SYNTHESIS AND SPECTROSCOPIC (IR AND ^{1}H, ^{13}C, ^{27}Al NMR) CHARACTERIZATION OF SEVERAL ALUMINIUM AND GALLIUM N-ARYLSALICYLALDIMINATE DERIVATIVES

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ABSTRACT

Several $[Al(OPr^i)_{3-x}(\eta^2\text{-}L)_x]_n$ (where $x = 1$, $n = 2$; $x = 2$, $n = 1$; $x = 3$, $n = 1$; η^2-L represents bidentate (O,N) ligating behaviour of the ligands) and $[Ga(\eta^2\text{-}L)_3]$ derivatives have been prepared by the reactions in benzene of $Al(OPr^i)_3$/$Ga(OPr^i)_3$ with a variety of N-arylsalicylaldimines (LH) (Scheme 1) in appropriate molar ratios and characterized spectroscopically along with elemental and molecular weight determinations. The $[Al(OPr^i)_2(\eta^2\text{-}L)]$ derivatives are dimers containing one octahedral and one tetrahedral aluminium atom bridged by isopropoxo groups. The derivatives $[Al(OPr^i)(\eta^2\text{-}L)_2]$ and $[M(\eta^2\text{-}L)_3]$ (M = Al or Ga) which are monomers in solution depict five- and six-coordination around aluminium/gallium, respectively.

INTRODUCTION

The preparation of Schiff base derivatives of group 13 elements is still a very active area of research [1]. A wide range of mixed-ligand complexes of aluminium have been investigated within the past few decades, among which β-diketonate-isopropoxide and related systems [2-5] have attracted special interest due to the presence of aluminium in two different coordination states within the same molecule. The possibility of enhanced hydrolytic and thermal stability of heteroleptic alkoxide derivatives containing chelating ligands [6] has added much fuel to the growing recent research activity in mixed ligand complexes of aluminium [7,8].

As part of a wide investigation of homo- and hetero-nuclear complexes of metal(loid)s [1,9-12], we have now studied the reactions of $Al(OPr^i)_3$ in benzene with a variety of N-arylsalicylaldimines (LH), shown in Scheme 1, to obtain three different types of complexes : $(\eta^2\text{-}L)_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2$ (**A**), $(\eta^2\text{-}L)_2Al(OPr^i)$ (**B**), and $Al(\eta^2\text{-}L)_3$ (**C**), where η^2-L represents the bidentate ligand involving deprotonated phenolic oxygen and azomethine nitrogen atoms. The spectroscopic properties and molecular weight data of the new complexes are consistent with the structures depicted by Figs. (**A**), (**B**), and (**C**).

MATERIALS AND METHODS

All experiments were performed under a moisture-free environment. Reagent grade (BDH) benzene, toluene, and *n*-hexane were dried by refluxing over sodium/benzophenone and distilled prior to use. Isopropoxides of aluminium [13] and gallium [14] were prepared by literature methods. Al and Ga were determined as oxinates [15]. Nitrogen and isopropoxy content in the azeotrope were determined by Kjeldahl's [15] and oxidimetric [16] methods, respectively.

All NMR spectra were recorded on a JEOL FX-90Q FT NMR spectrometer. ^{1}H NMR spectra in $CDCl_3$ were recorded at 89.55 MHz. ^{13}C NMR spectra in CCl_4 were recorded at 22.49 MHz. Chemical shifts are given in parts per million (ppm) relative to TMS. ^{27}Al NMR spectra in CCl_4 were recorded at 23.29 MHz using aqueous $Al(NO_3)_3$ as an external reference. IR spectra in Nujol were recorded on a Nicolet Magna 550 spectrophotometer using CsI optics. Molecular weights were measured using Gallenkamp ebulliometer.

