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Structural diversity and versatility for organoaluminum complexes supported by mono- and di-anionic aminophenolate bidentate ligands

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ABSTRACT

The present contribution describes the synthesis and structural characterization of structurally diverse organoaluminum species supported by variously substituted aminophenolate-type ligands: these Al complexes are all derived from the reaction of $AlMe_3$ with aminophenols 2-$CH_2NH(R)$-C_6H_3OH (**1a**, R = mesityl (Mes); **1b**, R = 2,6-di-isopropylphenyl (Diip)) and 2-$CH_2NH(R)$-4,6-$^tBu_2$-C_6H_2OH (**1c**, R = Mes; **1d**, R = Diip). The low temperature reaction of $AlMe_3$ with **1a**–**b** readily affords the corresponding Al dimeric species [μ-η^1,η^1-N,O-{2-$CH_2NH(R)$-C_6H_4O}]$_2AlMe_4$ (**2a**–**b**), consisting of twelve-membered ring aluminacycles with two μ-η^1,η^1-*N,O*-aminophenolate units, as determined by X-ray crystallographic studies. Heating a toluene solution of **2a** (80 °C, 3 h) affords the quantitative and direct formation of the dinuclear aluminium complex Al[η^2-N; μ,η^2-O-{2-CH_2N(Mes)-C_6H_4O}]($AlMe_2$) (**4a**) while species **2b**, under the aforementioned conditions, affords the formation of the Al dimeric species [η^2-N,O-{2-CH_2N(Dipp)-C_6H_4O}AlMe]$_2$ (**3b**), as deduced from X-ray crystallography for both **3b** and **4a**. In contrast, the reaction of bulky aminophenol pro-ligands **1c**–**d** with $AlMe_3$ afford the corresponding monomeric Al aminophenolate chelate complexes η^2-*N,O*-{2-$CH_2NH(R)$-4,6-$^tBu_2$-C_6H_2O}$AlMe_2$ (**5c**–**d**; R = Mes, Diip; Scheme 3) as confirmed by X-ray crystallographic analysis in the case of **5d**. Subsequent heating of species **5c**–**d** yields, via a methane elimination route, the corresponding Al-THF amido species η^2-*N,O*-{2-$CH_2N(R)$-4,6-$^tBu_2$-C_6H_2O}Al(Me)(THF) (**6c**–**d**; R = Mes, Diip). Compounds **6c**–**6d**, which are of the type {X_2}Al(R)(L) (L labile), may well be useful as novel well-defined Lewis acid species of potential use for various chemical transformations. Overall, the sterics of the aminophenol backbone and, to a lesser extent, the reaction conditions that are used for a given ligand/$AlMe_3$ set essentially govern the rather diverse "structural" outcome in these reactions, with a preference toward the formation of mononuclear Al species (i.e. species **5c**–**d** and **6c**–**d**) as the steric demand of the chelating *N,O*-ligand increases.

1. Introduction

Well-defined organoaluminum compounds supported by various *N*- and/or *O*-based multidentate chelating ligands, such as, for instance, salen- and salan-derived ligands have found numerous applications in homogeneous catalysis ranging from their use in the mediation of various Lewis acid-assisted organic reactions to that in polymerization catalysis of polar monomers (cyclic esters, epoxides) [1–3]. In general, the reactivity of such group 13 metal species is greatly influenced by their molecular structure which, to some extent, may be dictated by appropriate ligand design. In this regard, the well-known propensity of group 13 metal complexes towards aggregates formation (through diverse binding/bridging modes) often complicates their coordination chemistry and the obtainment of the envisioned species. Yet, despite the frequent requirement for thorough characterization, knowledge of the coordination trends (of a given class of ligand) towards Al appears to be crucial so that to gain insight on their potential reactivity and usefulness as catalysts.

Over the past few years, we have been interested into the coordination chemistry of LX^--type bidentate aminophenolate (**A**, chart 1) towards organoaluminum compounds and showed that the derived species may yield structurally diverse mono- and

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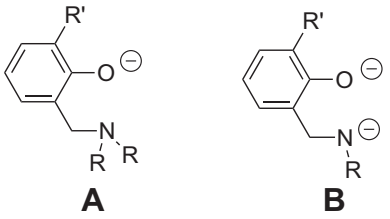


Chart 1. *N,O* bidentate aminophenolate ligands.

dinuclear aluminium species whose reactivity may greatly depend on the steric and electronic properties of the bidentate ligand [4]. These were thus far found to be effective in the mediation of several transformations ranging from the polymerization of polar monomers such cyclic esters and epoxides to the hydroalumination of aldehydes and ketones [2i,4b–f].

Over the past ten years, dianionic X^{2-}-type aminophenolate of (**B**, Chart 1) have been found to be suitable *N,O*-type chelating bidentate ligands for coordination to oxophilic and high-oxidation-state metals such group 4 metals and lanthanides frequently yielding complexes of interest as olefin polymerization catalysts [5]. In contrast, their coordination chemistry towards group 13 metals, in particular that of aluminium, remains essentially unexplored [6].

