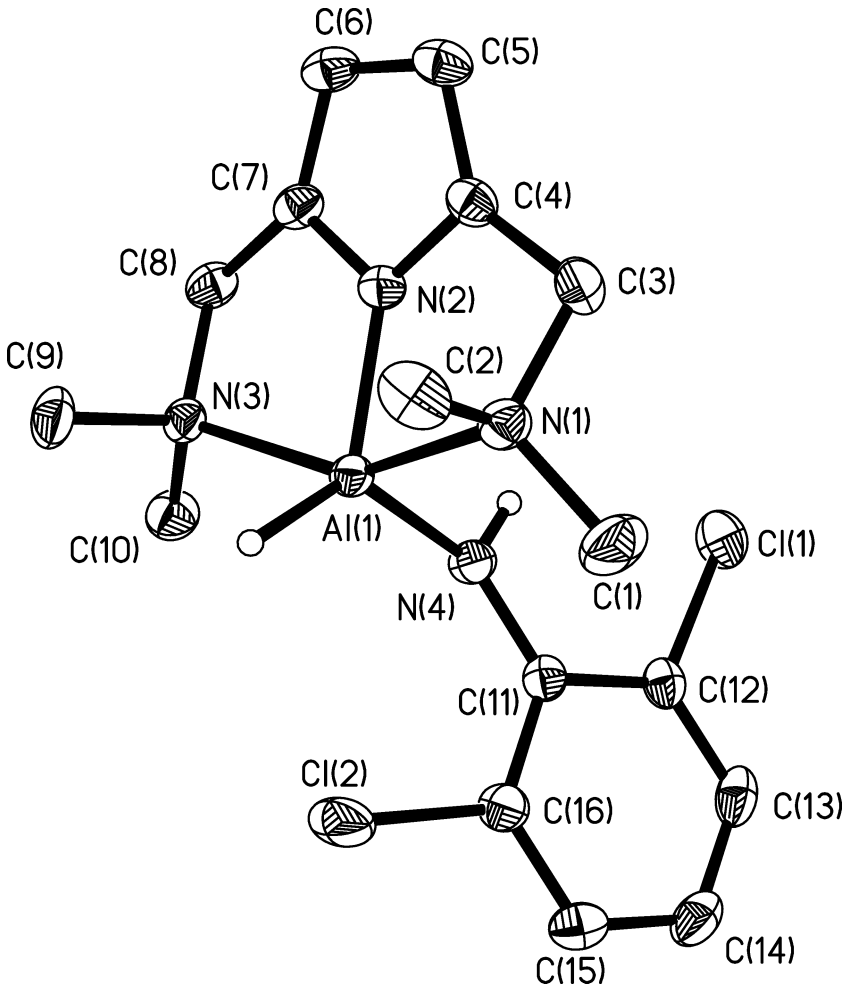


Fig. 3 The molecular structure of **2**, the ellipsoids were drawn at 50% probability level and all hydrogen atoms were omitted for clarity.

spectroscopic data analyses. We have chosen $[C_4H_2N(CH_2NMe_2)_2]AlH_2$ as a starting material because of its strong basicity and high reactivity towards functional organic molecules. It is also remarkable to draw our attention to monomeric compounds of the types mentioned above not only because of their underexplored structural chemistry but also due to the fact that monomeric compounds usually show higher volatilities compared to heterocyclic or cage compounds. Our next attempt is mainly to study the hydroalumination reactions of different organic molecules using asymmetric tridentate pyrrolyl ligands.

Experimental

Physical measurements and materials

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or a glove box. Toluene, diethyl ether, and tetrahydrofuran were dried by refluxing over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_2O_5. All solvents were distilled and stored in solvent reservoirs which contained 4 Å molecular sieves and were purged with nitrogen. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to the residual protons and ^{13}C of $CDCl_3$ (δ 7.24, 77.0) and C_6D_6 (δ 7.15, 128.0). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center, NCHU. $[C_4H_2N(CH_2NMe_2)_2]AlH_2$ was prepared according to a previously reported procedure.[21] All the chemicals (Aldrich, Acros) were used as received.

Preparation of the complexes

Complex 2. A solution of **1** (0.50 g, 2.39 mmol) in 15 mL methylene chloride was cooled to −78 °C, and a 2,6-dichloroaniline (0.40 g, 2.39 mmol)/methylene chloride (15 mL) solution was added dropwise *via* cannula. The solution then was warmed to −20 °C and stirred for 15 min. The pale yellow solution then was vacuum dried to yield an off-white solid powder. The solid was recrystallized from a diethyl ether/methylene chloride solution to yield colorless crystals of **2** (0.61 g, 68.5% yield). ^1H NMR ($CDCl_3$): 2.43 (s, 12H, N*Me*$_2$), 3.57, 3.80 (dd, $^2J_{HH}$ = 13.8 Hz, 4H, C*H*$_2$N), 3.85 (s, 1H, N*H*), 5.92 (s, 2H, pyrrole C*H*), 6.37 (t, 1H, *p*-Ph C*H*), 7.10 (d, 2H, *m*-Ph C*H*). ^{13}C NMR ($CDCl_3$): 47.1 (q, J_{CH} = 138 Hz, N*Me*$_2$), 59.6 (t, J_{CH} = 138 Hz, *C*H$_2$N), 104.3 (d, J_{CH} = 166 Hz, pyrrole *C*H), 114.6 (d, J_{CH} = 165 Hz, phenyl *C*H), 120.8 (s, phenyl, C_{ipso}), 127.9 (d, J_{CH} = 163 Hz, phenyl *C*H), 130.8 (s, pyrrole C_{ipso}), 146.5 (s, phenyl, C_{ipso}). IR (KBr) for Al-H: 1851 cm^{-1}. Anal. Calcd for $C_{16}H_{23}N_4Cl_2Al$: C, 52.04; H, 6.28; N,

