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Five-coordinate organoaluminum acetylides and crystal structure of the hydrosylate, [Salophen(^{t}Bu)Al]$_2$O

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Abstract

The first examples of five coordinate aluminum acetylide compounds chelated by a single ligand are reported in this paper. The combination of L(^{t}Bu)AlCl (where L = Salen (**1**), Salpen (**2**), Salophen (**3**), Salomphen (**4**)) with LiC≡CPh in THF at −78 °C leads to the formation of the four acetylides (**5**–**8**), LC≡CPh. These are extremely moisture sensitive and readily hydrolyze to form aluminum hydroxides and with condensation form compounds of formula [L(^{t}Bu)Al]$_2$O. The hydrosylate [Salophen(^{t}Bu)Al]$_2$O (**9**) has been structurally characterized.

Keywords: Aluminum; Acetylides; Five-coordinate; Salen

1. Introduction

Since the first aluminum acetylide was reported in 1960 [1], aluminum acetylides have been used as versatile tools in organic synthesis [2–4]. For instance, alkynyldiethyl alanes have been used to alkynylate acyclic epoxides [2] and diethylalkylnylalane reagents have been employed to add acetylene units to simple α,β-unsaturated ketones [3]. Chemo-, regio, and diastereoselective alkylation via Lewis acid promoted substitution of sulfones have been achieved with vinylalanaes [4]. Although aluminum acetylides are generally dimeric with bridging acetylide ligands between two four-coordinate aluminum atoms, monomeric terminal aluminum acetylides have been reported recently [5]. The only example of a six-coordinate aluminum acetylide was observed in a new kind of carbaalane [6]. However, there have been no reports of five-coordinate aluminum acetylides. The Salen ligands can be used to achieve this coordination number for soluble, stable, and higher-coordinate main group compounds [7]. For example, some five-coordinate compounds of aluminum [8–11], gallium [12], indium [13] have been reported. Some of these can act as precursors to six-coordinate cations [14]. Beyond their fundamental interest and novelty, these high coordinate Salen-main group compounds are finding applications in catalysis [15–17]. For example, the asymmetric addition of diorgano-H-phosphonates to carbonyls (the phospho-aldol reaction) has been found to be catalyzed by chiral complexes of aluminum containing the salycen ligand framework, [(*R*,*R*)-Salcyen]AlX (X = Me, OSiMe$_2$^{t}Bu) [17]. In this paper, we have reported the use of the Salen ligands to prepare five-coordinate aluminum compounds with a single terminal acetylide ligand. They are of formula L(^{t}Bu)AlC≡CPh (where L = Salen (**5**), Salpen (**6**), Salophen (**7**), and Salomphen (**8**)). Their syntheses and spectroscopic properties will be discussed along with the crystal structure of the hydrolyzed by-product of **7**, [Salophen(^{t}Bu)Al]$_2$O (**9**).

2. Results and discussion

2.1. Synthesis and characterization of 5–8

As the reactants to synthesize compounds **5**–**8**, the Salen aluminum chlorides of formula L(^{t}Bu)AlCl (where L = Salen (**1**), Salpen (**2**), Salophen (**3**), Salomphen (**4**))

