FULL PAPER



Novel aluminium compounds derived from Schiff bases: Synthesis, characterization and catalytic performance in hydroboration

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National Nature Science Foundation of China, Grant/Award Numbers: 21872005 and 21671018 Seven novel aluminium complexes supported by Schiff base ligands derived from o-diaminobenzene or o-aminothiophenol were synthesized and characterized. The reactions of AlMe₃ with L^1 (*N*,*N*'-bis(benzylidine)-o-phenylenediamine) and L^2 (*N*,*N*'-bis(2-thienylmethylene)-o-phenylenediamine) gave the complexes $L^{1}AlMe_{3}$ (1) and $L^{2}AlMe_{2}$ (2), respectively, which involved two types of reaction mechanisms: one was proton transfer and ring closure, and the other was alkyl transfer. Complexes $L^{3}AlMe_{2}$ (HL³ = 4-chlorobenzylidene-o-aminothiophenol) (3), L^4AlMe_2 (HL⁴ = 2-thiophenecarboxaldehyde-o-aminothiophenol) (4), $L^{3}AlH(NMe_{3})$ (5), $L^{4}AlH(NMe_{3})$ (6) and $L^{5}AlH(NMe_{3})$ (HL⁵ = 4methylbenzylidene-o-aminothiophenol) (7) were prepared by reacting HL^{3-5} with equimolar AlMe₃ or H₃Al·NMe₃, respectively. Compounds 3-7 feature an organic-inorganic hybrid containing CNAISC five-membered ring. All complexes were characterized using ¹H NMR and ¹³C NMR spectroscopy, X-ray crystal structure analysis and elemental analysis. The efficient catalytic performances of 1-7 for the hydroboration of carbonyl groups were investigated, with compound 4 exhibiting the highest catalytic activity among all the complexes.

KEYWORDS

aluminium compounds, catalytic, hydroboration, ring closure, Schiff bases

1 | INTRODUCTION

Organoboranes are important synthetic intermediates, which are widely used in scientific research and are easily obtained from hydroboration of carbonyl groups.^[1] During past decades, various transition metal complexes, such as those of Ni,^[2] Ru,^[3] Ti^[4] and Cu,^[5] have been utilized as catalysts for the hydroboration of carbonyl compounds. Compared to those transition metal catalysts, main group metal catalysts are cheap, widespread and less toxic.^[6] Hydroboration involving main group metal catalysts based on alkali metals,^[7] magnesium,^[8] group 14 metals^[9] and aluminium^[10] has been investigated widely. Our group was the first one to demonstrate that aluminium

hydride can be applied to facilitate hydroboration in high yield.^[11] Although the hydrogenation of aldehydes and ketones with aluminium hydroxide catalysts has been reported,^{10c,e,11} the reaction using an aluminium species has yet to be realized. We postulated that, with the correct aluminium complex design, increased Lewis acidity and reduced steric hindrance, the conversion of hydroboration with aldehydes and ketones would be improved. All these above considerations prompted us to continue to research aluminium compounds.

Furthermore, ligands play a synergistic role in the activation of chemical bonds. Quite a few complexes with Schiff base ligands have been synthesized.^[12] Schiff base ligands bearing diaminobenzene usually have O-donor

(such as *N*,*N'*-bis(salicylidene)diaminobenzene) to lead to [O–N–N–O] chelation, which can stabilize a metal center to form the expected well-defined catalysts.^[13] Nevertheless, without the modified functional group (–OH), it is not well studied for main group metals except some transition metals.^[14] Moreover, metal complexes containing N and S are attracting increasing attention because of their chemical and, especially, their promising biological properties,^[15] and both atoms play a vital role in the coordination of metal complexes.^[16] Since Jancik *et al.* first reported the synthesis of species containing Al–SH units in 2003,^[17] a mushrooming number of aluminium compounds with the Al–S–C core have been studied.^[18] However, few examples of compounds containing the S–Al–N moiety in a ring have been reported.^[19]