Preparation of new N-arylsalicylaldimines and their characterization

$HOC_6H_4CH{=}NC_6H_3Me_2$-2,6 (HL^1)

Equimolar amounts of salicylaldehyde (27.09 g, 222.04 mmol) and 2,6-dimethylaniline (30.81 g, 222.20 mmol) in benzene (~ 100 ml) and Pr^iOH (~ 15 ml) was refluxed for ~ 50 h, with the continuous removal of the liberated water. When the liberation of water ceased off, the refluxing was stopped and allowed to cool to room temperature. Removal of the volatile components from the solution afforded orange yellow viscious liquid (48.7 g, 98%). The analytically pure ligand was obtained in ~ 85% yield by distillation (150°C / 0.3 mm).

Other ligands (**HL^2**)-(**HL^4**) were prepared by the same procedure. Colour, state, boiling point (°C/mm), and characterization data for the N-arylsalicylaldimines (**HL^1**)-(**HL^4**) are summarized below.

(**HL^1**) : Orange yellow viscious liquid; b.p. 150/0.3 ; IR (Neat, cm^{-1}); 2920s ν(OH), 1624s ν(C=N), 1575s ν(C=C), 1472s, 1279s ν(C-O), 1179s, 1151m, 1118m, 1092m, 1028m, 984m, 903m, 845m, 756s, 613w, 554w; ^{1}H NMR ($CDCl_3$, ppm) : 13.80 (s, 1H, O**H**), 8.64 (s, 1H, C**H**=N) 7.83-7.02 (m, 7H, Ar-**H**), 2.28 (s, 6H, C**H**$_3$); ^{13}C NMR (CCl_4, ppm) : 166.52 (C-1), 161.32 (C-7), 148.16 (C-8), 132.88 (C-5), 131.85 (C-3), 128.17 (C-9), 127.79 (C-10), 124.78 (C-11), 118.52 (C-4 and C-6), 117.28 (C-2), 18.36 (**C**H$_3$). (**HL^2**) . Reddish yellow solid ; b.p. 155/0.3 ; IR (Nujol, cm^{-1}) : 2960s, 2345s ν(OH), 1626s ν(C=N), 1580s ν(C=C), 1481s ν(C-O), 1169s, 1131s, 1036s, 1036m, 907m, 880m, 751s, 657m, 615m, 430m, ^{1}H NMR ($CDCl_3$, ppm) : 13.76 (s, 1H, O**H**), 8.33 (s, 1H, C**H**=N), 7.40-6.91 (m, 6H, Ar-**H**), 3.48 (s, 3H, **Me**-4); 2.28 (s, 6H, **Me**-2,6); ^{13}C NMR (CCl_4, ppm) : 166.31 (C-1), 161.32 (C-7), 145.66 (C-8), 133.58 (C-11), 132.61 (C-5), 131.69 (C-3), 128.82 (C-9), 127.57 (C-10), 118.58 (C-4), 118.36 (C-6), 117.22 (C-2), 20.63 (**Me**-4), 18.25 (**Me**-2,6); (**HL^3**) : Yellow viscious liquid; b.p. 160/0.3; IR (Neat, cm^{-1}) : 2967s, 2932, 2874s ν(OH), 1624s ν(C=N), 1578s ν(C=C), 1496s, 1464s, 1402m, 1278s ν(C-O), 1217m, 1177s, 1157s, 1115m, 1037m, 988w, 909s, 847m, 785s, 756s, 556w, 444w; ^{1}H NMR ($CDCl_3$, ppm) : 13.52 (s, 1H, O**H**), 8.54 (s, 1H, C**H**=N), 7.47-6.82 (m, 7H, Ar-**H**), 2.61 (q, J = 6 Hz, 4H, C**H**$_2$CH$_3$), 1.26 (t, J = 6 Hz, 6H, CH$_2$C**H**$_3$); ^{13}C NMR (CCl_4, ppm) : 166.25 (C-1), 161.43 (C-7), 147.51 (C-8), 133.75 (C-9), 132.88 (C-5), 131.74 (C-3), 126.32 (C-10), 125.02 (C-11), 118.52 (C-4), 118.41 (C-6), 117.44 (C-2), 24.80 (**C**H$_2$CH$_3$), 14.78 (CH$_2$**C**H$_3$); and (**HL^4**) : Yellow solid; b.p. 170/0.4; IR (Nujol, cm^{-1}) : 3463m, 3063m, 2963s ν(OH), 1626s ν(C=N), 1578m ν(C=C), 1493m, 1462s, 1386m, 1362m, 1319m, 1279s ν(C-O), 1213m, 1175m, 1148m, 1111m, 1061m, 989w, 941w, 906m, 843m, 812m, 781m, 752s, 702w, 559w, 463w ; ^{1}H NMR ($CDCl_3$, ppm) : 14.18 (s, 1H, O**H**), 8.54 (s, 1H, C**H**=N), 8.34-7.56 (m, 7H, Ar-**H**), 3.35 (sept, J = 6 Hz, 2H, C**H**Me$_2$), 1.19 (d, J = 6 Hz, 12H, CH**Me**$_2$); ^{13}C NMR (CCl_4, ppm) : 166.47 (C-1), 161.38 (C-7), 146.32 (C-8), 138.19 (C-9), 133.99 (C-5), 131.90 (C-3), 125.30 (C-11), 123.02 (C-10), 119.23 (C-4), 118.63 (C-6), 117.39 (C-2), 28.00 (**C**HMe$_2$), 23.50 (CH**Me**$_2$).