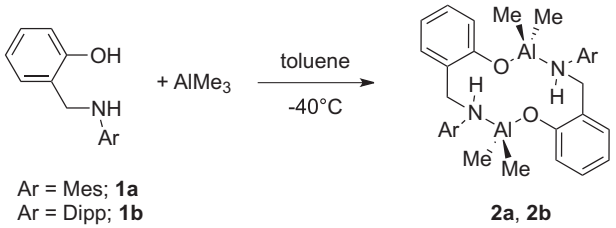
To widen the potential scope of applications of aminophenolate-supported aluminium compounds, we have become interested into studying the coordination chemistry of X_2^{2-} - type dianionic N,O-aminophenolate (type **B**, Chart 1) towards simple organoaluminum species of the type AlR_3. Apart from its fundamental interest, derived from the likely structural diversity of the envisioned aminophenolate Al compounds, we aimed at the synthesis of organoaluminium species of type $(X_2)Al(R)(L)$, where X_2^{2-} is an aminophenolate of type **B** and L labile. Organoaluminum compounds of the type $(X_2)Al(R)(L)$, which may be seen as well-defined Lewis acids, are widely used as such for the mediation of various chemical transformations [1].

Here we report a full account on the synthesis and structural characterization of aluminium complexes supported by LX- and X_2-type aminophenolate ligand of type **B**. As will be seen, various structural types/coordination modes may be observed for these Al complexes depending on the chelating ligand sterics and/or the reaction conditions.

2. Results discussion

2.1. Aminophenol pro-ligands *1a–d*

The aminophenol derivatives **1a–d** (Schemes 1 and 3) were synthesized following a classical amine condensation procedure (in the presence of Na_2SO_4 and a catalytic amount of formic acid) with a subsequent imine reduction ($NaBH_4$ for **1a–b** and $LiAlH_4$ for **1c–d**) [7].



Scheme 1. Synthesis of organoaluminum complexes **2a** and **2b**.

2.2. Organoaluminum complexes supported by sterically open aminophenolates (*2a–b*, *3b*, *4a–b*): synthesis and structural variety

As an entry point to organoaluminum complexes supported by X_2-type aminophenolate, the aminophenol derivatives **1a–b** were reacted with $AlMe_3$ under controlled and low temperature reaction conditions to disfavor the formation of a mixture of compounds. Thus, slow addition of $AlMe_3$ to one equiv. of pro-ligands 2-$CH_2NH(R)$-C_6H_4OH (**1a–b**) in toluene (−40 °C, 1 h) readily yields, via a methane elimination route, the corresponding Al dimers [μ-η^1,η^1-N,O-{2-$CH_2NH(R)$-C_6H_4O}]$_2Al_2Me_4$ (**2a–b**; R = Mes, Diip; Scheme 1), as deduced from NMR data and X-ray crystallographic analysis. An identical outcome was observed when pro-ligands **1a–b** were slowly added (−40 °C, 1 h) to a precooled $AlMe_3$ solution. Compounds **2a–b** were both isolated in high yields (91% and 82%, respectively) as air-sensitive colorless solids found to be sparingly soluble in common organic solvents with the exception of THF. In the case of compound **2a**, its dimeric nature in the solid state was unambiguously established by X-ray crystallographic analysis.

The molecular structure of **2a** is depicted in Fig. 1, and selected bond distances and angles are summarized in Fig. 1. The Al methyl compound **2a** may be described as a centrosymmetric dimer in which the two Al centers are connected to one another through two bridging LX^--type aminophenolate μ-η^1,η^1-*N,O*-2-$CH_2NH(Mes)$-$C_6H_4O^-$, resulting in the formation of a twelve-membered ring Al dimer. Both Al centers adopt a slightly distorted geometry due a small N–Al–O bond angle (92.4(1)° vs. 109.49° for an ideal tetrahedron), resulting, in turn, in an opening of the C(1)–Al–C(2) bond angle (120.4(2)°). The Al–O phenolate (1.777(2) Å) and Al–N amine (2.018(3) Å) bond distances lie within the expected range

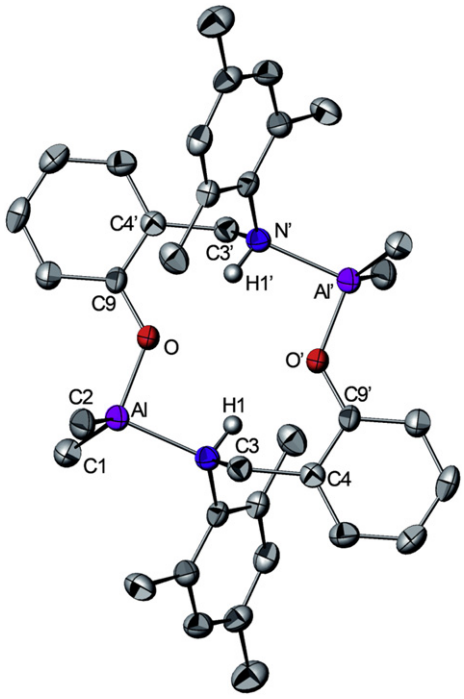


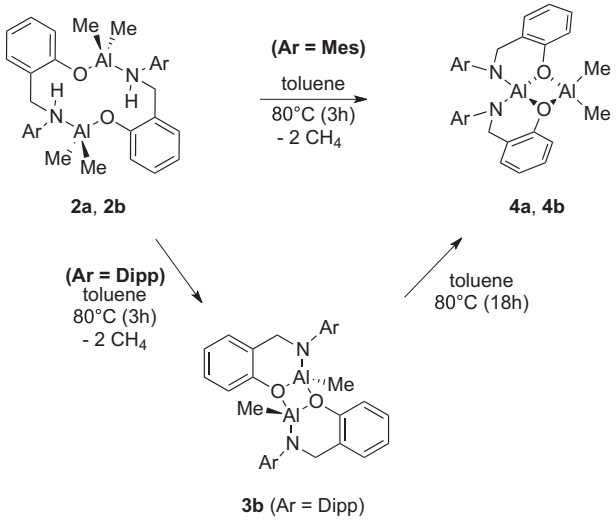
Fig. 1. ORTEP view of complex **2a**. The ellipsoids enclose 50% of the electronic density. The H atoms, except H1, as well as the solvent molecules (C_6H_6) are omitted for clarity. Symmetry codes for equivalent position': −x, −y, −z. Selected bond lengths (Å) and bond angles (°): Al–C(1), 1.950(4); Al–C(2), 1.956(4); Al–O, 1.777(2); Al–N, 2.018(3); N–Al–O, 92.4(1); C(1)–Al–C(2), 120.36(16); C(2)–Al–N, 108.03(13); C(1)–Al–O, 112.84(14); O–Al–C(2), 110.39(14).