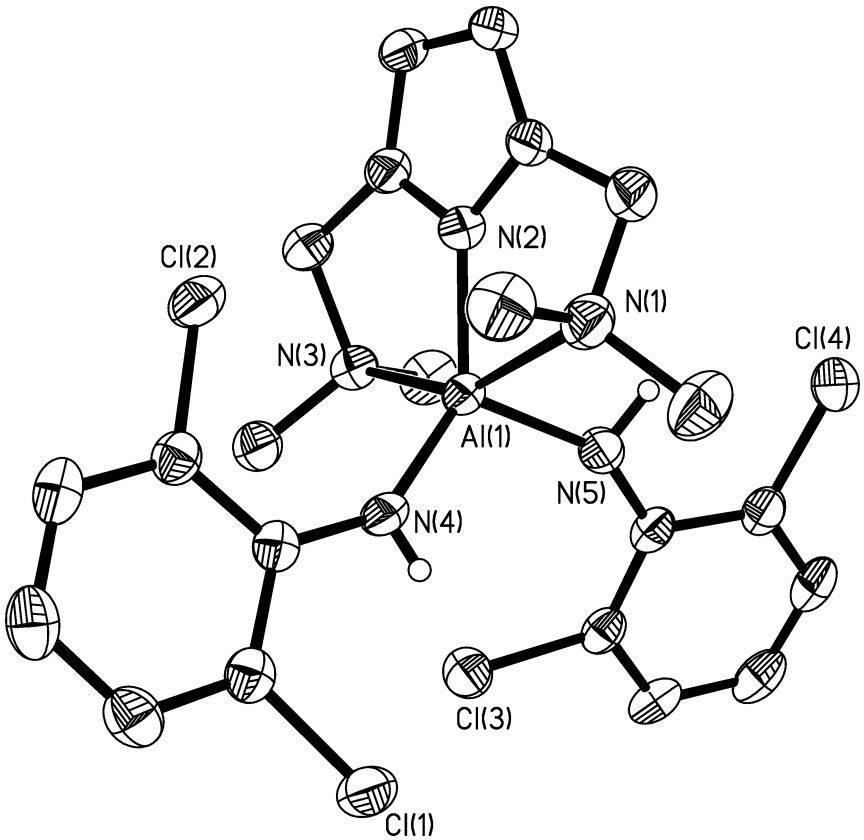


Fig. 4 The molecular structure of **3**, the ellipsoids were drawn at 50% probability level and all hydrogen atoms were omitted for clarity.

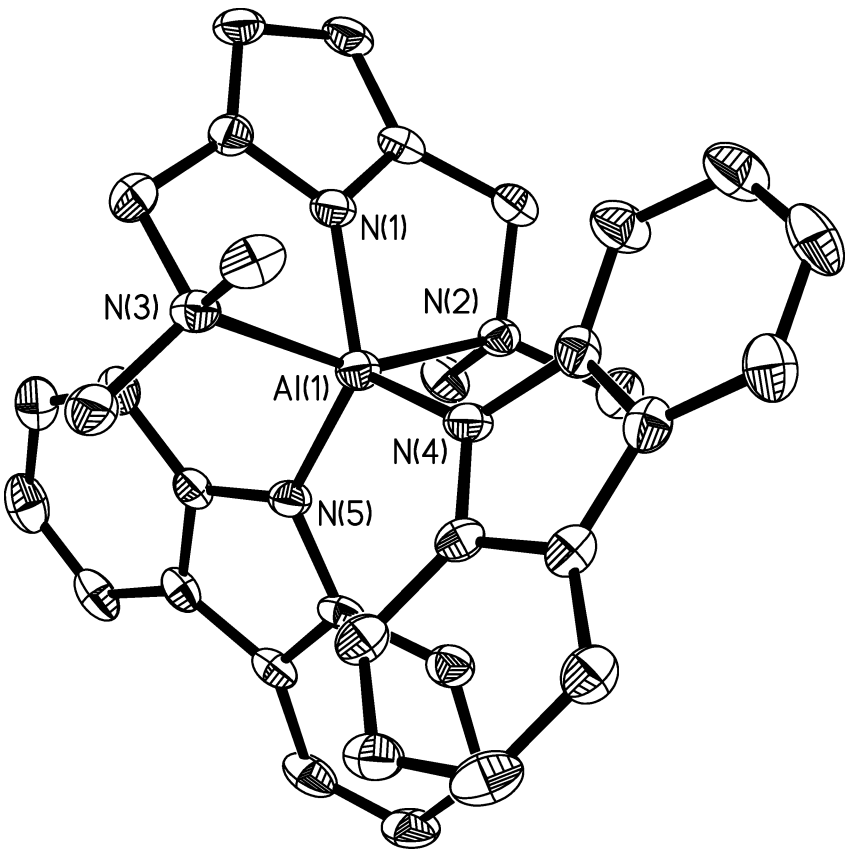


Fig. 5 The molecular structure of **5**, the ellipsoids were drawn at 50% probability level and all hydrogen atoms were omitted for clarity.