Herein, we report the synthesis and characterization of seven novel aluminium compounds bearing Schiff bases derived from *o*-diaminobenzene or *o*-aminothiophenol. We found alkyl transfer occurred when AlMe₃ reacted with N,N'-bis(2-thienylmethylene)-*o*-phenylenediamine (L²). In addition, when AlMe₃ reacted with N,N'-bis(benzylidine)-*o*-phenylenediamine (L¹), an unexpected process occurred which involved proton transfer and ring closure. We also synthesized five aluminium compounds forming the rare S—Al—N modified ring through the elimination of hydrogen from ligands. Finally, we investigated the application of all compounds in catalytic hydroboration of selected aldehydes and ketones.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis and characterization

Compounds **1** and **2** were prepared from reactions of L^1 and L^2 , respectively, with equimolar AlMe₃ in toluene at 0°C (Scheme 1). In the formation of compound **1**, AlMe₃ as an organic electrophile causes proton transfer. The proposed mechanism for the synthesis of compound **1** involved ring closure in a concerted manner (Scheme 2).





SCHEME 2 Plausible mechanism of complex 1 synthesis

Although ligands L^1 and L^2 are similar, the reaction mechanisms are quite different. In the formation of compound **2**, a methyl group was migrated from AlMe₃ onto the ligand backbone, resulting in formal insertion of the C=N bond on the ligand into an Al–C bond. Compounds **3–7** were prepared from reactions of HL³ (4-chlorobenzylidene-*o*-aminothiophenol), HL⁴ (2thiophenecarboxaldehyde-*o*-aminothiophenol) and HL⁵ (4-methylbenzylidene-*o*-aminothiophenol) with equivalent amount of AlMe₃ or H₃Al·NMe₃ in toluene at 0°C (Scheme 3).

Compounds 1-7 were characterized from their ¹H NMR and ¹³C NMR spectra in CDCl₃ solution as well as using elemental analysis. In the ¹H NMR spectrum of **1**, there was an absence of the N=CH resonance (9.30 ppm) of ligand L^{1.[20]} The resonances at 5.18 and -1.08 ppm revealed the existence of NCH₂ and three equivalent Me groups of AlMe₃. In the ¹H NMR spectrum of 2, the singlet peak (8.74 ppm), the quartet peak (4.8, 4.78, 4.77 and 4.75 ppm) integrated with 1:3:3:1 ratio and the doublet peak (1.68 and 1.67 ppm) integrated with 1:1 ratio could be assigned to N=CH, NCH and CHCH₃, respectively. In addition, there were resonances for the AlCH₃ groups in the high-field region (-0.63 and-0.72 ppm), which indicated the two Me groups were not in the same chemical environment. Both ¹³C NMR spectra were consistent with the ¹H NMR spectra, showing characteristic signals for N=CH (153.15 ppm for 1



SCHEME 1 Preparation of compounds 1 and 2



SCHEME 3 Preparation of compounds 3-7

and 150.93 ppm for **2**) of the ligands and Al*Me* (-14.22 ppm for **1** and -8.29, -9.11 ppm for **2**) in the high-field region. In the ¹H NMR spectra of compounds **3-7**, the disappearance of *SH* resonances (3.4 to 4.3 ppm) in the ligands^[21] and the appearance of Al*Me*₂ resonances at high-field region (-0.75 to -0.6 ppm) or N*Me*₃ group resonances at 2.3 ppm and *CH*₂ resonances at 4.46 to 4.66 ppm indicated the formation of desired complexes.

2.2 | Crystal structures

X-ray-quality single crystals of **1–7** were obtained in toluene. The X-ray single-crystal structures show that compounds **1** and **3–7** belong to the monoclinic crystal system while **2** belongs to the triclinic crystal system. All crystals are soluble in common organic solvents, such as toluene, dichloromethane and tetrahydrofuran. The molecular structures (**1**, **2**, **3** and **5**) are shown in Figures 1–4, with selected bond lengths and angles in the captions of, while other similar structures (**4**, **6** and **7**) are shown in the supporting information (Figures S1–S3).