and are comparable to those observed in related *N,O*-supported aluminium species reported so far [4,8]. From a general structural point of view, dimer **2a**, which features two *N,O*-bidentate adopting a μ-η^1,η^1 bridging mode, may be related to dimeric eight-membered ring amidate and amidinate Al complexes of the type $Me_2Al\{\mu,\eta^1,\eta^1-(N(R)C(R')O)\}_2AlMe_2$ and $Me_2Al\{\mu$-η^1,η^1-$(N(R)C(R')N(R))\}_2AlMe_2$, respectively [9,10]. The latter two classes of compounds were also found to readily form upon reaction of $AlMe_3$ with relatively unhindered amides or amidines.

The NMR data for complexes **2a**–**b** under the studied conditions (thf-d^8, room temperature) closely relate to one another and are all consistent with effective C_s-symmetric structures for both complexes which, in the case of **2a**, agree with its solid state structure being retained in solution. In particular, the NMR spectrum for complex **2a** features two characteristic doublet resonances (δ 3.22 and 4.34, 4H) corresponding to the Ph*CHH'* moieties along with a typical resonance for the N*H* moiety (δ 4.74, 2H).

While the organoaluminum dimers **2a**–**b** are stable for weeks under inert atmosphere in thf solution, they both readily react upon heating, yet in a somewhat different manner. Thus, heating a toluene solution of **2a** (80 °C, 3 h) affords the quantitative and direct formation of the dinuclear aluminium complex $Al[\eta^2$-N; μ,η^2-O-{2-CH_2N(Mes)-C_6H_4O}$](AlMe_2)$ (**4a**, Scheme 2); in contrast, species **2b** yields under the aforementioned conditions the formation of $[\eta^2$-N,O-{2-CH_2N(Dipp)-C_6H_4O}$AlMe]_2$ (**3b**, Scheme 2) as the major product. Both Al species **4a** and **3b** were isolated as colorless solids and, unlike compounds **2a**–**b**, solubilize well in common aromatic solvents. The molecular structures of both complexes were determined by X-ray crystallography analysis and are depicted in Figs. 2 and 3; their overall structural features are briefly discussed below (for **3b** and **4a**, see captions of Figs. 2 and 3 for selected bond distances and angles).

As illustrated in Fig. 2, compound **3b** $[\eta^2$-N,O-{2-CH_2N(Dipp)-C_6H_4O}$AlMe]_2$ crystallizes as a centrosymmetric dimer and its molecular structure may be formally described as two three-coordinate η^2-N,O-{2-CH_2N(Dipp)-C_6H_4O}AlMe moieties being linked to one another via the two μ,η^2-O phenolates; this results in the formation of a centrally located and nearly planar Al_2O_2 core with the two Al-bonded methyl groups being disposed in a *trans* fashion relative to the Al_2O_2 core. Both bridging oxygens are symmetrically bonded to each Al center as reflected from the nearly identical Al–O and Al'–O bond distances (1.856(1) and 1.863(1) Å). These values are comparable to related bridging phenolate Al



Scheme 2. Synthesis of aminophenolate dinuclear aluminum species **3b**, **4a** and **4b**.

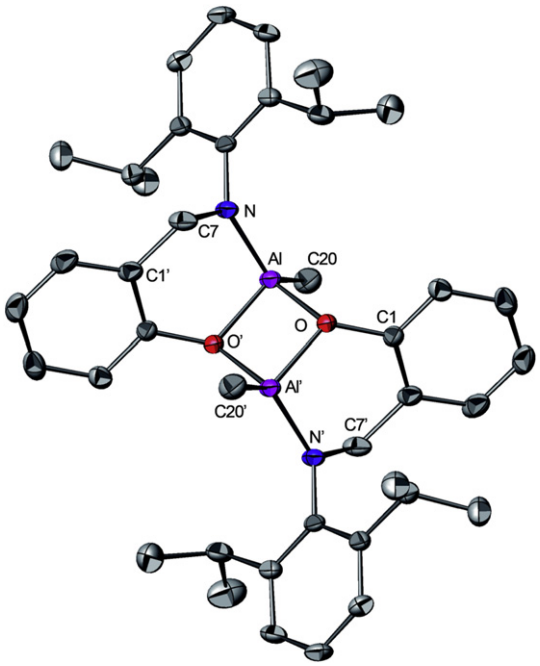


Fig. 2. ORTEP view of complex **3b**. The ellipsoids enclose 50% of the electronic density. The H atoms are omitted for clarity. Symmetry codes for equivalent position ': −x, −y, 1−z. Selected bond lengths (Å) and bond angles (°): Al–C(20), 1.931(2); Al–N, 1.786(1); Al–O, 1.856(1); Al′–O, 1.863(1); N–Al–O, 98.21(7); C(20)–Al–O, 121.86(4); C(20)–Al–N, 122.77(5); Al–O–Al′, 99.97(6); O′–Al–O, 80.03(6).