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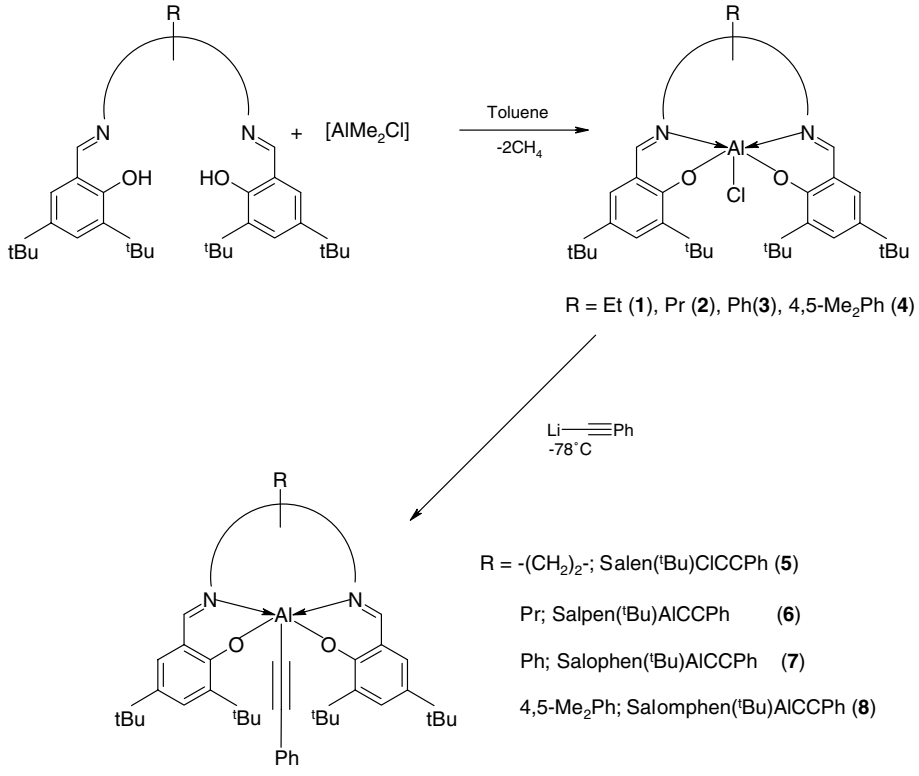
were prepared by combining the ligand with dimethyl aluminum chloride in a 1:1 ratio in toluene (Scheme 1) [9]. The NMR, IR and mass spectrometry data for compounds **1**–**9** are summarized in Table 1. The ^{27}Al NMR shifts in the range 43–57 ppm unambiguously confirm the existence of five-coordinate aluminum atoms in these compounds. Depending on the nature of the connection between the two nitrogen atoms of the ligand (the "backbone" of the ligand) [18], the compounds are either square pyramidal (with aryl backbones) or trigonal bipyramidal (with alkylene backbones). The acetylides **5**–**8** can be prepared in high yields by combining **1**–**4** with LiC≡CPh in THF at −78 °C (Scheme 1). The compounds can be isolated in good yields by filtration in CH_2Cl_2.

The ^{1}H NMR data for **5**–**8** contain two singlets for the ^{t}Bu groups and one singlet for the azomethine hydrogen, which are closely comparable to those in the chloride derivatives **1**–**4**. The acetylide phenyl resonances were observed as multiplets in the range δ 7.12–7.17 ppm. The integrated areas of protons of the phenyl and protons of the azomethine carbons are in the expected ratio of 5:2. ^{13}C NMR data for **5**–**8** display one relatively broad singlet at δ 105.5 ppm for the α-C of the



Scheme 1. Syntheses of five-coordinate aluminum acetylides.

Table 1
Selected spectroscopic Data for compounds **5**–**9**

Compound	^{1}H NMR (ppm)				^{27}Al NMR	^{13}C NMR	MS	IR
	^{t}Bu	Backbone	N–C*H*R	CCPh-*H*	(ppm) ($W_{1/2}$)	$\delta_{C\equiv C}$ (ppm)	[M$^+$]	$\nu_{C\equiv C}$ (cm^{-1})
Salen(^{t}Bu)AlC≡CPh (**5**)	1.33 (s) 1.59 (s)	3.73 (m) 4.18 (m)	8.35 (s)	7.17 (m)	39 (1042 Hz)	106.0 (br) 122.0 (s)	618, 100%	2119
Salpen(^{t}Bu)AlC≡CPh (**6**)	1.32 (s) 1.54 (s)	2.20 (m) 3.63 (m) 4.07 (m)	8.24 (s)	7.17 (m)	41 (1302 Hz)	105.5 (br) 122.0 (s)	632, 100%	2121
Salophen(^{t}Bu)AlC≡CPh (**7**)	1.40 (s)	7.68 (d) 1.69 (s)	8.91 (s) 7.77 (m)	7.15 (m)	40 (834 Hz)	105.1 (br)	666, 100% 122.1 (s)	2121
Salomphen(^{t}Bu)AlC≡CPh (**8**)	1.38 (s) 1.66 (s)	2.38 (s) 7.22 (d)	8.87 (s)	7.12 (m)	40 (625 Hz)	105.1 (br) 122.0 (s)	694, 100%	2121
[Salophen(^{t}Bu)Al]$_2$O (**9**)	1.30 (s) 1.46 (s)	7.35 (m) 7.49 (d)	7.90 (s)		48 (3751 Hz)		1147, 12%	