Preparation of N-arylsalicylaldiminate derivatives of aluminium and gallium

The procedure essentially involved the intimate mixing of desired stoichiometric quantities of $Al(OPr^i)_3/Ga(OPr^i)_3$ and $HOC_6H_4CH=NAr$ (Ar = $C_6H_3Me_2$-2,6, $C_6H_2Me_3$-2,4,6, $C_6H_3Et_2$-2,6, $C_6H_3Pr^i_2$-2,6) in anhydrous benzene and refluxing at 105-110°C for about 6 to 18 h. During this period the liberated isopropyl alcohol was continuously fractionated out azeotropically and estimated periodically to check progress of the reaction. After completion of the reaction, excess solvent was removed under *vacuo*, and analytically pure product was recrystallized from a mixture of toluene and *n*-hexane at –20°C in quantitative yield.

Adopting the above general procedure the compounds listed below were prepared from appropriate reactants in required amounts shown in parentheses.

(**1**) : from $Al(OPr^i)_3$ (1.94 g, 9.53 mmol) and HL^2 (2.26 g, 9.46 mmol); (**2**) : from $Al(OPr^i)_3$(0.93 g, 4.56 mmol) and HL^2 (2.18 g, 9.11 mmol); (**3**) : from $Al(OPr^i)_3$(0.66 g, 3.23 mmol), and HL^2 (2.29 g, 9.57 mmol); (**4**) : from $Al(OPr^i)_3$ (2.82 g, 13.82 mmol) and HL^3 (3.49 g, 13.79 mmol); (**5**): from $Al(OPr^i)_3$ (1.56 g, 7.65 mmol) and HL^3 (3.88 g, 15.31 mmol); (**6**) : from $Al(OPr^i)_3$ (1.63 g, 8.01 mmol) and HL^3 (6.07 g, 23.97 mmol) ; (**7**) : from $Al(OPr^i)_3$ (1.45 g, 7.09 mmol) and HL^4 (1.98 g, 7.04 mmol); (**8**) : from $Al(OPr^i)_3$ (1.04 g, 5.11 mmol) and HL^4 (0.86 g, 10.17 mmol); (**9**) : from $Al(OPr^i)_3$(0.34 g, 1.66 mmol) and HL^4 (1.41 g, 5.0 mmol); (**10**) : from $Ga(OPr^i)_3$(0.75 g, 3.04 mmol) and HL^1 (2.04 g, 9.09 mmol) ; and (**11**) : from $Ga(OPr^i)_3$(0.74 g, 3.01 mmol) and HL^3 (2.29 g, 9.03 mmol).

RESULTS AND DISCUSSION

$M(OPr^i)_3$ (M = Al or Ga) reacts in benzene with different N-arylsalicylaldimines (LH shown in Scheme 1) in 1:1, 1:2, and 1:3 molar ratios to give derivatives (**1**)-(**11**) in which the coordination numbers of Al or Ga are six/four (**A**), five (**B**), and six (**C**), respectively according to the following reaction.