complexes with, for instance, an Al–O bond distance of 1.875(2) Å (average) for the dimer $[(^iBu)_2Al(\mu$-OPh$)]_2$ [11]. Both Al centers feature distorted tetrahedral geometries as a result of the geometrical constraints imposed by the O-bridging phenolates and the η^2-(NO)Al chelate [N–Al–O = 98.21(7)° compensated for by an opening of the C(20)–Al–O and C(20)–Al–N bond angles, 121.86(4) and 122.77(5)°, respectively]. It is finally noteworthy that the terminal amido Al–N bond distance (Al–N = 1.786(1) Å) is among the shortest reported to date (typical range 1.78–1.86 Å), which, given the fact that the nature of the Al–N bond is very likely to be essentially electrostatic based on various reports on that matter,

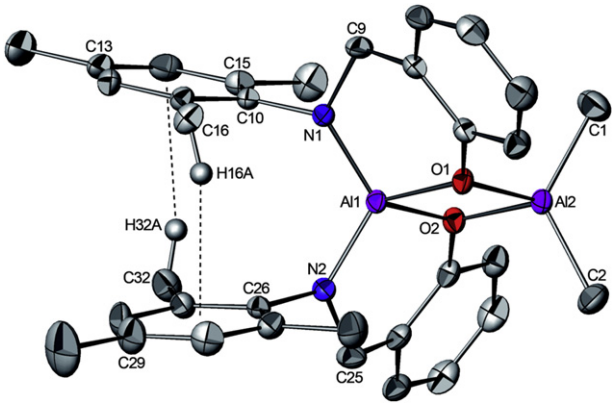


Fig. 3. ORTEP view of complex **4a**. The ellipsoids enclose 50% of the electronic density. The H atoms are omitted for clarity with the exception of H16A and H32A which are implicated in CH-π interactions (dashed lines). Selected bond lengths (Å) and bond angles (°): Al(1)–N(1), 1.776(3); Al(1)–N(2), 1.774(3); Al(1)–O(1), 1.843(3); Al(1)–O(2), 1.845(3); Al(2)–O(1), 1.856(3); Al(2)–O(2), 1.864(3); Al(2)–C(1), 1.940(5); Al(2)–C(2), 1.936(5); H(16a)–Ar, 3.557(5); H(32a)–Ar, 3.539(5); N(1)–Al(1)–N(2), 118.57(14); O(1)–Al(1)–O(2), 80.12(12); O(1)–Al(2)–O(2), 79.29(11); C(1)–Al(2)–C(2), 125.2(2); O(1)–Al(2)–O(2)–Al(1), 0.90(12).

most probably reflects a highly polar Al–N bond in **3b** [12]. In solution, the ^{1}H and ^{13}C NMR data for **3b** are all consistent with the presence of center of inversion, and thus with an effective C_i-symmetric structure, under the studied conditions (room temperature, C_6D_6). In addition, species **3b** appears to be rather robust at room temperature in solution with no sign of dissociation in a coordinative solvent such as THF. In contrast, **3b** readily reacts in hot THF (60 °C), yet to yield an untractable mixture of products.

Structurally different from dimer **3b**, compound **4a**, whose molecular structure is depicted in Fig. 3, is a dinuclear Al species featuring two μ,η^2-aminophenolate units bridging two Al centers, both of which being in a quite different coordination environment. Thus, while Al(1) is η^2-chelated by two X_2-type *N,O*-aminophenolate to adopt a distorted tetrahedral environment, Al(2) is connected to Al(1) via two μ-O oxygen phenolates (O(1) and O(2)) with the rest of its coordination sphere being completed by two methyl groups. Overall, species **4a** nearly exhibits a C_2-symmetric structure (with a C_2 axis defined by the two Al atoms Al(1) and Al(2)) and, with the exception of rather short terminal amido Al–N bond distances (1.775(6) Å average), its structural features (as deduced from bonding and geometrical parameters, Fig. 3) are rather normal. As for the solution structure of **4a**, the room temperature NMR data agree with a C_2-symmetric species under the studied conditions: it thus appears likely that **4a** retains its solid-state molecular structure in solution.

The difference of reactivity (upon heating) between the twelve-membered ring Al dimer **2a** and its analogue **2b**, which only differ by the size of the N-*R* amido substituent (Mes vs. Diip, respectively), prompted us to also investigate the relative reactivity of the derived products (**4a** and **3b**, respectively) so that to gain a better understanding of these Al aminophenolate systems. Thus, while dinuclear Al compound **4a** is stable for days in refluxing toluene with no sign of decomposition (as deduced from an NMR monitoring), the Al dimer **3b** was found to quantitatively afford in toluene (80 °C, 18 h) the dinuclear Al species Al[η^2-N; μ,η^2-O-{2-CH_2N(Diip)-C_6H_4O}]($AlMe_2$) (**4b**, Scheme 2), isostructural to species **4a** as determined by X-ray crystallographic studies (see Fig. 4 for the molecular structure and selected bonding parameters). In addition, as may be expected, a prolonged heating of dimer **2b** (toluene, 80 °C, 24 h) afforded the quantitative and direct formation of **4b**.