acetylides and another singlet at 122.0 ppm for the β-carbon. The ^{27}Al NMR for **5–8** display sharp resonances ($W_{1/2}$ ranging between 625 and 1302 Hz) compared to those for **1–4** ($W_{1/2}$ ranging between 5000 and 6500 Hz). The chemical shifts of **5–8** in ^{27}Al NMR, δ 39–41 ppm, are in the normal range for five-coordinate complexes [19]. The spectroscopic data show that **5–8** have monomeric structures and the acetylide group is terminally bound to the aluminum center.

Mass spectral data (EI) afford further support for the presence of monomeric compounds, whose molecular ion peaks were observed as m/z 618, 632, 666, and 694, respectively. It should be noted that these molecular ion peaks are base peaks. This reflects the stability of Al–C≡CPh unit in the absence of protic reagents such as H_2O.

The C≡C stretching bands for **5–8** are observed in the range, 2119–2121 cm^{-1}. When compared to LiC≡CPh (2036 cm^{-1}), they clearly confirm the presence of aluminum acetylides. Other terminal aluminum acetylides [5] such as [(^{t}Bu$_2$Pz)Al(C≡CPh)$_2$]$_2$ (2129, 2143 cm^{-1}), (^{t}Bu$_2$Pz)Al(C≡CPh)$_2$(HCCSiMe$_3$) (2075 cm^{-1}) as well as aluminum compounds with bridging acetylide ligands between two aluminum atoms such as [(CH$_3$)$_2$AlC≡CCH$_3$]$_2$ (2101 cm^{-1}) [20] have C≡C stretching frequencies comparable with those in **5–8**. However, the C≡C stretching band in carbaalane (AlMe)$_8$(CCH$_2$Ph)$_5$(C≡CPh) [6] (1957 cm^{-1}), where the acetylide ligand is bridging between four aluminum atoms, is lower than those in **5–8**. It is not possible to assign the bonding mode of acetylides in **5–8** from infrared spectroscopy. The variation of the Salen ligand seems to have no effect on the C≡C stretch.

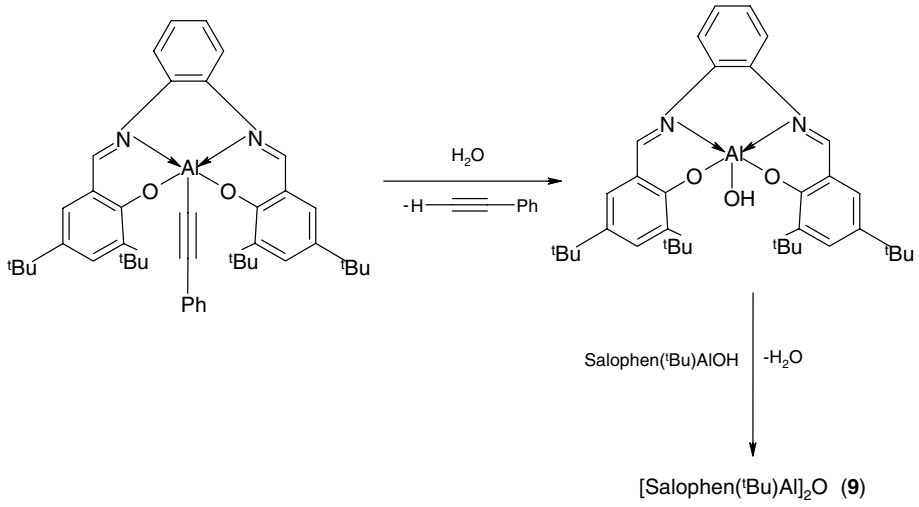
2.2. Synthesis and characterization of *9*

Like Salen aluminum amides [9] and azides [18], **5–8** are very moisture sensitive. In the presence of trace amounts of water, acetylides **5–8** hydrolyze to form aluminum hydroxides (e.g., Salophen(^{t}Bu)AlOH (Scheme 2)). The hydroxides then undergo intermolecular condensation to form dimeric molecules of formula [L(^{t}Bu)Al]$_2$O, (L = Salen, Salpen, Salophen, Salomphen) (Scheme 1).