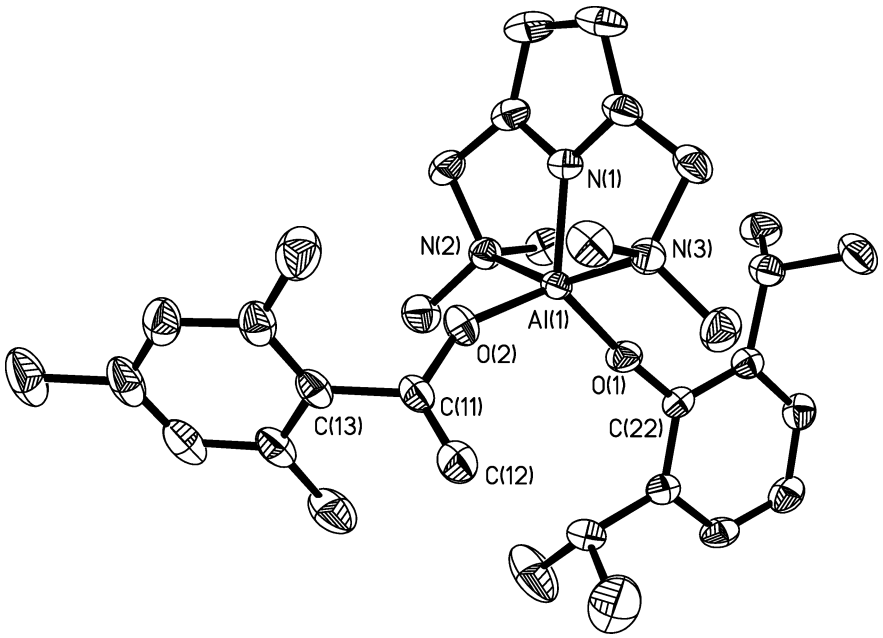


Fig. 6 The molecular structure of **7**, the ellipsoids were drawn at 50% probability level and all hydrogen atoms were omitted for clarity.

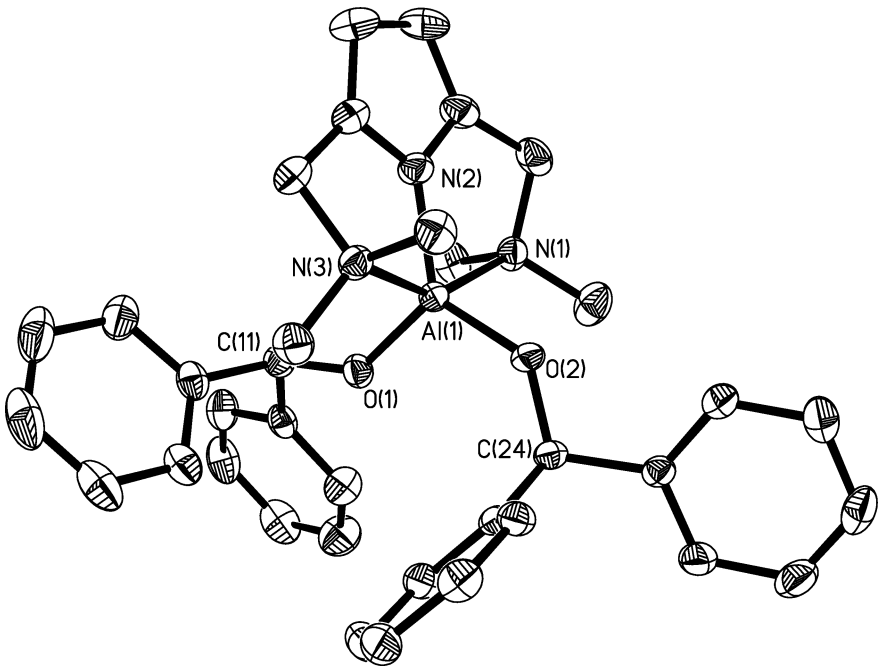


Fig. 7 The molecular structure of **9**, the ellipsoids were drawn at 50% probability level and all hydrogen atoms were omitted for clarity.

15.17. Found: C, 51.46; H, 6.22; N: 15.35%. The corresponding deuterium compound $[C_4H_2N(CH_2NMe_2)_2]AlD(NHC_6H_3$-2,6-$Cl_2$) (**2-D**) was synthesized with the same method and the NMR spectra are essentially the same as compound **2**. The IR (KBr) for Al–D: 1344 cm^{-1} (calculated: 1333 cm^{-1}).

Complex 3. A solution of **1** (0.50 g, 2.39 mmol) in 15 mL diethyl ether was cooled to −78 °C, then a 2,6-dichloroaniline (0.79 g, 4.78 mmol)/diethyl ether (15 mL) solution was added slowly *via* cannula. The solution then was warmed to –20 °C and stirred for an additional 15 min. Volatiles were removed under vacuum and the resulting solid was recrystallized from a diethyl ether solution to yield colorless crystals of **3** (0.76 g, 60% yield). ^{1}H NMR ($CDCl_3$): 2.44 (s, 12H, NMe_2), 3.83 (s, 4H, CH_2N), 4.15 (s, 2H, NH), 5.93 (s, 2H, pyrrole, CH), 6.40 (t, 2H, *p*-Ph-CH), 7.12 (d, 4H, *m*-Ph CH). ^{13}C NMR ($CDCl_3$): 48.0 (q, J_{CH} = 136 Hz, NMe_2), 60.3 (t, J_{CH} = 137 Hz, CH_2NMe_2), 105.1 (d, J_{CH} = 162 Hz, pyrrole *C*H), 115.2 (d, J_{CH} = 166 Hz, phenyl *C*H), 120.9 (s, phenyl C_{ipso}), 128.2 (d, J_{CH} = 164 Hz, phenyl *C*H), 130.8 (s, pyrrole C_{ipso}), 146.3 (s, phenyl C_{ipso}). Anal. Calcd for $C_{22}H_{26}N_5Cl_4Al$: C, 49.92; H, 4.95; N, 13.23. Found: C, 49.33; H, 5.21; N: 13.02%.