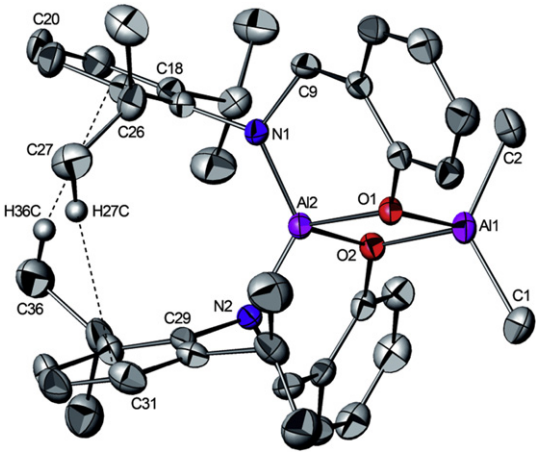


Fig. 4. ORTEP view of complex **4b**. The ellipsoids enclose 50% of the electronic density. The H atoms are omitted for clarity, with the exception of H27C and H37C which are implicated inCH-π interactions (dashed lines). Selected bond lengths (Å) and bond angles (°): Al(2)–N(1), 1.7816(19); Al(2)–N(2), 1.7759(19); Al(2)–O(1), 1.8402(14); Al(2)–O(2), 1.8463(15); Al(1)–O(1), 1.8591(15); Al(1)–O(2), 1.8678(15); Al(1)–C(1), 1.932(3); Al(2)–C(2), 1.937(3); H(27C)–Ar, 3.724(3); H(36C)–Ar, 3.822(4); N(1)–Al(2)–N(2), 125.47(8); O(1)–Al(2)–O(2), 80.60(6); O(1)–Al(1)–O(2), 79.55(6); O(1)–Al(1)–C(1), 110.42(10); C(1)–Al(1)–C(2), 126.61(2).

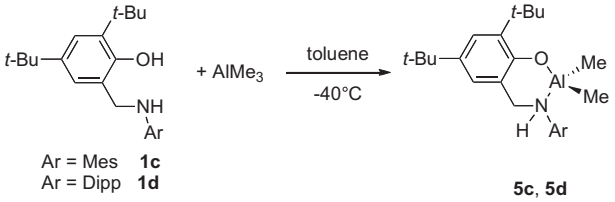
Altogether, the latter observations and experimental data for the **2b** system clearly show the initial formation of **3b** as a kinetic product, susceptible to be converted to the thermodynamically more stable dinuclear species **4b**. In the case of the more sterically open mesityl-substituted amido analogue **2a**, despite the use of various reaction conditions, the formation of a putative kinetic product "[η^2-N,O-{2-CH_2N(Dipp)-C_6H_4O}$AlMe]_2$" analogous to **3b**, was not observed: this strongly suggests that such a species, if it forms, is merely an intermediate that readily reacts (to yield **4a**) under the conditions required for its formation.

2.3. Organoaluminum complexes supported by sterically bulky aminophenolates (*5c–d, 6c–d*)

The reaction of bulky aminophenol pro-ligands **1c–d**, which both contain *tert*-butyl *ortho*-substituted phenol groups, with $AlMe_3$ was studied as the derived aminophenolate Al complexes, for steric reasons, may be less prone to the formation of aggregates and thus favour the obtainment of mononuclear Al species structurally different from those reported herein thus far. The use of chelating ligands containing ^{t}Bu-*ortho*-substituted phenol entities has been previously shown to promote the formation of well-defined mononuclear Al species. Representative examples in this area include the synthesis of various alumatranes, in which the Al metal center is effectively η^4-chelated by an amino-trisphenolate tri-anionic tetradentate ligand [13].

The aminophenol derivative 2-CH_2NH(R)-4,6-^{t}Bu$_2$-C_6H_2OH (**1c–d**; R = Mes or Diip) readily reacted with one equiv. $AlMe_3$ via a methane elimination route (toluene, −40 °C to 0 °C, 1 h) to afford the corresponding monomeric Al aminophenolate chelate complexes η^2-*N,O*-{2-CH_2NH(R)-4,6-^{t}Bu$_2$-C_6H_2O}$AlMe_2$ (**5c–d**; R = Mes, Diip; Scheme 3), as deduced from NMR data and X-ray crystallographic analysis. Compounds **5c–d** were isolated as colorless solids in high yield and are highly soluble species in common hydrocarbon solvents. In the case of **5d**, its molecular structure was determined by X-ray crystallographic studies unambiguously establishing **5d** as a monomeric species. As depicted in Fig. 5, compound **5d** crystallizes as a four-coordinate Al dimethyl species effectively η^2-*N,O*-chelated by the LX$^-$-type 2-CH_2NH(Diip)-4,6-^{t}Bu$_2$-$C_6H_2O^-$ anionic aminophenolate ligand. The Al center in **5d** adopts a slightly distorted tetrahedral structure with a (NO)Al bite angle (O(1)–Al(1)–N(1) = 95.43(7)°) along with larger along with larger C(28)–Al(1)–C(29) etc.

C(28)–Al(1)–C(29) and N(1)–Al(1)–C(29) bond angles (117.0(1)° and 116.90(9)°, respectively). The six-membered-ring Al metallacycle is significantly puckered with the Al-NH(Diip) moiety well above the nearly planar C(15)–C(6)–O(1)–Al(1) backbone, as shown by the O(1)–C(1)–C(15)–N(1) and C(15)–C(6)–Al(1)–O(1) torsion angles (54.73 and 50.57°, respectively), thus resulting in an overall C_1 symmetry for compound **5d** in the solid state. The Al–O and Al–N bond distances (1.768(2) and 2.049(2) Å, respectively) are in the normal range found for aluminium phenolates (1.640(5)-1.773(2) Å) [14] and for Al–N dative bonds (1.957(3)-2.238(4) Å) [15], respectively. As for the behaviour of compound **5d** in the



Scheme 3. Preparation of mononuclear organoaluminum **5c** and **5d**.