The hydrolysate [Salophen(^{t}Bu)Al]$_2$O (**9**) was isolated and fully characterized. In the ^{1}H NMR the azomethine hydrogen (δ 7.90 ppm) shifts upfield compared to those for **1–8** (δ 8.24–8.97 ppm). A relatively broad resonance was observed at δ 48 ppm ($W_{1/2}$ = 3751 Hz) in the ^{27}Al NMR, which confirms the presence of five-coordinate aluminum atoms. The molecular ion peak (m/z 1147) with an intensity of 12% in the mass spectrum could be attributed to a dimer.

2.3. Structural description of [Salophen(^{t}Bu)Al]$_2$O (*9*)

The structure is unambiguously confirmed in the single crystal analysis (Fig. 1). Table 2 summarizes the crystal data and Table 3 the bond angles and lengths of **9**. In one molecule, two Salophen(^{t}Bu)Al units are connected together through a bridging oxygen atom. This is similar to the reported dimeric structure of [Salen(^{t}Bu)Al]$_2$O [9]. The largest Al–O–Al bond angle (173.1(1)°) was reported for **9** (Table 2) in comparison with other Al analogues (e.g., 159.5(5)° in [Salen(^{t}Bu)Al]$_2$O, 152.0(3)° in (SalenAl)$_2$O [21]) and (139.1–144.6°) in (SalenFe)$_2$O [22]). The large Al–O–Al bond angle and staggered conformation of the salophen(^{t}Bu) ligands result from steric contact between the ligands. The Al–(μ-O) bond distance (1.6840(4) Å) in **9** is shorter than that observed in [Salen(^{t}Bu)Al]$_2$O (1.696(3)Å). According to the reported method, the value τ (Tau), which measures how closely a distorted five-coordinate compound approximates either a trigonal bipyramidal or square pyramidal geometry, was calculated [23]. The τ value (0.23) of **9** suggests that the



Scheme 2. Hydrolysis mechanism of five-coordinate aluminum acetylides.

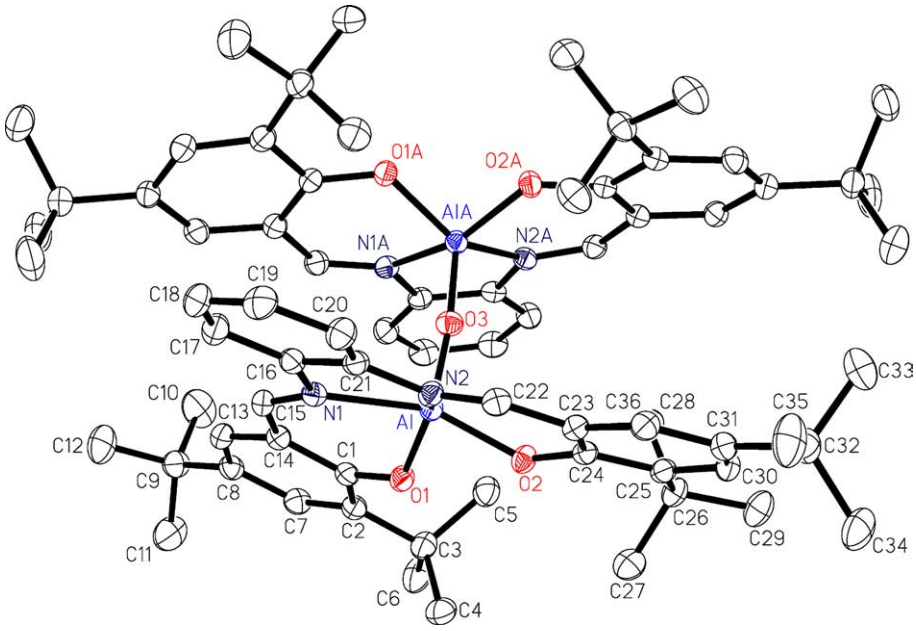


Fig. 1. Structure of [Salophen(^{t}Bu)Al]$_2$O (**9**).