Table 1 Summary of data collections for compounds **2**, **3**, **5**, **7**, **10**, and **11**

	2	**3**	**5**	**7**	**9**	**10**
formula	$C_{16}H_{23}AlCl_2N_4$	$C_{22}H_{26}AlCl_4N_5$	$C_{35}H_{36}AlCl_2N_5$	$C_{33}H_{48}AlN_3O_2$	$C_{36}H_{40}AlN_3O_2$	$C_{24}H_{30}AlN_5S_2$
fw	369.26	529.26	624.57	545.72	573.69	479.63
crystal syst	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	Cc	$Pccn$	$P2_1/c$	P-1	$P2_1/c$
a (Å)	13.3892(4)	21.4849(5)	20.656(3)	8.7168(3)	9.7181(3)	10.2678(3)
b (Å)	10.8311(4)	9.0569(2)	36.021(7)	17.7020(6)	11.9863(4)	21.9497(6)
c (Å)	15.3524(4)	25.5170(6)	8.4360(14)	21.6908(7)	14.7312(5)	14.2669(4)
α (deg)					90.608(2)	
β (deg)	124.500(2)	90.4260(10)	90	106.796(2)	107.021(2)	128.105(2)
γ (deg)					104.025(2)	
V (Å^3), Z	1834.83(10), 4	4965.1(2), 8	6276.8(18), 8	3204.21(19), 4	1585.71(9), 2	2530.14(12), 4
D_{calc} (Mg m^{-3})	1.337	1.416	1.322	1.131	1.202	1.259
Abs coeff (mm^{-1})	0.406	0.533	0.269	0.095	0.100	0.267
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
F(000)	776	2192	2624	1184	612	1016
no. of reflns collected	29329	23086	35323	34891	28937	26122
no. of ind reflns	4425 ($R_{int} = 0.0257$)	11124 ($R_{int} = 0.0207$)	7517 ($R_{int} = 0.1226$)	7730 ($R_{int} = 0.0593$)	7625 ($R_{int} = 0.0475$)	6099 ($R_{int} = 0.0482$)
data/restraints/ params	4425/0/216	11124/2/585	7517/0/392	7730/0/363	7625/0/383	6099/0/293
Flack parameter		-0.01(2)				
goodness of fit on F^2	1.037	1.057	0.918	1.023	1.047	1.057
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0309$	$R1 = 0.0280$	$R1 = 0.0660$	$R1 = 0.0482$	$R1 = 0.0439$	$R1 = 0.0376$
	$wR2 = 0.0781$	$wR2 = 0.0644$	$wR2 = 0.1494$	$wR2 = 0.1061$	$wR2 = 0.1002$	$wR2 = 0.0885$
R indices (all data)	$R1 = 0.0353$	$R1 = 0.0346$	$R1 = 0.1812$	$R1 = 0.0879$	$R1 = 0.0772$	$R1 = 0.0635$
	$wR2 = 0.0812$	$wR2 = 0.0666$	$wR2 = 0.1893$	$wR2 = 0.1207$	$wR2 = 0.1120$	$wR2 = 0.0960$
largest diff peak and hole (e Å^{-3})	0.677 and -0.708	0.226 and -0.194	0.366 and -0.645	0.242 and -0.283	0.259 and -0.304	0.501 and -0.239

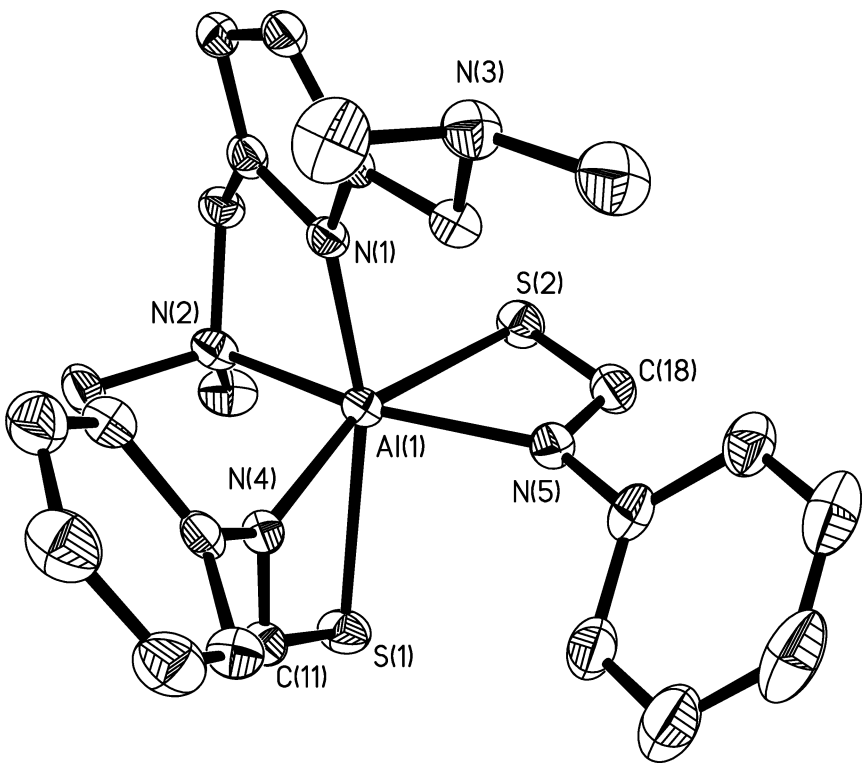


Fig. 8 The molecular structure of **10**, the ellipsoids were drawn at 50% probability level and all hydrogen atoms were omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for compounds **2**, **3**, **5**, **7**, **9** and **10**