In compound **1**, the aluminium center exhibits a distorted tetrahedral geometry including a nitrogen atom on the ligand and three carbon atoms from three methyl groups. The bond angles around the aluminium atom range from 102.08 (11)° to 115.79 (16)°. The bond length of Al \leftarrow N is 2.014 (2) Å, which is shorter than the corresponding Al \leftarrow N bond length in [AlMe₃{NH(Bu^t)Ph}] (2.067(4) Å)^[22] and AlMe₃(NMe₃) (2.099(10) Å).^[23] Meanwhile, the three bound angles of C—Al—N (108.91(12)°,



FIGURE 1 Molecular structure of 1 in crystals. Thermal ellipsoids are drawn at 50% level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–C(22) 1.962(3), Al(1)–C(21) 1.980(3), Al(1)–C(23) 1.989(3), Al(1)–N(1) 2.014(2); C(22)–Al(1)–C(21) 115.79(16), C(22)–Al(1)–C(23) 109.84(14), C(21)–Al(1)–C(23) 114.77(14), C(22)–Al(1)–N(1) 108.91(12), C(21)–Al(1)–N(1) 102.08(11), C(23)–Al(1)–N(1) 104.37(11)



FIGURE 2 Molecular structure of 2 in crystals. Thermal ellipsoids are drawn at 50% level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–N(1) 1.874(3), Al(1)–C(1) 1.969(4), Al(1)–C(2) 1.970(4), Al(1)–N(2) 1.996(3), N(1)–C(4) 1.460(4), N(2)–C(3) 1.296(4); N(1)–Al(1)–C(1) 114.31(15), N(1)–Al(1)–C(2) 115.17(15), C(1)–Al(1)–C(2) 118.1(2), N(1)–Al(1)–N(2) 85.69(11), C(1)–Al(1)–N(2) 110.12(16), C(2)–Al(1)–N(2) 108.36(16)



FIGURE 3 Molecular structure of 3 in crystals. Thermal ellipsoids are drawn at 50% level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–S(1) 2.2877(8), Al(1)–N(1) 2.0181(18), Al(1)–C(8) 1.966(2), Al(1)–C(7) 1.977(2); C(8)–Al(1)–C(7) 119.93(10), C(8)–Al(1)–N(1) 114.65(9), C(7)–Al(1)–N(1) 104.98(8), C(8)–Al(1)–S(1) 112.10(8), C(7)–Al(1)–S(1) 112.41(8), N(1)–Al(1)–S(1) 88.19(5)



FIGURE 4 Molecular structure of **5** in crystals. Thermal ellipsoids are drawn at 50% level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)-S(1) 2.2263(6), Al(1)-N(2) 1.8194(14), Al(1)-N(1) 1.9999(15); N(2)-Al(1)-N(1) 107.96(6), N(2)-Al(1)-S(1) 93.93(5), N(1)-Al(1)-S(1) 108.46(4)

104.37(11)° and 102.08(11)°) are similar to those in $[AlMe_3{NH(Bu^t)Ph}]$ (108.5(4)°, 107.8(2)° and 106.14(16)°).

In compound **2**, L^2 forms a five-membered N–N chelate moiety with Al. The aluminium center is described as a four-coordinated distorted tetrahedron, being surrounded by two nitrogen atoms on the ligand and two carbon atoms from methyl groups. The sum of the inner angles of the C-N-Al-C-N five-membered ring is 538.33°, which is close to that of the ideal planar ring of 540°. The Al \leftarrow N coordinate bond (1.996(3) Å) is slightly shorter than that in compound 1. The Al-N single bond (1.874(3) Å) is significantly shorter than the Al \leftarrow N coordinate bond, and both are slightly longer than those in $[Cy[NC(CH_2)-2-(C_5H_4N)AlMe_2]_2]$ (1.861(1) Å for Al-N and 1.973(1) Å for Al \leftarrow N),^[24] respectively. The N(2)= C(3) (1.296(4) Å) double bond is much shorter than and distinct from the N(1)–C(4) single bond (1.460(4) Å). The N(1)–Al–N(2) angle $(85.69(11)^\circ)$ is larger than that in (^{DiPP}DAB (Me₂)) (84.40(4)°).^[25]

In compounds **3** and **4**, the central aluminium exhibits a distorted tetrahedral geometry with a sulfur atom, a nitrogen atom and two carbon atoms. The sums of the inner angles of C–N–Al–S–C five-membered ring are 539.04° and 531.23°, respectively. In **3**, the bond lengths of Al–S (2.2877(8) Å) and Al←N (2.0181(18) Å) are shorter than those of Al(1)–S(2) (2.3137(7) Å) and Al(1)–N(5) (2.1208(17) Å) in [LAl[(*m*-S)(*m*-pyrimidine)(CH₂)₂]₂] reported by our group previously.^[26] In **4**, the Al–S bond length (2.2939(11) Å) is longer than that in **3**, while the Al←N bond length (2.005(3) Å) is shorter than that in **3**.