Table 2
Crystal data for compound [Salophen(^{t}Bu)Al]$_2$O (**9**)

Formula weight	665.86
Color	Yellow
Crystal size (mm^3)	$0.38 \times 0.32 \times 0.30$
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	24.489(2)
b (Å)	17.0210(10)
c (Å)	18.9950(10)
α (°)	89.89
β (°)	106.263(10)
γ (°)	89.97
V (Å^3)	7600.8(9)
Z	8
F(000)	2872
D(calcd) (g cm^{-3})	1.164
μ (mm^{-1})	0.092
Unique data measured	8684
S (goodness of fit)	1.05

Table 3
Selected bond lengths (Å) and angles (°) for [Salophen(^{t}Bu)Al]$_2$O (**9**)

Al–O(1)	1.8168(10)	O(2)–C(24)	1.3125(16)
Al–O(2)	1.8074(10)	O(3)–Al(A)	1.6842(4)
Al–O(3)	1.6840(4)	N(1)–C(15)	1.2957(18)
Al–N(1)	2.0479(12)	N(1)–C(16)	1.4218(17)
Al–N(2)	2.0341(12)	N(2)–C(21)	1.4211(17)
O(1)-C(1)	1.3188(17)	N(2)–C(22)	1.3008(18)
O(1)–Al–O(2)	89.69(4)	C(15)–N(1)–C(16)	121.03(12)
O(1)–Al–O(3)	110.63(4)	Al–N(2)–C(21)	115.83(9)
O(2)–Al–O(3)	107.23(6)	Al–N(2)–C(22)	124.07(10)
O(1)–Al–N(1)	86.44(5)	C(21)–N(2)–C(22)	119.66(12)
O(2)–Al–N(1)	152.67(5)	O(1)–C(1)–C(2)	120.82(12)
O(3)–Al–N(1)	99.43(5)	O(1)–C(1)–C(14)	121.22(12)
O(1)–Al–N(2)	139.00(5)	N(1)–C(15)–C(14)	124.79(13)
O(2)–Al–N(2)	87.87(5)	N(1)–C(16)–C(17)	126.13(13)
O(3)–Al–N(2)	109.15(4)	N(1)–C(16)–C(21)	113.73(12)
Al–O(1)–C(1)	129.20(9)	N(2)–C(22)–C(23)	126.49(13)
Al–O(2)–C(24)	132.79(9)	N(2)–C(21)–C(16)	114.40(12)
Al–O(3)–Al(A)	173.1(1)	N(2)–C(21)–C(20)	126.35(13)
Al–N(1)–C(15)	123.04(10)	O(2)–C(24)–C(23)	120.57(12)
Al–N(1)–C(16)	115.30(9)	O(2)–C(24)–C(25)	121.41(12)

structure is best described as distorted square pyramidal. This value is comparable with Salophen(^{t}Bu)AlOSiPh$_3$ (τ 0.17) [18]. For the analogue [Salen(^{t}Bu)Al]$_2$O, however, the τ value is 0.46. A value of 0.50 is intermediary between trigonal bipyramidal and square pyramidal.

3. Experimental

3.1. General

All manipulations were conducted using Schlenck techniques in conjunction with an inert atmosphere Glove box. All solvents were rigorously dried prior to use. NMR data were obtained on JEOL-GSX-400 and −270 instruments at 270.17 (^{1}H), 62.5 (^{13}C), and 104.5 (^{27}Al) MHz. Chemical shifts are reported relative to $SiMe_4$ and are in ppm. Elemental analyses were obtained on a Perkin–Elmer 2400 analyzer and were found to be within acceptable limits for **5**–**9**. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. LiC≡CPh was purchased from Aldrich and used without further purification. L(^{t}Bu)AlCl (where L = Salen (**1**), Salpen (**2**), Salophen (**3**), Salomphen (**4**)) were prepared by the literature method [9].

The common names of the Salen-ligands are created by inserting the backbone abbreviation between "Sal-" and "en".