2			
Al(1)–N(4)	1.8642(11)	Al(1)–N(1)	2.2318(11)
Al(1)–N(2)	1.8534(10)	Al(1)–N(3)	2.2275(10)
Al(1)–H	1.477(17)	N(4)–Al(1)–N(1)	99.20(5)
N(2)–Al(1)–N(4)	105.90(5)	N(1)–Al(1)–N(2)	78.13(4)
N(4)–Al(1)–N(3)	102.86(5)	N(2)–Al(1)–N(3)	78.40(4)
N(1)–Al(1)–N(3)	151.32(4)	Al(1)–N(4)–C(11)	139.92(9)
3			
Al(1)–N(4)	1.8253(17)	Al(2)–N(10)	1.8298(17)
Al(1)–N(2)	1.8432(16)	Al(2)–N(7)	1.8412(18)
Al(1)–N(5)	1.8497(15)	Al(2)–N(9)	1.8527(15)
Al(1)–N(3)	2.1872(17)	Al(2)–N(8)	2.1995(16)
Al(1)–N(1)	2.4171(18)	Al(2)–N(6)	2.3472(18)
N(4)–Al(1)–N(2)	136.33(7)	N(10)–Al(2)–N(7)	138.67(7)
N(4)–Al(1)–N(5)	111.60(7)	N(10)–Al(2)–N(9)	114.23(7)
N(2)–Al(1)–N(5)	109.64(7)	N(7)–Al(2)–N(9)	105.71(8)
N(4)–Al(1)–N(3)	104.73(7)	N(10)–Al(2)–N(8)	102.22(7)
N(2)–Al(1)–N(3)	79.44(7)	N(7)–Al(2)–N(8)	78.93(8)
N(5)–Al(1)–N(3)	102.53(7)	N(9)–Al(2)–N(8)	101.67(7)
N(4)–Al(1)–N(1)	92.51(7)	N(10)–Al(2)–N(6)	93.79(7)
N(2)–Al(1)–N(1)	74.42(7)	N(7)–Al(2)–N(6)	75.04(7)
N(5)–Al(1)–N(1)	88.93(7)	N(9)–Al(2)–N(6)	90.67(7)
N(3)–Al(1)–N(1)	153.72(6)	N(8)–Al(2)–N(6)	153.40(7)
5			
Al(1)–N(1)	1.832(3)	Al(1)–N(4)	1.868(3)
Al(1)–N(3)	2.247(3)	Al(1)–N(5)	1.862(3)
Al(1)–N(2)	2.319(3)	N(1)–Al(1)–N(5)	121.99(13)
N(5)–Al(1)–N(4)	114.16(13)	N(5)–Al(1)–N(3)	102.67(12)
N(1)–Al(1)–N(2)	76.39(11)	N(4)–Al(1)–N(2)	99.79(11)
N(1)–Al(1)–N(4)	123.75(13)	N(1)–Al(1)–N(3)	78.06(11)
N(4)–Al(1)–N(3)	93.46(12)	N(5)–Al(1)–N(2)	91.76(11)
N(2)–Al(1)–N(3)	154.43(11)		
7			
Al(1)–N(1)	1.8308(12)	Al(1)–N(2)	2.1952(14)
Al(1)–N(3)	2.1885(14)	Al(1)–O(1)	1.6956(12)
Al(1)–O(2)	1.7208(11)	O(2)–C(11)	1.3433(18)
C(12)–C(11)	1.321(3)	O(1)–C(22)	1.3459(18)
O(1)–Al(1)–O(2)	118.97(6)	O(1)–Al(1)–N(1)	126.16(6)
O(2)–Al(1)–N(1)	114.70(6)	O(1)–Al(1)–N(3)	96.24(6)
O(2)–Al(1)–N(3)	100.09(6)	N(1)–Al(1)–N(3)	78.14(6)
O(1)–Al(1)–N(2)	95.65(6)	O(2)–Al(1)–N(2)	92.91(6)
N(1)–Al(1)–N(2)	77.37(6)	N(3)–Al(1)–N(2)	155.32(5)
C(22)–O(1)–Al(1)	172.55(10)	C(11)–O(2)–Al(1)	149.89(12)
O(2)–C(11)–C(12)	124.68(16)	O(2)–C(11)–C(13)	113.03(14)
C(12)–C(11)–C(13)	122.29(15)		
9			
Al(1)–O(1)	1.7241(10)	Al(1)–O(2)	1.7248(10)
Al(1)–N(1)	2.2680(14)	Al(1)–N(2)	1.8453(13)
Al(1)–N(3)	2.2641(14)	O(1)–Al(1)–O(2)	113.33(5)
O(1)–Al(1)–N(2)	121.59(6)	O(2)–Al(1)–N(2)	127.08(6)
O(1)–Al(1)–N(3)	101.91(5)	O(2)–Al(1)–N(3)	94.84(5)
N(2)–Al(1)–N(3)	75.89(5)	O(1)–Al(1)–N(1)	99.32(5)
O(2)–Al(1)–N(1)	94.98(5)	N(2)–Al(1)–N(1)	76.82(5)
N(1)–Al(1)–N(3)	151.46(5)	Al(1)–O(1)–C(11)	135.75(9)
Al(1)–O(2)–C(24)	128.06(9)		

Table 2 (*Contd.*)

10			
Al(1)–N(1)	1.9064(13)	Al(1)–N(2)	2.1093(14)
Al(1)–N(4)	1.9852(14)	Al(1)–S(1)	2.5226(6)
Al(1)–N(5)	2.0201(14)	Al(1)–S(2)	2.4894(6)
S(1)–C(11)	1.7021(18)	C(11)–N(4)	1.306(2)
S(2)–C(18)	1.6978(18)	C(18)–N(5)	1.302(2)
N(1)–Al(1)–N(4)	99.32(6)	N(4)–Al(1)–S(2)	161.52(5)
N(1)–Al(1)–N(5)	101.00(6)	N(5)–Al(1)–S(2)	68.37(4)
N(4)–Al(1)–N(5)	98.15(6)	N(2)–Al(1)–S(2)	90.49(4)
N(1)–Al(1)–N(2)	83.82(6)	N(1)–Al(1)–S(1)	164.33(5)
N(4)–Al(1)–N(2)	101.63(6)	N(4)–Al(1)–S(1)	68.21(4)
N(5)–Al(1)–N(2)	158.60(6)	N(5)–Al(1)–S(1)	90.47(4)
N(1)–Al(1)–S(2)	95.78(4)	N(2)–Al(1)–S(1)	89.36(4)
S(2)–C(18)–N(5)	116.82(13)	S(1)–C(11)–N(4)	116.49(13)