In compounds 5-7, the central aluminium atom is four-coordinated, being surrounded by a nitrogen atom and a sulfur atom on the ligand, one nitrogen atom from the NMe₃ group and one hydrogen atom. The imino groups have been transformed into amido functionality, forming cyclopentyl-bearing aluminium metallacycles. Their Al-S bond lengths (2.2263(6) Å for 5, 2.2291(6) Å for 6 and 2.2294(4) Å for 7) are close to each other and shorter than those in 3 and 4. Their Al-N bond lengths (1.8194(14) Å for 5, 1.8200(12) Å for 6 and 1.8208(10) Å for 7) are significantly shorter than those of the Al \leftarrow N coordinate bonds in 3 and 4. Meanwhile, compared to the corresponding bond lengths and angle in the structure of $[LAI[(\mu-N)(\mu-S)]]$ $(o-C_6H_4)$] (Al(1)-S(1), 2.2274(15) Å; Al(1)-N(3), 1.799(4) Å; N(3)-Al(1)-S(1), 93.52(12)°),^[19] the Al-S bond lengths are quite similar, the Al-N bond lengths are longer and the N-Al-S angles (108.46(4)° for 5, 105.88(4)° for $\boldsymbol{6}$ and 108.81(3)° for $\boldsymbol{7})$ are more obtuse. Their Al \leftarrow NMe₃ bond lengths (1.9999(15) Å for 5, 1.9906(13) Å for 6 and 1.9982(11) Å for 7) are comparable to that in $[(2,6-iPr_2C_6H_3)NC(Me)]_2AlH(NMe_3)]$ (2.0027(8) Å).^[27] Each of the C–S–Al–N–C fivemembered rings is approximately coplanar and the three sums of the inner angles are 538.91°, 539.10° and 538.99°, respectively.

2.3 | Catalytic performance

The catalytic performance of all the complexes in hydroboration with selected aldehydes and ketones was evaluated. We carried out the reactions by adding catalysts 1-7 to an equimolar mixture of HBpin and carbonyl compounds in C_6D_6 . The results are presented in Table 1. We noticed that compounds 1-7 are active catalysts for hydroboration of benzaldehyde and the yields were 99% within 1 h at room temperature. The conversions were concluded from ¹H NMR analysis. In contrast, the catalyst-free hydroboration of benzaldehyde displayed little conversion. The hydroboration of ketone with HBpin using all compounds as catalysts at room temperature showed slower progress than that of aldehydes. However, on heating the reaction mixture to 60°C, the acetophenone conversion was significantly improved for all cases, with the highest up to 92% yield in 5 h. From Table 1, it is evident that the catalytic efficiency of 1-4 is higher than that of 5-7. It might be that the methyl group directly attached to aluminium as electron-donating group improved the catalytic efficiency. Meanwhile, the -NMe₃ group attached to aluminium might reduce the catalytic efficiency due to its steric hindrance. Moreover, we found that 4 exhibits the highest catalytic activity among the seven complexes and the catalytic efficiency is comparable to that of other similar complexes reported previously.^{10a,c}

The mechanism of aluminium hydride-catalyzed hydroboration of carbonyl compounds (insertion/ σ -bond metathesis type) was previously investigated by our group^[11] and others.^{10c,e} Herein, we proposed an insertion/ σ -bond metathesis type of mechanism (Scheme 4). For compound **4**, we proposed that Al–Me, similar to Mg–ⁿBu,^[28] reacted with HBpin to form hydride. And then, Al–H bond inserted into the C=O functional group to form the corresponding aluminum alkoxide intermediate. Finally, the reaction of the metal alkoxide with HBpin via σ -bond metathesis to yield the alkoxyboronate product regenerates the aluminum hydride catalyst for further reaction.