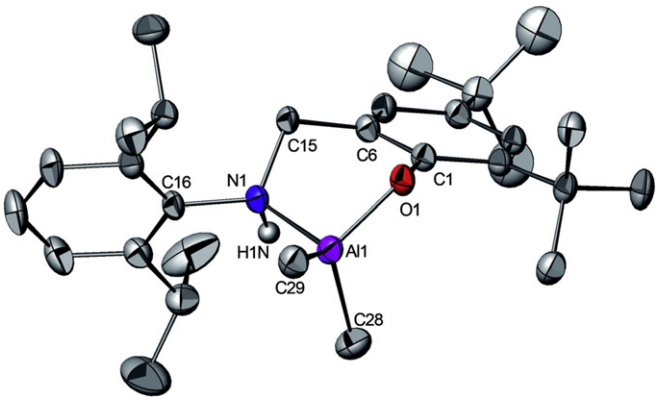


Fig. 5. ORTEP view of complex **5d**. The ellipsoids enclose 50% of the electronic density. The H atoms are omitted for clarity except for H(1N). Selected bond lengths (Å) and bond angles (°): C(28)–Al(1), 1.970(3); C(29)–Al(1), 1.945(2); N(1)–Al(1), 2.049(2); O(1)–Al(1), 1.7679(16); O(1)–Al(1)–C(29), 112.99(11); C(29)–Al(1)–C(28), 117.01(11); O(1)–Al(1)–N(1), 95.43(7); C(29)–Al(1)–N(1), 116.90(9); N(1)–Al(1)–C(28), 99.30(10).

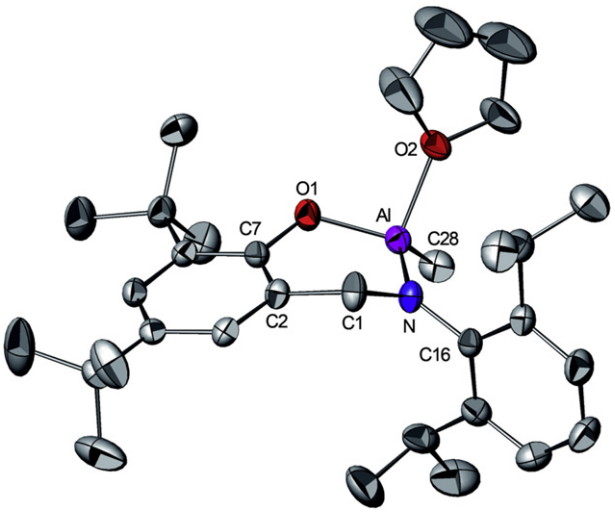
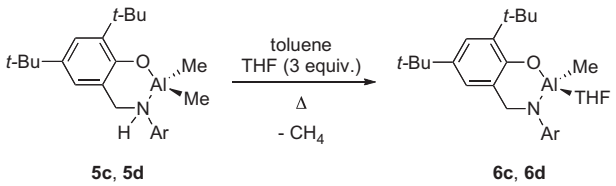


Fig. 6. ORTEP view of complex **6d**. The ellipsoids enclose 50% of the electronic density. The H atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al–O(1), 1.740(2); Al–N, 1.795(3); Al–O(2), 1.896(3); Al–C(18), 1.948(4); O(1)–Al–N, 101.79(12); O(2)–Al–C(28), 104.06(14); N–Al–O(2), 110.18(13).

solution, all NMR data agree with the effective chelation of the LX^--type $\{2\text{-}CH_2NH(Diip)\text{-}4,6\text{-}^tBu_2\text{-}C_6H_2O\}^-$ anion onto Al along with an overall C_1 symmetry. For instance, the ^1H NMR spectrum contains two Al-*Me* singlet resonances (δ −0.49 and −0.18), two sets of signals for the PhC*HH'* groups (δ 3.31 and 4.75) and a doublet resonance (δ 5.18, $^3J_{HH}$ = 11Hz) assigned to the N*H* entity. The observation of such a doublet (due to a strong $^2J_{HH}$ vicinal coupling of the N*H* moiety to one of the PhCH_2 hydrogens) versus, for instance, a triplet-type resonance has to be related to quite different H-C-N-H dihedral angles for the two PhCH_2 hydrogens in **5d**: the latter, based on classical Karplus curve correlations, may greatly impact the values of coupling constants [16]. In the present case, from a solution structure point of view, this suggests that the six-membered-ring Al aminophenolate metallacycle in **5d** is rather rigid in solution under the studied conditions (room temperature, C_6D_6) with, presumably, slow conformation changes on the NMR time scale. As a comparison, under similar conditions, related Al aminophenolate complexes such as η^2-*N,O*-$\{2\text{-}CH_2NR_2\text{-}6\text{-}^tBu\text{-}C_6H_3O\}AlMe_2$ (R = alkyl) were found to undergo a fast conformation change of the six-membered metallacycle [2i]. In the case of complex **5d**, the severe steric crowding along with bonding requirements within the Al metallacycle rationalizes such a robustness. Based on NMR data, the mesityl analogue **5c** is structurally similar to **5d**.