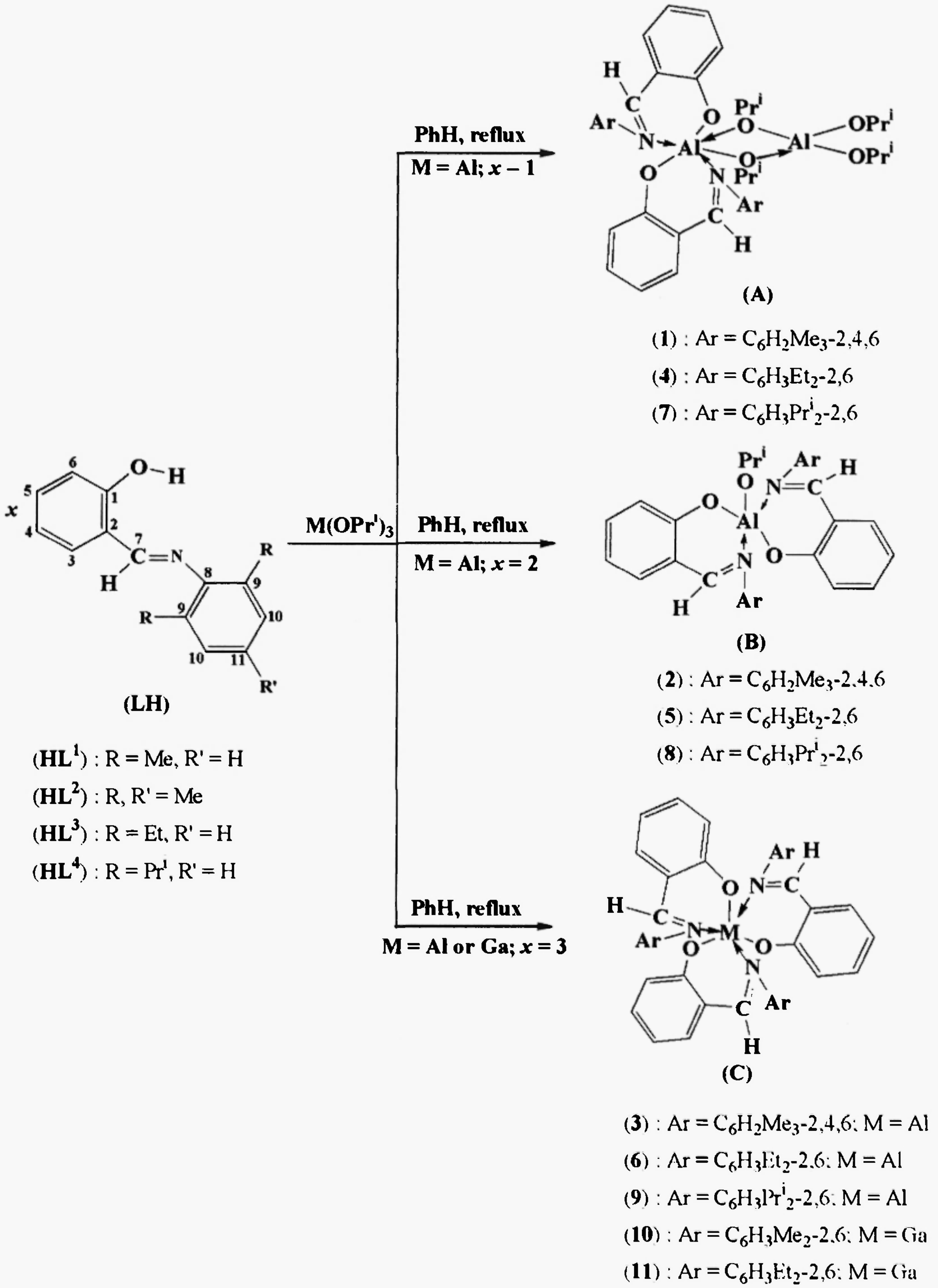
$$M(OPr^i)_3 + x\,LH \xrightarrow[\text{reflux}]{\text{benzene}} [M(OPr^i)_{3-x}(\eta^2\text{-}L)_x]_n + x\,Pr^iOH\uparrow$$

where LH = HL^1, HL^2, HL^3, and HL^4; x = 1, 2 or 3 ; M = Al or Ga ; n = 2 when x = 1, whereas in all other cases n is one.