3 | EXPERIMENTAL

3.1 | General procedures

All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside

TABLE 1 Hydroboration of aldehydes and ketones catalyzed by $1-7^a$

		R'=alk	$R^{+} HB O + Cat. 0-2$ $Cat. 0-2 C_6 D_6$ $C_6 D_6$ $C_6 D_6$ $C_6 D_6$	Bpin Brin R'HR"		
Entry	Substrate	Catalyst	Loading (mol%)	Temperature (°C)	Time (h)	Yield (%) ^b
a	O H	None	0	25	1	Trace
b	ОН	1	1	25	1	99
c	ОЦН	1	1	25	1	99
d	O	1	2	60	5	86
e	ОН	2	1	25	1	99
f	оЦ	2	1	25	1	99
g	°↓	2	2	60	5	89
h	O H	3	1	25	1	99
i	оЩн	3	1	25	1	99
j	°,	3	2	60	5	88
k	O H	4	1	25	1	99
1	о Ц	4	1	25	1	99
m	°↓	4	2	60	5	92
n	O H	5	1	25	1	99
0	ОЦН	5	1	25	1	99
р	O C	5	2	60	5	85

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TABLE 1 (Continued)

		R'	$\begin{array}{c} & & \\ & & \\ & & \\ & \\ & \\ & \\ & \\ & \\ $	Bpin 6 R' H R*		
Entw	Substrate	R ⁱ =alk	yl or aryl; R [°] =alkyl or H	Tomporature (°C)	Time (h)	Viold (07)b
Entry	Substrate	Catalyst	Loading (mor%)	Temperature (C)	Time (II)	rielu (%)
q	ОН	6	1	25	1	99
r	о Ц н	6	1	25	1	99
S	°,	6	2	60	5	82
t	O H	7	1	25	1	99
u	ОЦН	7	1	25	1	99
V	O	7	2	60	5	76

^aAll reactions carried out in benzene- d_6 using 1 equiv. of HBpin.

^bConversion was determined by NMR spectroscopy on the basis of the consumption of the aldehyde/ketone, and the identity of the product was confirmed by R' CH₂OBpin or R'R"CHOBpin signal in NMR spectra.



SCHEME 4 Proposed mechanism for hydroboration of carbonyl compounds catalyzed by compound **4**

an Etelux MB 200G glovebox. All solvents were refluxed with the appropriate drying agent and distilled prior to use. Commercially available chemicals were purchased from J&K chemical or VAS and used as received. L^{1-2} and HL^{3-5} were prepared as previously described in the literature.^[20,21,29] Elemental analyses were performed at

the Analytical Instrumentation Center of the Beijing Institute of Technology. NMR spectra were recorded with a Bruker AM 400 spectrometer. Melting points were measured in sealed glass tubes.

3.2 | Preparation of complexes

3.2.1 | Synthesis of L^1AlMe_3 (1)

AlMe₃ (1 M in toluene, 1 ml, 1 mmol) was added drop by drop to a solution of L¹ (0.284 g, 1 mmol) in toluene (10 ml) at 0°C. After the addition was completed, the reaction mixture was allowed to warm to room temperature and stirring was continued for 24 h. And then the solution was filtered. The filtrate was concentrated to 5 ml and was stored at -20° C in a freezer for 3 days to afford compound **1** as yellow crystals. Yield 0.20 g (56%); m.p. 235°C decomposed. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 7.45–7.11 (m, 14 H, Ar–*H*), 5.18(s, 2 H, NC*H*₂), -1.08 (s, 9 H, Al*Me*₃). ¹³C NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 153.15 (NCN), 142.19, 135.39, 135.05, 129.09, 128.87, 128.37, 128.32, 128.24, 128.03, 127.71, 127.32, 126.74, 126.65, 124.95, 121.99, 121.63, 118.99, 109.48 (C of Ar), 47.37 (*C*H₂), -14.22 (Al*Me*₃). Elemental analysis, calcd for C₂₃H₂₅AlN₂ (356.44) (%): C 77.50, H 7.07, N 7.86; found (%): C 78.08, H 7.14, N 7.99.