Complex 4. To a solution of **1** (0.50 g, 2.39 mmol) in 15 mL tetrahydrofuran, a carbazole (0.36 g, 2.15 mmol)/tetrahydrofuran (15 mL) solution was added at 0 °C slowly *via* cannula. The solution was stirred at room temperature for 12 h and volatiles were removed under vacuum to generate pale yellow solids of **4** (0.65 g, 72.6% yield). ^{1}H NMR ($CDCl_3$): 1.87 (s, 6H, NMe_2), 2.58 (s, 6H, NMe_2), 3.70, 3.79 (dd, 4H, J_{HH} = 14.0 Hz, CH_2N), 6.14 (s, 2H, pyrrole C*H*), 6.48 (d, 1H, phenyl C*H*), 7.18 (m, 3H, phenyl C*H*), 7.44 (t, 1H, phenyl C*H*), 8.11 (m, 3H, phenyl C*H*). ^{13}C NMR ($CDCl_3$): 46.2 (q, J_{CH} = 136 Hz, NMe_2), 48.0 (q, J_{CH} = 136 Hz, NMe_2), 60.4 (t, J_{CH} = 139 Hz, CH_2N), 105.7 (d, J_{CH} = 166 Hz, pyrrole *C*H), 112.9 (d, J_{CH} = 158 Hz, phenyl *C*H), 113.8 (d, J_{CH} = 164 Hz, phenyl *C*H), 117.7 (d, J_{CH} = 150 Hz, phenyl *C*H), 119.7 (d, J_{CH} = 149 Hz, phenyl *C*H), 124.7 (d, J_{CH} = 159 Hz, phenyl *C*H), 125.2 (d, J_{CH} = 158 Hz, phenyl *C*H), 125.4 (s, phenyl C_{ipso}), 130.6 (s, pyrrole C_{ipso}), 146.7 (s, phenyl C_{ipso}), 147.6 (s, phenyl C_{ipso}). IR (KBr) for Al–H: 1830 cm^{-1}.

Complex 5. Same procedure as for synthesizing **4** has been applied. Amount used: **1**, 0.50 g, 2.39 mmol; carbazole, 0.75 g, 4.49 mmol. Yield: 1.01 g, 78.2%. ^{1}H NMR ($CDCl_3$): 1.55 (s, 6H, NMe_2), 2.35 (s, 6H, NMe_2), 3.65, 4.57 (dd, 4H, J_{HH} = 15.0 Hz, CH_2N), 6.29 (s, 2H, pyrrole C*H*), 6.97 (t, 2H, phenyl C*H*), 7.23 (m, 10H, phenyl C*H*), 8.11 (m, 4H, phenyl C*H*). ^{13}C NMR ($CDCl_3$): 47.9 (q, J_{CH} = 137 Hz, NMe_2), 48.0 (q, J_{CH} = 135 Hz, NMe_2), 62.2 (t, J_{CH} = 142 Hz, CH_2N), 106.9 (d, J_{CH} = 171 Hz, pyrrole *C*H), 110.5 (d, J_{CH} = 159 Hz, phenyl *C*H), 112.6 (d, J_{CH} = 157 Hz, phenyl *C*H), 117.1 (d, J_{CH} = 159 Hz, phenyl *C*H), 118.6 (d, J_{CH} = 160 Hz, phenyl *C*H), 118.8 (d, J_{CH} = 160 Hz, phenyl *C*H), 119.1 (d, J_{CH} = 159 Hz, phenyl *C*H), 119.4 (d, J_{CH} = 170 Hz, phenyl *C*H), 119.9 (d, J_{CH} = 159 Hz, phenyl *C*H), 120.2 (d, J_{CH} = 159 Hz, phenyl *C*H), 122.9 (s, phenyl C_{ipso}), 124.4 (d, J_{CH} = 158 Hz, phenyl *C*H), 125.4 (d, J_{CH} = 159 Hz, phenyl *C*H), 125.6 (d, J_{CH} = 162 Hz, phenyl *C*H), 125.8 (s, phenyl C_{ipso}), 126.0 (s, phenyl C_{ipso}), 131.0 (s, pyrrole C_{ipso}), 139.2 (s, phenyl C_{ipso}), 145.9 (s, phenyl C_{ipso}), 147.1 (s, phenyl C_{ipso}). Anal. Calcd. for $C_{34}H_{34}AlN_5 \cdot CH_2Cl_2$: C, 67.31; H, 5.81; N, 11.21. Found: C, 67.44; H, 6.47; N, 11.34%.

Complex 6. A solution of **1** (3.0 g, 14.3 mmol) in 40 mL diethyl ether was cooled to 0 °C, and a 2,6-diisopropylphenol (2.6 g, 14.4 mmol)/diethyl ether (40 mL) solution was added dropwise *via* cannula. The solution was stirred at room temperature for another 3 h after the completion of addition. The volatiles were removed under vacuum to yield pale yellow solid of the final product **2**