The new derivatives (**1**)-(**11**) (Table I) are yellow solids (having sharp melting points), soluble in organic solvents (e.g., PhH, PhMe, CCl_4, CH_2Cl_2) but sparingly soluble in *n*-hexane. Derivatives (**1**), (**4**), and (**7**) are dimeric, whereas all others depict monomeric behaviour (ebullioscopically) in benzene solution.

Infrared spectra

The IR spectra (Table I) of derivatives (**1**)-(**11**) as expected do not show absorptions due to hydrogen bonded phenolic OH group in the 3400-2900 cm^{-1} region. Absorptions due to ν(C=N) and phenolic ν(C-O) appear in the 1624-1632 and 1285-1291 cm^{-1} regions, respectively. The bands due to C=N stretching vibrations appear to be almost in the same region at ~ 1625 ± 1 cm^{-1}, in the ligands as well as the aluminium (III) derivatives (**1**)-(**9**). This is consistent with the observations of some other workers [17-21] in the field. The tris-derivatives (**10**) and (**11**) of gallium, however, exhibit an increase of about 7 ± 1 cm^{-1} in C = N stretching frequency. Phenolic ν(C-O), appearing at ~ 1280 ± 2 cm^{-1} in the IR spectra of N-arylsalicylaldimines shows a shift towards higher frequencies by 5-13 cm^{-1} in comparison to the spectra of the free ligands. These observations have been generally considered to be diagnostic of chelate formation involving deprotonation of phenolic OH proton and intramolecular coordination through azomethine nitrogen [19-21]. The mixed isopropoxo-N-arylsalicylaldimino derivatives (**1**), (**2**), (**4**), (**5**), (**7**), and (**8**) exhibit additional absorptions characteristic of isopropoxo groups attached to a metal centre. For example, absorptions due to gem-dimethyl group(s) and isopropoxo ν(C-O) appear in the regions 1173-1115 and 1010-950 cm^{-1} respectively. Appearance of new medium to weak intensity bands in cases of derivatives (**1**)-(**9**) in the 673-688 and 415-440 cm^{-1} regions are assigned to ν(Al-O) [1,18,19] and ν(Al←N) [19], respectively. The absorptions due to metal-oxygen and metal-nitrogen bonds for gallium derivatives (**10**) and (**11**) appear at 515-518 and 590-595 cm^{-1}, respectively.



(LH)

(**HL^1**) : R = Me, R' = H
(**HL^2**) : R, R' = Me
(**HL^3**) : R = Et, R' = H
(**HL^4**) : R = Pr^i, R' = H

(A)

(**1**) : Ar = $C_6H_2Me_3$-2,4,6
(**4**) : Ar = $C_6H_3Et_2$-2,6
(**7**) : Ar = $C_6H_3Pr^i{}_2$-2,6

(B)

(**2**) : Ar = $C_6H_2Me_3$-2,4,6
(**5**) : Ar = $C_6H_3Et_2$-2,6
(**8**) : Ar = $C_6H_3Pr^i{}_2$-2,6

(C)

(**3**) : Ar = $C_6H_2Me_3$-2,4,6; M = Al
(**6**) : Ar = $C_6H_3Et_2$-2,6; M = Al
(**9**) : Ar = $C_6H_3Pr^i{}_2$-2,6; M = Al
(**10**) : Ar = $C_6H_3Me_2$-2,6; M = Ga
(**11**) : Ar = $C_6H_3Et_2$-2,6; M = Ga

Scheme 1. Synthesis of the compounds (1)-(11)

Table I. Physical, Analytical and Some Important Infrared Spectral Data for the New Compounds