3.2. Syntheses

3.2.1. Salen(^{t}Bu)AlC≡CPh (**5**)

Salen(^{t}Bu)AlCl (0.500 g, 0.904 mmol) was dissolved in 40 mL of THF and cooled to −78 °C, and then a cooled solution (−78 °C) of lithium phenylacetylide (0.098 g, 0.905 mmol) in 40 mL of THF was added. The solution was gradually warmed to ambient temperature and stirred for an additional 4 h, and then the solvent was removed under reduced pressure to give a pale yellow solid, which was extracted using 80 mL of dichloromethane and then filtered. Compound **5** was isolated by removing the solvent from the filtrate. Yield: 0.47 g (84%). Melting point 244–246 °C.

Spectroscopic data: δ ^{1}H NMR (200 MHz, $CDCl_3$) 1.33 (s, 18H, CCH_3), 1.59 (s, 18H, CCH_3), 3.73 (m, 2H, NCH_2), 4.18 (m, 2H, NCH_2), 7.04 (d, 2H, Ph-*H*), 7.17 (m, 5H, C≡CPh-*H*), 7.56 (d, 2H, Ph-*H*), 8.35 (s, 2H, NC*H*). δ ^{13}C NMR (50 MHz, $CDCl_3$) 29.7 (CCH_3), 31.3 (CCH_3), 33.9 (CCH_3), 35.5 (CCH_3), 54.9 (NCH_2), 106.0 (br, Al*C*≡), 122.0 (C≡*C*Ph), 118.3, 127.1, 131.7, 138.0, 141.2, 163.3 (*Ph*-ligand), 126.0, 126.4, 127.6, 130.7 (C≡C*Ph*), 169.8 (N*C*H). δ ^{27}Al NMR (52.1 MHz, $CDCl_3$) 39 ($W_{1/2} = 1042$ Hz). MS(EI, positive): *m*/*z*: 618 ([M$^+$], 100%). IR (KBr, *v*, cm^{-1}): 2956(s), 2905(m), 2868(m), 1648(s), 1625(vs), 1556(m), 1541(m), 1486(m), 1474(m), 1444(m), 1418(m), 1390(m), 1361(m), 1336(m), 1311(m), 1276(m), 1256(m), 1236(m), 1203(m), 1177(m), 865(m), 754(m). *Anal*. Calc. for $C_{40}H_{51}N_2O_2Al$: C, 77.64; H, 8.31. Found: C, 77.48; H, 8.29%.

3.2.2. Salpen(^{t}Bu)AlC≡CPh (**6**)

Salpen(^{t}Bu)AlCl (1.000 g, 1.763 mmol) was dissolved in 40 mL of THF and cooled to −78 °C, and then a cooled solution (−78 °C) of lithium phenylacetylide (0.191 g, 1.767 mmol) in 40 mL of THF was added. The solution was gradually warmed to ambient temperature and stirred for an additional 4 h, and then the solvent was removed under reduced pressure to give a pale yellow solid, which was extracted using 80 mL of dichloromethane and then filtered. Compound **6** was isolated by removing the solvent from the filtrate. Yield: 0.98 g (88%). Melting point 217–219 °C.

Spectroscopic data: δ ^{1}H NMR (200 MHz, $CDCl_3$) 1.32 (s, 18H, CCH_3), 1.54 (s, 18H, CCH_3), 2.20 (m, 2H, CH_2CH_2), 3.63 (m, 2H, NCH_2), 4.07 (m, 2H, NCH_2), 7.03 (d, 2H, Ph-*H*), 7.17 (m, 5H, CCPh-*H*), 7.52 (d, 2H, Ph-*H*), 8.24 (s, 2H, NC*H*). δ ^{13}C NMR (50 MHz, $CDCl_3$) 27.5 (CH_2CH_2), 29.7 (CCH_3), 31.4 (CCH_3), 34.0 (CCH_3), 35.4 (CCH_3), 54.9 (NCH_2), 105.5 (br, Al*C*≡), 122.0 (C≡*C*Ph), 118.1, 127.0, 131.7, 137.9, 141.0, 163.0 (*Ph*-ligand), 126.1, 126.4, 127.7, 130.6 (C≡C*Ph*), 171.1 (N*C*H). δ ^{27}Al NMR (52.1 MHz, $CDCl_3$) 41 ($W_{1/2} = 1302$ Hz). MS(EI, positive): *m*/*z*: 632 ([M$^+$], 100%). IR (KBr, *v*, cm^{-1}): 2957(vs), 2905(m), 2868(m), 1640(s), 1619(vs), 1604(s), 1556(m), 1542(m), 1485(m), 1475(s), 1461(s), 1440(m), 1417(m), 1391(m), 1361(m), 1343(m), 1315(m), 1278(m), 1258(m), 1238(m), 1202(m), 1177(s), 860(m), 844(m), 757(m), 633(m). *Anal*. Calc. for $C_{41}H_{53}N_2O_2Al$: C, 77.81; H, 8.44. Found: C, 77.97; H, 8.39%.