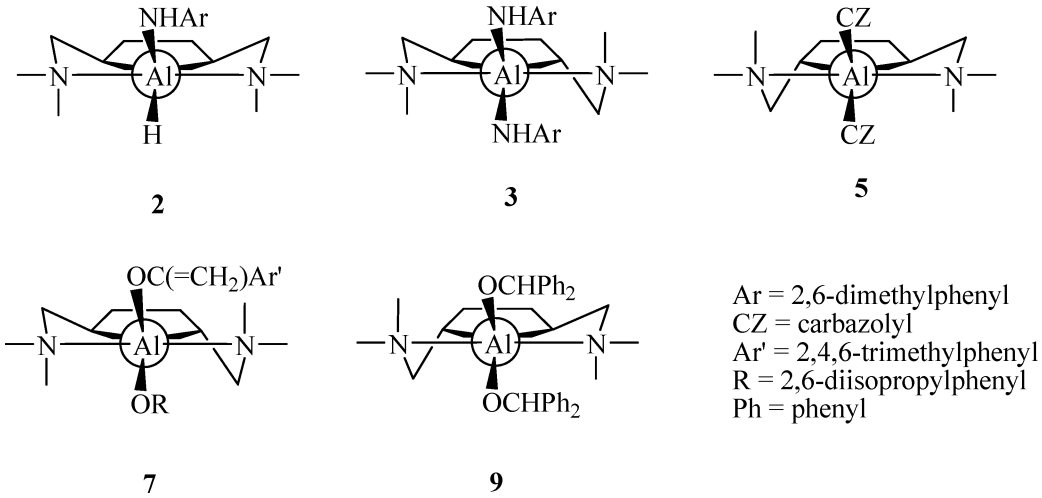


Fig. 9 Schematic drawings the molecular structures of **2**, **3**, **5**, **7**, and **9** presenting the relative geometries of all crystal structures.

(4.5 g, 81% yield). ^{1}H NMR ($CDCl_3$): 1.16 (d, 12H, CHMe_2), 2.42 (s, 12H, NMe_2), 3.32 (m, 4H, CHMe$_2$), 3.63 (d, 2H, CH_2NMe$_2$), 3.75 (d, 2H, CH_2NMe$_2$), 5.95 (s, 2H, pyrrole CH), 6.78 (t, 2H, phenyl CH), 7.02 (d, 2H, phenyl CH). ^{13}C NMR ($CDCl_3$): 23.5 (q, J_{CH} = 125 Hz, CHMe_2), 26.5 (d, J_{CH} = 127 Hz, CHMe$_2$), 46.9 (q, J_{CH} = 137 Hz, NMe_2), 59.9 (t, J_{CH} = 139 Hz, CH$_2$NMe$_2$), 104.3 (d, J_{CH} = 165 Hz, pyrrolyl CH), 117.9 (d, J_{CH} = 159 Hz, phenyl CH), 123.0 (d, J_{CH} = 155 Hz, phenyl CH), 130.3 (s, C_{ipso}), 136.9 (s, C_{ipso}), 153.2 (s, C_{ipso}). IR (KBr) for Al–H: 1853 cm^{-1}.

Complex 7. A solution of **6** (0.88 g, 2.28 mmol) in 20 mL methylene chloride was cooled to −78 °C, and a 2,4,6-trimethylacetophenone (0.37 g, 2.28 mmol)/methylene chloride (15 mL) solution was added slowly *via* cannula. The solution then was stirred at −20 °C for 2 h after addition to be completed. The volatiles were removed under vacuum and a white solid was obtained (1.05 g, 84%). ^{1}H NMR ($CDCl_3$): 1.15 (d, ^3J = 13.5 Hz, 12H, CHMe_2), 2.29 (s, 3H, *p*-PhMe), 2.36 (s, 6H, *o*-PhMe), 2.38 (s, 12H, NMe_2), 3.41 (m, 2H, CHMe$_2$), 3.57, 3.64 (dd, ^2J = 21.0 Hz, ^3J = 13.5 Hz, 4H, CH_2N), 4.08 (s, 1H, OC=CH_2), 4.38 (s, 1H, OC=CH_2), 5.98 (s, 2H, pyrrole CH), 6.80-7.07 (m, 5H, phenyl CH). ^{13}C NMR ($CDCl_3$): 20.5 (q, J_{CH} = 126 Hz, *o*-PhMe), 21.0 (q, J_{CH} = 120 Hz, *p*-PhMe), 24.2 (q, J_{CH} = 125 Hz, CHMe_2), 25,7 (d, J_{CH} = 126 Hz, CHMe$_2$), 47.3 (q, J_{CH} = 137 Hz, NMe_2), 60.6 (t, J_{CH} = 138 Hz, CH$_2$N), 91.6(dd, J_{CH} = 159, 158 Hz, OC=CH$_2$), 104.5 (d, J_{CH} = 166 Hz, pyrrole CH), 118 (d, J_{CH} = 160 Hz, phenyl CH), 123.2 (d, J_{CH} = 155 Hz, phenyl CH), 128.0 (d, J_{CH} = 154 Hz, phenyl CH), 130.3 (s, pyrrole C), 135.4 (s, phenyl C_{ipso}), 136.3 (s, phenyl C_{ipso}), 137.2 (s, phenyl C_{ipso}), 138.5 (s, phenyl C_{ipso}), 152.3 (s, OCC), 157.4 (s, OC=CH$_2$). Anal. Calcd. for $C_{33}H_{48}N_3O_2Al$: C, 72.63; H, 8.87; N, 7.70. Found: C, 72.87; H, 8.62; N, 7.45%.

Complex 8. A solution of **1** (0.30 g, 1.44 mmol) in 20 mL methylene chloride wad cooled to −20 °C, and a methylene chloride (15 mL) solution of 2′,4′,6′-trimethylacetophenone (0.47 g, 2.89 mmol) was added dropwise *via* cannula. The solution was stirred at −20 °C for 30 min and then volatiles were removed under vacuum to yield a pale yellow solid of **4** (0.42 g, 55.3% yield). ^{1}H NMR ($CDCl_3$): 2.25 (s, 6H, p-PhMe), 2.32 (s, 12H, o-PhMe), 2.37 (s, 12H, NMe_2), 3.51 (s, 4H, CH_2N), 3.99 (s, 2H, OCCH_2), 4.46 (s, 2H, OCCH_2), 5.87 (s, 2H, pyrrole CH), 6.80 (s, 4H, Ph CH). ^{13}C NMR ($CDCl_3$): 20.5 (q, J_{CH} = 126 Hz, o-PhMe), 20.9 (q, J_{CH} = 126 Hz, p-PhMe), 46.9 (q, J_{CH} = 137 Hz, NMe_2), 60.3 (t, J_{CH} = 139 Hz, CH$_2$N), 91.4 (dd, J_{CH} = 158 Hz, 158 Hz, OCCH$_2$), 104.1 (d, J_{CH} = 167 Hz, pyrrole CHCCH$_2$), 128.0 (d, J_{CH} = 150 Hz, phenyl CH), 130.7 (s, pyrrole C_{ipso}), 135.4 (s, phenyl C_{ipso}), 136.0 (s, phenyl C_{ipso}), 138.5 (s, OCCH$_2$), 157.6 (s, phenyl C_{ipso}).