Compound[a]	Yield[b] g(%)	M.P. °C	Analysis Found (Calcd.)		M.wt. Found (Calcd.)	IR (cm^{-1})
			M	N		
(1)	3.02 (83)	150 (dec.)	7.14 (7.04)	3.52 (3.65)	758 (383)	1624s ν(C=N), 1578s ν(C=C), 1285s ν(C-O), 678m ν(Al-O), 425m ν(Al←N)
(2)	1.98 (77)	165	4.65 (4.79)	4.79 (4.97)	572 (563)	1624s ν(C=N), 1540s ν(C=C), 1285s ν(C-O), 680m ν(Al-O), 425m ν(Al←N)
(3)	1.76 (74)	145	3.59 (3.63)	5.44 (5.66)	754 (742)	1626s ν(C=N), 1541s ν(C=C), 1286s ν(C-O), 685m ν(Al-O), 440m ν(Al←N)
(4)	3.94 (72)	200 (dec.)	6.69 (6.78)	3.45 (3.52)	800 (398)	1625s ν(C=N), 1588s ν(C=C), 1288s ν(C-O), 688m ν(Al-O), 428w ν(Al←N)
(5)	3.35 (75)	180	4.55 (4.56)	4.72 (4.73)	605 (591)	1625s ν(C=N), 1586s ν(C=C), 1288s ν(C-O), 685m ν(Al-O), 436m ν(Al←N)
(6)	4.96 (79)	145	3.48 (3.44)	5.27 (5.35)	771 (784)	1626s ν(C=N), 1588s ν(C=C), 1288s ν(C-O), 673m ν(Al-O), 415m ν(Al←N)
(7)	2.56 (85)	150 (dec.)	6.28 (6.34)	3.25 (3.29)	841 (425)	1626s ν(C=N), 1578s ν(C=C), 1287s ν(C-O), 685m ν(Al-O), 423w ν(Al←N)
(8)	2.64 (80)	125	4.25 (4.17)	4.35 (4.33)	729 (647)	1626s ν(C=N), 1541s ν(C=C), 1288s ν(C-O), 685m ν(Al-O), 425m ν(Al←N)
(9)	1.25 (86)	100	3.01 (3.10)	4.81 (4.84)	860 (868)	1626s ν(C=N), 1543s ν(C=C), 1285s ν(C-O), 688m ν(Al-O), 440m ν(Al←N)
(10)	1.80 (80)	155	9.43 (9.38)	5.58 (5.65)	735 (743)	1632s ν(C=N), 1580s ν(C=C), 1291s ν(C-O), 515m ν(Ga-O), 595w ν(Ga←N)
(11)	1.94 (78)	110	8.45 (8.43)	4.91 (5.08)	820 (827)	1630s ν(C=N), 1580s ν(C=C), 1291s ν(C-O), 518m ν(Ga-O), 592w ν(Ga←N)

[a] All are yellow solids

[b] Refers to the recrystallized product.

NMR spectra

The NMR spectral data are summarized in Tables II and III, and only a few salient features are being discussed here.

Table II. ^{1}H and ^{27}Al NMR Spectral Data for the New Compounds (1)-(11)