3.2.3. Salomphen(^{t}Bu)AlC≡CPh (**7**)

Salomphen(^{t}Bu)AlCl (0.500 g, 0.795 mmol) was dissolved in 40 mL of THF and cooled to −78 °C, and then a cooled solution (−78 °C) of lithium phenylacetylide (0.086 g, 0.796 mmol) in 40 mL of THF was added. The solution was gradually warmed to ambient temperature and stirred for an additional 4 h, and then the solvent was removed under reduced pressure to give a deep red solid. This was then extracted using 50 mL of dichloromethane, filtered and the compound isolated by removing the solvent from the filtrate. Yield: 0.51 g (92%). Melting point 270–273 °C.

Spectroscopic data: δ ^{1}H NMR (200 MHz, $CDCl_3$) 1.38 (s, 18H, CCH_3), 1.66 (s, 18H, CCH_3), 2.38 (s, 6H, Ph-CH_3), 7.12 (m, 5H, C≡CPh-*H*), 7.22 (d, 2H, Ph-*H*), 7.53 (s, 2H, Ph-*H*), 7.64 (d, 2H, Ph-*H*), 8.87 (s, 2H, NC*H*). δ ^{13}C NMR (50 MHz, $CDCl_3$) 20.0 (Ph-*C* H_3), 29.9 (CCH_3), 31.3 (CCH_3), 34.0 (CCH_3), 35.4 (CCH_3), 105.1 (br, Al*C*≡), 122.0 (C≡*C*Ph), 116.4, 118.8, 127.6, 131.9, 136.3, 137.3, 138.7, 141.5, 161.4 (*Ph*-ligand), 126.0, 126.3, 128.0, 131.7 (C≡C*Ph*), 164.4 (N*C*H). δ ^{27}Al NMR (52.1 MHz, $CDCl_3$) 40 ($W_{1/2} = 625$ Hz). MS(EI, positive): *m*/*z*: 694 ([M$^+$], 100%). IR (KBr, *v*, cm^{-1}): 2955(vs), 2905(m), 2868(m), 1619(vs), 1590(s), 1552(s), 1537(vs), 1501(m), 1486(m), 1470(s), 1441(m), 1418(m), 1386(m), 1360(m), 1278(m), 1255(m), 1234(m), 1202(m), 1193(m), 1178(s), 1045(m), 846(m), 788(m), 755(m), 639(m). *Anal*. Calc. for $C_{46}H_{55}N_2O_2Al$: C, 79.50; H, 7.98. Found: C, 79.11; H, 8.25%.

3.2.4. Salophen(^{t}Bu)AlC≡CPh (**8**)

Salophen(^{t}Bu)AlCl (1.000 g, 1.663 mmol) was dissolved in 40 mL of THF and cooled to −78 °C, and then a cooled solution (−78 °C) of lithium phenylacetylide (0.180 g, 1.664 mmol) in 40 mL of THF was added. The solution was gradually warmed to ambient temperature and stirred for an additional 4h, and then the solvent was removed under reduced pressure to give a deep red solid, which was then extracted using 50 mL of dichloromethane, filtered and compound (**8**) was isolated by removing the solvent from the filtrate. Yield: 0.98 g (88%). Melting point 98–103 °C.