3.2.2 | Synthesis of L^2AlMe_2 (2)

Compound **2** was synthesized using the same procedure as for **1**, using AlMe₃ (1 M in toluene, 1 ml, 1 mmol) with L² (0.296 g, 1 mmol) in toluene (10 ml) to afford black crystals. Yield 0.15 g (51%); m.p. 132–134°C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 8.74 (s, 1 H, NCH), 7.76–6.84 (m, 10 H, H of Ar or thiophene), 4.78 (q, J = 4 Hz, 1 H, CHCH₃), 1.67(d, J = 8 Hz, 3 H, CHCH₃), -0.63 (s, 3 H, AlCH₃), -0.72 (s, 3 H, AlCH₃). ¹³C NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 150.93 (NCH), 150.09, 148.89, 135.69, 135.46, 134.39, 131.52, 130.23, 127.89, 125.51, 122.00, 121.90, 114.49, 111.89, 111.57 (C of Ar or thiophene), -8.29, -9.11 (AlMe₂). Elemental analysis, calcd for C₁₉H₂₁AlN₂S₂ (368.49) (%): C 61.93, H 5.74, N 7.60; found (%): C 62.62, H 5.85, N 7.86.

3.2.3 | Synthesis of L^3AlMe_2 (3)

Compound 3 was synthesized using the same procedure as for 1, using AlMe₃ (1 M in toluene, 1 ml, 1 mmol) with HL³ (0.248 g, 1 mmol) in toluene (10 ml) to afford red crystals. Yield 0.21 g (70%); m.p. 140-142°C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS, δ, ppm): 8.71 (s, 1 H, NCH), 7.71-6.95 (m, 8 H, Ar-H), -0.75 (s, 6 H, AlMe₂). ¹³C NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 166.48 (NCH), 145.88, 141.26, 140.97, 133.26, 132.00, 130.61, 130.43, 129.73, 128.92, 127.96, 123.87, 119.23(C of Ar), -7.37 (AlMe₂). Elemental analysis, calcd for C₁₅H₁₅AlClNS (303.79) (%): C 59.31, H 4.98, N 4.61; found (%): C 60.02, H 5.11, N 4.83.

3.2.4 | Synthesis of L^4AlMe_2 (4)

Compound **4** was synthesized using the same procedure as for **1**, reacting AlMe₃ (1 M in toluene, 1 ml, 1 mmol) with HL⁴ (0.219 g, 1 mmol) in toluene (10 ml) to afford red crystals. Yield 0.18 g (65%); m.p. 132–133°C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 8.73 (s, 1 H, NC*H*), 7.88–6.92 (m, 8 H, H of Ar or thiophene), -0.60 (s, 6 H, Al*Me*₂). ¹³C NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 156.74 (NCH), 144.51, 139.84, 136.65, 136.35, 135.04, 132.14, 128.80, 128.36, 122.67, 117.78 (C of Ar or thiophene), -8.32 (Al*Me*₂). Elemental analysis, calcd for $\rm C_{13}H_{14}AlNS_2$ (275.37) (%): C 56.70, H 5.12, N 5.09; found (%): C 57.21, H 5.01, N 5.36.

3.2.5 | Synthesis of $L^3AlH(NMe_3)$ (5)

Compound **5** was synthesized using the same procedure as for **1**, reacting H₃Al·NMe₃ (1 M in toluene, 1 ml, 1 mmol) with HL³ (0.248 g, 1 mmol) in toluene (10 ml) to afford colorless crystals. Yield 0.29 g (87%); m.p. 155–156°C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 7.29–6.17 (m, 8 H, Ar–H), 4.49 (s, 2 H, NCH₂), 2.33 (s, 9 H, NMe₃). ¹³C NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 150.47, 138.37, 130.54, 128.53, 127.50, 127.14, 127.00, 124.03, 122.94, 115.04, 114.26, 109.69 (C of Ar), 47.26 (CH₂), 45.80 (NMe₃). Elemental analysis, calcd for C₁₆H₂₀AlClN₂S (334.84) (%): C, 57.39; H, 6.02; N, 8.37; found (%): C, 58.05; H, 6.12; N, 8.58.