Complex 9. A solution of **1** (0.30 g, 1.44 mmol) in 20 mL methylene chloride was cooled to −78 °C, and a methylene chloride (15 mL) solution of benzophenone (0.53 g, 2.88 mmol) was added dropwise *via* cannula. The solution was stirred at −20 °C for 2 h and then volatiles were removed under vacuum to yield a solid of **10** which then was recrystallized from a diethyl ether/methylene chloride mixed solvent to generate 0.36 g (44% yield) of final product **10**. ^{1}H NMR ($CDCl_3$): 2.06 (s, 12H, NMe_2), 3.32 (s, 4H, NCH_2), 5.91 (s, 2H, pyrrole CH), 5.91 (s, 2H, OCH), 7.17 (t, 4H, phenyl CH), 7.26 (t, 8H, phenyl CH), 7.39 (d, 8H, phenyl CH). ^{13}C NMR ($CDCl_3$): 46.7 (q, J_{CH} = 137 Hz, NMe_2), 59.9 (t, J_{CH} = 138 Hz, NCH_2), 77.0 (d, J_{CH} = 139 Hz, OCH), 103.9 (d, J_{CH} = 166 Hz, pyrrole CH), 126.3 (d, J_{CH} = 160 Hz, phenyl CH), 126.7 (d, J_{CH} = 158 Hz, phenyl CH), 127.9 (d, J_{CH} = 159 Hz, phenyl CH), 131.2 (s, pyrrole CHCN), 148.2 (s, phenyl OCHCCH). Anal. Calcd. for $C_{36}H_{40}N_3O_2Al$: C: 75.37; H: 7.03; N: 7.32; Found: C: 74.50; H: 6.73; N: 6.90%.

Complex 10. A solution of **1** (1.00 g, 4.78 mmol) in 15 mL diethyl ether was cooled to −78 °C, and a diethyl ether (15 mL) solution of phenyl isothiocyanate (1.30 g, 9.6 mmol) was added dropwise *via* cannula. The solution was slowly warmed to −20 °C and stirred for 1 h. The clear solution became cloudy with white precipitation. The solid was filtered off and recrystallized from a diethyl ether and methylene chloride solution to yield 1.40 g of **10** (61% yield). ^{1}H NMR ($CDCl_3$, 240 K): 1.61 (s, 6H, NMe_2), 2.09 (d, $^2J_{HH}$ = 14.7 Hz, 1H, CH_2N), 2.54 (s, 3H, NMe_2), 2.83 (s, 3H, NMe_2), 2.90 (d, $^2J_{HH}$ = 14.2 Hz, 1H, CH_2N), 3.60 (d, $^2J_{HH}$ = 14.2 Hz, 1H, CH_2N), 4.14 (d, $^2J_{HH}$ = 14.2 Hz, 1H, CH_2N), 5.95 (s, 1H, pyrrole CH), 6.03 (s, 1H, pyrrole CH), 6.36 (d, 2H, phenyl CH), 7.15 (m, 8H, phenyl CH), 9.13 (s, 1H, SCHNPh), 9.46 (s, 1H, SCHNPh). ^{13}C NMR ($CDCl_3$, 230 K): 46.1 (q, J_{CH} = 129 Hz, NMe_2), 46.7 (q, J_{CH} = 135 Hz, NMe_2), 50.2 (q, J_{CH} = 139 Hz, NMe_2), 60.2 (t, J_{CH} = 135 Hz, CH$_2$N), 60.7 (t, J_{CH} = 130 Hz,

CH_2N), 104.5 (d, J_{CH} = 168 Hz, pyrrole *C*H), 106.7 (d, J_{CH} = 162 Hz, pyrrole *C*H), 121.0 (d, J_{CH} = 159 Hz, phenyl CH), 121.6 (d, J_{CH} = 160 Hz, phenyl *C*H), 126.3 (d, J_{CH} = 162 Hz, phenyl CH), 129.2 (d, J_{CH} = 162 Hz, phenyl CH), 129.6 (d, J_{CH} = 161 Hz, phenyl *C*H), 131.2 (s, pyrrole C_{ipso}), 135.8 (s, pyrrole C_{ipso}), 144.6 (s, phenyl C_{ipso}), 146.0 (s, phenyl C_{ipso}), 184.9 (d, J_{CH} = 181 Hz, S*C*HNPh), 189.6 (d, J_{CH} = 179 Hz, S*C*HNPh). Anal. Calcd. for $C_{24}H_{30}N_5S_2Al$: C, 60.10; H, 6.30; N, 14.60. Found: C, 59.92; H, 6.51; N, 14.42%.

X-Ray crystallography

The crystals were mounted on capillaries and transferred to a goniostat and were collected at 150 K under a nitrogen stream. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo-K_α radiation. The structures were solved by direct and difference Fourier methods and refined by full matrix least-squares on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic computing was performed using the SHELXTL[22] package of programs. All refinements were carried out by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. All the relevant crystallographic data and structure refinement parameters for **2**, **3**, **5**, **7**, **9** and **10** are summarized in Table 1.

Acknowledgements

The authors gratefully acknowledge the National Science Council of Taiwan for the financial assistance. JHH would also like to thank the National Changhua University of Education for providing the X-ray facility.

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