Spectroscopic data: δ ^{1}H NMR (200 MHz, $CDCl_3$) 1.40 (s, 18H, CCH_3), 1.69 (s, 18H, CCH_3), 7.15 (m, 5H, C≡CPh-*H*), 7.24 (d, 2H, Ph-*H*), 7.41 (m, 2H, Ph-*H*), 7.68 (d, 2H, Ph-*H*), 7.77 (m, 2H, Ph-*H*), 8.91 (s, 2H,

NC*H*). δ ^{13}C NMR (50 MHz, $CDCl_3$) 29.8 (C*C*H$_3$), 31.3 (C*C*H$_3$), 34.0 (*C*CH$_3$), 35.6 (*C*CH$_3$), 105.1 (br, Al*C*≡), 122.1 (C≡*C*Ph), 115.6, 118.6, 127.5, 131.5, 132.3, 138.4, 138.7, 141.4, 162.3 (*Ph*-ligand), 125.8, 126.3, 128.0, 131.6 (C≡C*Ph*), 164.7 (NCH). δ ^{27}Al NMR (52.1 MHz, $CDCl_3$) 40 ($W_{1/2} = 834$ Hz). MS (EI, positive): *m*/*z*: 666 ([M$^+$], 100 %). IR (KBr, *v*, cm^{-1}): 2956(vs), 2904(m), 2868(m), 1617(vs), 1583(s), 1552(s), 1538(vs), 1487(m), 1470(m), 1441(m), 1414(m), 1388(m), 1360(m), 1275(m), 1261(m), 1200(m), 1180(m), 1047(m), 845(m), 788(m), 755(m), 639(m), 598(m). *Anal*. Found: C, 79.40; H, 7.75. Calc. for $C_{44}H_{51}N_2O_2Al$: C, 79.25; H, 7.71.

3.2.5. [Salophen(^{t}*Bu)Al]$_2$O (**9**)*

(a) Salophen(^{t}Bu)AlC≡CPh (0.01 g, 0.015 mmol) was dissolved in 5 mL of toluene in an NMR tube. Yellow crystals of compound **9** were observed in the tube after being left close-capped in air for one week. The byproduct HC≡CPh was observed by ^{1}H NMR.

(b) Salophen(^{t}Bu)AlCl (1.000 g, 1.663 mmol) was dissolved in 40 mL of THF and cooled to −78 °C, and then a cooled solution (−78 °C) of lithium phenylacetylide (0.180 g, 1.664 mmol) in 40 mL of THF was added. The solution was gradually warmed to ambient temperature and stirred for an additional 4h, and then the solvent was removed under reduced pressure to give a deep red solid. The red solid was added into 20 mL of toluene and heated at reflux for 30 min. Overnight a large number of yellow crystals of [Salophen(^{t}Bu)Al]$_2$O were observed. Yield: 0.830 g (87%). Melting point 400 °C.

Spectroscopic data: δ ^{1}H NMR (200 MHz, $CDCl_3$) 1.30(s, 36H, CC*H*$_3$), 1.46(s, 36H, CC*H*$_3$), 6.80(d, 4H, Ph-*H*), 7.26 (m, 4H, Ph-*H*), 7.35 (m, 4H, Ph-*H*), 7.49(d, 4H, Ph-*H*), 7.90(s, 4H, NC*H*). δ ^{27}Al NMR (52.1 MHz, $CDCl_3$) 48 ($W_{1/2} = 3751$ Hz). MS(EI, positive): *m*/*z*: 1147 ([M$^+$], 12%). IR (KBr, *v*, cm^{-1}): 2956(vs), 2904(m), 2866(m), 1618(vs), 1586(s), 1549(s), 1535(s), 1471(m), 1443(m), 1415(m), 1386(m), 1359(w), 1296(m), 1262(m), 1241(m), 1200(m), 1035(s), 840(m), 738(m), 583(m). *Anal*. Calc. for $C_{72}H_{92}N_4O_5Al_2$: C, 75.36; H, 8.08. Found: C, 75.34; H, 8.19%.

3.3. X-ray crystallography

Crystals of **9** were mounted in oil on a Nonius kappa CCD diffractometer. The structures were solved by direct methods and successive interpretation of difference Fourier maps, followed by least squares refinement. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters. Crystallographic details are summarized in Table 2.

4. Supplementary Material

Crystallographic data for the structure described in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC number 223833. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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