Though compounds **5c**–**d** were found to afford an untractable mixture of product upon heating in toluene (80 °C), well-defined Al species may be obtained under the latter conditions but in the presence of a few equiv. of a Lewis base such as THF. Thus, compounds **5c**–**d** can be cleanly converted (80 °C, toluene, 3 equiv. of THF), via a methane elimination route, to the corresponding X_2-aminophenolate Al methyl complexes η^2-*N,O*-$\{2\text{-}CH_2N(R)\text{-}4,6\text{-}^tBu_2\text{-}C_6H_2O\}Al(Me)(THF)$ (**6c**–**d**; R = Mes, Diip; Scheme 4). Compounds **6c**–**d** were isolated in reasonable yields as analytically pure colourless solids found to be highly soluble in hydrocarbon solvents. As depicted in Fig. 6, the X-ray-determined molecular structure of **6d** features a monomeric Al species in which the Al center is effectively chelated in a η^2- fashion by the dianionic chelating aminophenolate η^2-*N,O*-$2\text{-}CH_2N(Diip)\text{-}4,6\text{-}^tBu_2\text{-}C_6H_2O^{2-}$, resulting in the formation of a severely distorted six-membered Al metallacycle. The structural and bonding parameters for **6d** (see Fig. 6) overall relate to those for **5d** discussed above. As expected when going from an Al amino to an Al-amido bond, the Al-N bond distance in **6d** (1.795(3) Å) is significantly shorter than that in **5d** (2.049(2) Å). The NMR data for species **6c**–**d** in solution (C_6D_6, room temperature) are consistent an overall C_1-symmetric structure, the effective coordination of THF to the Al center and, in the case of **6d**, with its solid state structure being retained in solution under the studied conditions. Thus, for instance, the ^1H NMR spectrum for **6c** exhibits three *Me*-mesityl singlet resonances while that for **6d** displays four distinct doublets for the *Me*-^{i}Pr groups. In contrast, species **6c** and **6d** both feature an effective C_s-symmetric structure in the presence of excess THF suggesting fast coordination/decoordination process (presumably via an associative mechanism) of THF on the NMR time scale under the studied conditions (C_6D_6, room temperature). The latter observations also establish compounds **6c**–**6d** as species of the type $\{X_2\}Al(R)(L)$ (L labile), thus susceptible to act as well-defined Lewis acids and/or to be interest for the activation/polymerization of polar monomers.



Scheme 4. Synthesis of the Al-THF adducts **6c** and **6d**.

3. Summary – conclusion

The present work shows that the reaction of variously substituted *N,O*-X_2-type aminophenol pro-ligands **1a**–**d** with $AlMe_3$ may open the way to structurally diverse and well-defined di- and mononuclear organoaluminum species bearing either a monoanionic LX^--type or a dianionic X_2^{2-}-type aminophenolate chelating ligand. The observed structural variety is clearly related to the bonding versatility of the aminophenolate moiety as reflected by the diverse bonding modes that may be adopted upon coordination to Al, which include: (i) an LX^--type $\mu\text{-}\eta^1\text{-}N,\eta^1\text{-}O$ bridging mode for **2a**–**b**, (ii) a X_2^{2-}-type μ–O,η^2-N,O bridging mode for compounds **3b** and **4a**–**b**, (iii) an LX^--type η^2-N,O chelating mode for compounds **5c**–**d** and (iv) a X_2^{2-}-type η^2-N,O chelating mode for derivatives **6c**–**d**. Overall, the sterics of the aminophenol backbone

and, to a lesser extent, the reaction conditions that are used for a given ligand/$AlMe_3$ set essentially govern the "structural" outcome in these reactions, with a preference toward the formation of mononuclear Al species (i.e. species **5c**–**d** and **6c**–**d**) as the steric demand of the chelating *N,O*-ligand increases.

4. Experimental section

4.1. General procedures

All experiments were carried out under N_2 using standard Schlenk techniques or in a Mbraun Unilab glovebox, with the exception of those involving the synthesis of the aminophenol proligands **1a**–**d**. Toluene, pentane, diethyl ether and tetrahydrofuran were collected after going through drying columns (SPS apparatus, MBraun) and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. CD_2Cl_2, C_6D_6 and thf-d^8 were distilled from CaH_2, degassed under a N_2 flow and stored over activated molecular sieves (4 Å) in a glovebox prior to use. $AlMe_3$ was purchased from Strem and used as received. All deuterated solvents were obtained from Eurisotop (CEA, Saclay, France). All other chemicals were purchased from Aldrich and were used as received. NMR spectra were recorded on Bruker AC 300 or 400 MHz NMR spectrometers at ambient temperature and in Teflon-valved J-Young NMR tubes for all aluminum complexes. ^1H and ^{13}C chemical shifts are reported vs. $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent peaks. Elemental analysis for all compounds were performed at the Services de Microanalyse of the Université Pierre et Marie Curie (Paris, France) and the Université de Strasbourg (Strasbourg, France).

4.2. Synthesis of aminophenol ligands ***1a*–*d***

The aminophenol precursors **1a**–**d** were prepared by condensation of the amine with the 2-hydroxybenzaldehyde derivative in methanol and in the presence of Na_2SO_4 and a catalytic amount of formic acid. The crude product was then reduced using $NaBH_4$ in methanol (for **1a**–**b**) or $LiAlH_4$ in diethyl ether (for **1c**–**d**) to yield the desired product after purification by flash chromatography (SiO_2, CH_2Cl_2).

4.2.1. 2-[(Mesitylamino)methyl]phenol (*1a*)

70% yield. ^1H NMR ($CDCl_3$): δ 7.24 (dd, ^3J = 7.8 Hz, 1H, C*H*$_{meta}$), 7.06 (d, ^3J = 7.5 Hz, 1H, C*H*$_{ortho}$), 6.95 (d, ^3J = 8.0 Hz, 1H, C*H*$_{meta}$), 6.91 (s, 2H, C*H*$_{mesityl}$), 6.83 (dd, ^3J = 7.5 Hz, 1H, C*H*$_{para}$); 4.15 (s, 2H, C*H*$_2$), 2.38 (s, 6H, C*H*$_{3\ ortho}$), 2.28 (s, 3H, C*H*$_{3\ para}$); ^{13}C {^1H} NMR ($CDCl_3$): δ 157.9, 140.8, 134.4, 131.7, 129.9, 129.2, 128.4, 122.6, 119.5, 116.8, 52.8 (*C*H$_2$), 20.7 (*C*H$_{3\ ortho}$), 18.3 (*C*H$_{3\ para}$); MS (ESI) *m/z*: 242.156 $(M + H)^+$.