3.2.6 | Synthesis of $L^4AlH(NMe_3)$ (6)

Compound **6** was synthesized using the same procedure as for **1**, reacting H₃Al·NMe₃ (1 M in toluene, 1 ml, 1 mmol) with HL⁴ (0.219 g, 1 mmol) in toluene (10 ml) to afford colorless crystals. Yield 0.25 g (82%); m.p. 103–105°C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 7.29–6.47 (m, 7 H, H of Ar or thiophene), 4.66 (s, 2 H, NCH₂), 2.29 (s, 9 H, NMe₃). ¹³C NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 150.75, 144.76, 129.32, 125.75, 125.15, 123.84, 123.14, 122.81, 115.15, 109.27 (C of Ar or thiophene), 45.06 (CH₂), 44.85 (NMe₃). Elemental analysis, calcd for C₁₄H₁₉AlN₂S₂ (306.43) (%): C 54.87, H 6.25, N 9.14; found (%): C 55.65, H 6.36, N 9.44.

3.2.7 | Synthesis of $L^5AlH(NMe_3)$ (7)

Compound 7 was synthesized using the same procedure as for 1, reacting H₃Al·NMe₃ (1 M in toluene, 1 ml, 1 mmol) with HL⁵ (0.227 g, 1 mmol) in toluene (10 ml) to afford colorless crystals. Yield 0.26 g (83%); m.p. 123–125°C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 7.28–6.25 (m, 8 H, H of Ar), 4.46 (s, 2 H, NCH₂), 2.26 (s, 12 H, NMe₃ and ArMe). ¹³C NMR (400 MHz, CDCl₃, 298 K, TMS, δ , ppm): 151.19, 136.84, 135.38, 129.18, 128.06, 127.62, 126.57, 126.03, 125.06, 123.13, 114.71, 109.36 (C of Ar), 49.22 (CH₂), 45.50 (NMe₃), 20.04 (ArMe). Elemental analysis, calcd for C₁₇H₂₃AlN₂S (314.42) (%): C 64.94, H 7.37, N 8.91; found (%): C 65.66, H 7.29, N 9.15. 8 of 10 WILEY-Organometallic

3.3 | X-ray crystallography

The crystallographic data for compounds 1–7 were collected using a Rigaku AFC10 Saturn 724+ (2 × 2 bin mode) diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Empirical absorption correction was applied using the SADABS program.^[30] Structures were solved by direct methods^[31] and refined by full matrix least squares on F^2 using the SHELXL-97 program.^[32] Crystallographic data are provided in Table 2. CCDC 1840545, 1840546, 1840547, 1840549, 1840548, 1841410 and 1841411 contain

TABLE 2 Crystal data and structure refinement for 1-7

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the supplementary crystallographic data for compounds **1–7**, respectively, and can be obtained free of charge via www.ccdc.cam.ac.uk/deposit.

3.4 | Hydroboration catalyzed by complexes 1–7

Benzaldehyde (0.1 ml, 1 mmol), HBpin (0.15 ml, 1 mmol) and C_6D_6 (1 ml) were loaded in a dried J-Young tube under nitrogen atmosphere. The mixture was placed in a sealed