Compound	^{1}H (δ)	^{27}Al (δ)
(1)	1.21(d, J = 6 Hz, 12H, OCH**Me**$_2$), 2.21 (s, 6H, **Me**-2,6), 2.32 (s, 3H, **Me**-4), 4.10 (sept, J = 6 Hz, 2H, OC**H**Me$_2$), 6.75-7.64 (m, 6H, Ar-**H**), 8.45 (s, 1H, **CH**=N)	+ 38.0, + 4.08
(2)	1.20 (d, J = 6 Hz, 6H, OCH**Me**$_2$), 2.23 (s, 12H, **Me**-2,6), 2.32 (s, 6H, **Me**-4), 4.08 (sept, J = 6 Hz, 1H, OC**H**Me$_2$), 6.93-7.60 (m, 12H, Ar-**H**), 8.45 (s, 2H, C**H**=N)	+ 30.4
(3)	2.14 (s, 18H, **Me**-2,6), 2.28 (s, 9H, **Me**-4), 6.70-7.59 (m, 18H, Ar-**H**), 8.45 (s, 3H, C**H**=N)	+ 1.80
(4)	1.11 (d, J = 6 Hz, 12H, OCH**Me**$_2$), 1.17 (t, J = 6 Hz, 6H, CH$_2$C**H$_3$**), 2.50 (q, J = 6 Hz, 4H, C**H$_2$**CH$_3$), 4.50 (sept, J = 6 Hz, 2H, OC**H**Me$_2$), 6.61-7.78 (m, 7H, Ar-**H**), 8.52 (s, 1H, C**H**=N)	+ 38.5, + 3.50
(5)	1.15 (d, J = 6 Hz, 6H, OCH**Me**$_2$), 1.19 (t, J = 6 Hz, 12H, CH$_2$C**H$_3$**), 2.45 (q, J = 6 Hz, 8H, C**H$_2$**CH$_3$), 4.51 (sept, J = 6 Hz, 1H, OC**H**Me$_2$), 6.61-7.78 (m, 14H, Ar-**H**), 8.62 (s, 2H, C**H**=N)	+ 29.0
(6)	1.17 (t, J = 6 Hz, 18H, CH$_2$C**H$_3$**), 2.51 (q, J = 6 Hz, 12H, C**H$_2$**CH$_3$), 6.66-7.78 (m, 21H, Ar-**H**), 8.59 (s, 3H, C**H**=N)	+ 1.40
(7)	1.12 (d, J = 6 Hz, 12H, CH**Me$_2$**), 1.20 (d, J = 6 Hz, 12H, OCH**Me$_2$**), 2.97 (sept, J = 6 Hz, 2H, C**H**Me$_2$), 4.06 (sept, J = 6 Hz, 2H, OC**H**Me$_2$), 6.93-7.64 (m, 7H, Ar-**H**), 8.40 (s, 1H, C**H**=N)	+ 37.2, +2.67
(8)	1.20 (d, J = 6 Hz, 24H, CH**Me$_2$**), 1.25 (d, J = 6 Hz, 6H, OCH**Me$_2$**), 2.99 (sept, J = 6Hz, 4H, C**H**Me$_2$), 4.05 (sept, J = 6 Hz, 1H, OC**H**Me$_2$), 6.93-7.64 (m, 14H, Ar-**H**), 8.40 (s, 2H, C**H**=N)	+ 28.0
(9)	1.17 (d, J = 6 Hz, 36H, CH**Me$_2$**), 2.97 (sept, J = 6 Hz, 6H, C**H**Me$_2$), 6.88-7.51 (m, 21H, Ar-**H**), 8.40 (s, 3H, C**H**=N)	+ 1.88
(10)	2.27 (s, 18H, **Me**-2,6), 6.14-7.83 (m, 21H, Ar-**H**), 8.66 (s, 3H, C**H**=N)	-
(11)	1.20 (t, J = 6 Hz, 18H, CH$_2$C**H$_3$**), 2.65 (q, J = 6 Hz, 12H, C**H$_2$**CH$_3$), 7.11-7.86 (m, 21H, Ar-**H**), 8.67 (s, 3H, C**H**=N)	-

A signal due to hydrogen bonded phenolic proton at δ 13.85 ± 0.33 for parent ligands is absent in the ^{1}H NMR of new derivatives, which is characteristic of the replacement of OH group proton by a metal(loid) atom. A singlet due to the azomethine proton (-C**H**=N-) which appears at δ 8.40-8.67 exhibits a small (0.05 to 0.1 ppm) shift to downfield with respect to the parent ligands. It would not be out of place to record that there are numerous examples available in the literature [21,22], wherein similar observations have been considered to support the formation of a chelate involving deprotonation of phenolic proton and coordination of the azomethine nitrogen atom to a metal centre. The aromatic protons appear as multiplets in the region δ 6.14-7.86. Ethyl groups on the aniline moiety in (**4**), (**5**), (**6**) and (**11**) appear as a triplet and quartet in the δ 1.17-1.20 (CH$_2$**CH**$_3$) and 2.45-2.65 (**CH**$_2$CH$_3$) regions, respectively.