Compound	1	2	3	4	5	6	7
Empirical formula	$C_{23}H_{25}AlN_2$	$C_{27}H_{32}AlN_2S_2$	C ₁₅ H ₁₅ AlClNS	$C_{13}H_{14}AlnS_2$	C ₁₆ H ₂₀ AlClN ₂ S	$\mathrm{C}_{14}\mathrm{H}_{19}\mathrm{AlN}_{2}\mathrm{S}_{2}$	C ₁₇ H ₂₃ AlN ₂ S
Formula weight	356.43	475.64	303.77	275.35	333.82	306.41	314.41
Temperature (K)	153.1500	153.1500	153.1500	153.1500	153.1500	153.1500	153.1500
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_{1}/c$	<i>P</i> -1	$P2_{1}/c$	$P2_{1}/n$	$P2_{1}/n$	$P2_{1}/c$	$P2_{1}/n$
a (Å)	10.277(2)	9.3370(10)	9.4300(6)	9.4743(5)	11.3508(11)	11.0474(8)	11.3366(7)
b (Å)	22.465(5)	10.9234(12)	7.8023(5)	7.9722(4)	10.1156(9)	9.6300(7)	10.2462(6)
c (Å)	8.8469(19)	13.3951(15)	20.4565(13)	18.1371(9)	15.3560(14)	18.2395(13)	15.3908(9)
α (deg)	90.00	67.141(3)	90.00	90.00	90.00	90.00	90.00
β (deg)	96.993(7)	75.170(3)	90.591(2)	93.550(1)	97.067(2)	103.748(2)	97.781(2)
γ (deg)	90.00	87.410(3)	90.00	90.00	90.00	90.00	90.00
$V(\text{\AA}^3)$	2027.3(7)	1214.7(2)	1505.02(17)	1367.29(12)	1749.8 (3)	1884.8(2)	1771.29(18)
Ζ	4	2	4	4	4	4	4
$\rho_{\rm c} ({\rm g}~{\rm cm}^{-3})$	1.168	1.300	1.341	1.338	1.267	1.080	1.179
$\mu (\mathrm{mm}^{-1})$	0.108	0.274	0.436	0.430	0.383	0.319	0.228
Crystal size (mm)	$0.3 \times 0.15 \times 0.1$	$0.2 \times 0.15 \times 0.1$	$0.3 \times 0.15 \times 0.1$	$0.3 \times 0.15 \times 0.1$	$0.3 \times 0.15 \times 0.1$	$0.2 \times 0.15 \times 0.1$	$0.2 \times 0.15 \times 0.1$
θ range (deg)	1.813-25.048	1.708-25.047	1.991-25.049	2.250-28.277	2.112-25.049	1.898-28.302	2.101-28.244
Reflections collected	2513	3828	2459	3184	2736	3837	3865
R _(int)	0.0792	0.0310	0.0240	0.0222	0.0434	0.0279	0.0278
Data/restraints	3589/0	4297/52	2674/0	3389/12	3087/1	4674/1	4358/0
Parameters	235	289	172	154	194	176	194
F(000)	760.0	506.0	632.0	576.0	704.0	648.0	672.0
$R1^{a}, wR2^{b}$ $(I > 2\sigma(I))$	0.0572, 0.1484	0.0745, 0.2186	0.0359, 0.0997	0.0690, 0.2177	0.0308, 0.0821	0.0349, 0.1187	0.0315, 0.0898
R1 ^a , wR2 ^b (all data)	0.0888, 0.1668	0.0806, 0.2265	0.0388, 0.1017	0.0718, 0.2211	0.0359, 0.0856	0.0433, 0.1292	0.0358, 0.0923

 ${}^{a}R = \Sigma ||F_{0}| - |F_{c}||/\Sigma |F_{0}|.$

^b $wR2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma (F_0^2)]^{1/2}.$

environment and stirred at room temperature and the progress was followed by ¹H NMR and ¹³C NMR spectroscopy.

Compound 1 (0.01 or 0.02 mmol) was added to a solution of aldehyde (1 mmol) or ketone (1 mmol) with HBpin (0.15 ml, 1 mmol) in C_6D_6 (1 ml) under nitrogen atmosphere. The mixture was placed in a sealed environment and stirred at room temperature. The reaction was terminated by exposing the mixture to air. The conversion was determined by ¹H NMR and ¹³C NMR spectroscopy.

Hydroboration of aldehydes and ketones catalyzed by compounds **2–7** was conducted using a similar method to that mentioned above.

4 | CONCLUSIONS

In summary, seven novel aluminium complexes supported by Schiff bases have been synthesized and fully characterized. The possible mechanism for the synthesis of **1** was investigated. The catalytic performances of all complexes towards hydroboration of aldehydes and ketones were evaluated. Compound **4** exhibits the highest catalytic activity among the seven complexes. Moreover, complexes **3–7** are interesting precursors for the preparation of new aluminium compounds. We are concentrating on synthesizing some novel compounds based on these and expanding their applications.

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