^{13}C NMR spectra of (**1**), (**3**) and (**6**)-(**9**) (Table III) show signals at δ 169.13 ± 2.76 due to **C**-O of N-arylsalicylaldiminate moiety, which are at ~ 0-5 ppm downfield from those observed for the parent ligands (δ 166.25-166.52). The azomethine carbon signals observed at δ 161.07-164.47, also exhibit a downfield shift of ~ 3 ppm from the **C**H=N chemical shifts (δ 161.32-161.43) observed in the case of parent ligands. The positions of other aromatic carbons are almost unaltered.

^{27}Al NMR spectra of (**3**), (**6**) and (**9**) exhibit signals at δ +1.40-1.88, consistent with hexacoordinated [1,2,23] aluminium complexes (structure **C**). Appearance of broad ($W_{1/2}$ = 3405 ± 180 Hz) signals centred at δ 29.20 ± 1.20 for the derivatives (**2**), (**5**) and (**8**) is in accordance with pentacoordinate aluminium compounds [1,23] as depicted by the structure **B**. The appearance of two signals for each of the derivatives (**1**), (**4**) and (**7**) respectively at δ 38/4.08, 38.5/3.5, and 37.2/2.67 supports an asymmetric structural form (structure **A**) with four- and six- coordinated aluminium atoms within the same molecule.

Table III. ^{13}C NMR Spectral Data (δ, ppm) for the New Compounds (1), (3), (6)-(9).

Compound	
(1)	18.05 (**Me**-2,6), 20.43 (**Me**-4), 25.31 (OCH**Me**$_2$), 67.45 (O**C**HMe$_2$), 116.97 (C-2), 118.56 (C-6), 118.37 (C-4), 127.61 (C-10), 128.80 (C-9), 131.60 (C-3), 132.68 (C-5), 133.35 (C-11), 145.41 (C-8), 161.07 (C-**7**), 166.48 (C-1)
(3)	18.31 (**Me**-2,6), 20.80 (**Me**-4), 117.72 (C-2), 118.79 (C-6), 118.99 (C-4), 127.71 (C-10), 128.78 (C-9), 131.80 (C-3), 132.58 (C-5), 134.41 (C-11), 146.26 (C-8), 162.08 (C-7), 167.07 (C-1)
(6)	14.78 (CH$_2$**C**H$_3$), 24.80 (**C**H$_2$CH$_3$), 117.44 (C-2), 118.44 (C-6), 118.58 (C-4), 125.02 (C-11), 126.39 (C-10), 131.91 (C-3), 132.80 (C-5), 133.69 (C-9), 148.71 (C-8), 161.38 (C-7), 166.52 (C-1)
(7)	23.45 (CH**Me**$_2$), 24.97 (OCH**Me**$_2$), 28.38 (**C**HMe$_2$), 66.53 (O**C**HMe$_2$), 118.01 (C-2), 118.38 (C-6), 119.39 (C-4), 123.17 (C-10), 125.43 (C-11), 131.90 (C-3), 133.25 (C-5), 138.27 (C-9), 148.59 (C-8), 164.42 (C-7), 171.89 (C-1)
(8)	23.45 (CH**Me**$_2$), 24.86 (OCH**Me**$_2$), 28.38 (**C**HMe$_2$), 66.79 (O**C**HMe$_2$),117.82 (C-2), 118.57 (C-6), 119.20 (C-4), 123.3 (C-10), 125.67 (C-11), 132.30 (C-3), 133.53 (C-5), 138.64 (C-9), 148.59 (C-8), 164.47 (C-7), 171.89 (C-1)
(9)	23.07 (CH**Me**$_2$), 27.30 (**C**HMe$_2$), 117.44 (C-2), 118.53 (C-6), 119.11 (C-4), 122.89 C-10), 125.53 (C-11), 131.74 (C-3), 133.35 (C-5), 138.39 (C-9), 147.89 (C-8), 163.87 (C-7), 171.02 (C-1)

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