4.2.2. 2-[(2,6-Diisopropylphenylamino)methyl]phenol (*1b*)

71% yield. ^1H NMR ($CDCl_3$): δ 7.25 (dd, ^3J = 7.8 Hz, 1H, C*H*$_{meta}$), 7.19 (s, 3H, C*H*$_{2\text{-}6\text{-}disopro.}$), 7.07 (d, ^3J = 7.4 Hz, 1H, C*H*$_{ortho}$), 6.97 (d, ^3J = 8.2 Hz, 1H, C*H*$_{meta}$), 6.86 (dd, ^3J = 8.5 Hz, 1H, C*H*$_{para}$); 4.16 (s, 2H, C*H*$_2$), 3.29 (m, ^3J = 6.8 Hz, 2H, -C*H*Me$_2$), 1.30 (d, ^3J = 6.8 Hz, 12H, -CH*Me*$_2$); ^{13}C {^1H} NMR ($CDCl_3$): δ 157.8, 143.0, 140.3, 129.3, 128.5, 125.9, 124.0, 122.5, 119.5, 116.8, 55.9 (*C*H$_2$), 28.2 (*C*HMe$_2$), 24.3 (CH*Me*$_2$); MS (ESI) *m/z*: 284.203 $(M + H)^+$.

4.2.3. 2-[(Mesitylamino)methyl]-4,6-di-tert-butylphenol (*1c*)

53% yield. ^1H NMR ($CDCl_3$, 298 K): δ 10.4 (broad s, 1H, O*H* or N*H*), 7.22 (s, 1H, C*H*$_{arom.}$), 6.93 (s, 1H, C*H*$_{arom.}$), 6.91 (s, 2H, C*H*$_{mes}$), 4.12 (s, 2H, CH2), 3.4 (broad s, 1H, X*H*), 2.39 (s, 6H, C*H*$_{3\ ortho}$), 2.28 (s, 3H, C*H*$_{3\ para}$), 1.48 (s, 9H, ^{t}Bu), 1.32 (s, 9H, ^{t}Bu); ^{13}C {^1H} NMR ($CDCl_3$, 298 K): δ 154.5, 150.4, 141.0, 136.5, 131.8, 129.9, 124.9, 123.6, 123.4, 122.2, 53.5 (*C*H$_2$), 35.1, 34.2, 31.7 (^{t}Bu), 29.7 (^{t}Bu), 20.7, 18.4; MS (ESI): *m/z*: 354.276 $(M + H)^+$.

4.2.4. 2-[(2,6-Disopropylphenylamino)methyl]-4,6-di-tert-butylphenol (*1d*)

42% yield. ^1H NMR ($CDCl_3$, 298 K): δ 10.1 (broad s, 1H, O*H* or N*H*), 7.33 (m, 1H, C*H*$_{arom.}$), 7.19 (s, 3H, C*H*$_{2\text{-}6\text{-}disopro.}$), 6.92 (s, 1H, C*H*$_{arom}$), 4.14 (s, 2H, C*H*$_2$), 3.33 (m, ^3J = 6.8 Hz, 2H, –C*H*Me$_2$), 1.48 (s, 9H, ^{t}Bu), 1.32–1.16 (m, 21H, ^{t}Bu, CH*Me*$_2$); ^{13}C {^1H} NMR ($CDCl_3$, 298 K): δ 154.5, 150.4, 141.0, 136.5, 131.8, 129.9, 124.9, 123.6, 123.4, 122.2, 53.5 (*C*H$_2$), 35.1, 34.2, 31.7 (^{t}Bu), 29.7 (^{t}Bu), 20.7, 18.4; MS (ESI): *m/z*: 354.276 $(M + H)^+$.

4.2.5. [μ-η^1,η^1-*N,O*-{2-CH_2NH(Mes)-C_6H_4O}]$_2Al_2Me_4$ (*2a*)

To a precooled toluene solution (−40 °C, 2 mL) of the aminophenol derivative **1a** (89.0 mg, 0.373 mmol), a toluene solution (1 mL) of $AlMe_3$ (26.9 mg, 0.373 mmol), also precooled at −40 °C, was added dropwise via a pipette. Upon addition of $AlMe_3$, the initial colorless solution immediately became cloudy to eventually a colorless suspension. After the addition, the mixture was allowed to warm to room temperature and stirred for 1 h, after which it was filtered through a glass frit under reduced pressure. The collected solid was washed twice with pentane and dried *in vacuo* to afford the Al compound **2a** (110 mg, 91% yield) as an analytically pure colorless solid. The outcome and yield of the latter reaction are identical when a precooled toluene solution of ligand **2a** is slowly added a precooled toluene solution of $AlMe_3$. Anal. Calcd for $C_{36}H_{48}Al_2N_2O_2$: C, 72.70; H, 8.13; N, 4.71. Found: C, 72.93; H, 8.34; N, 4.85. ^1H NMR (300 MHz, thf-d^8): δ −0.67 (s, 6H, $AlMe_2$), −0.54 (s, 6H, $AlMe_2$), 1.71 (s, 6H, Mes), 1.98 (s, 6H, Mes), 2.17 (s, 6H, Mes), 3.22 (d, $^3J_{HH}$ = 11.1 Hz, 2H, PhC*H*H'), 4.34 (t, J_{HH} = 11.5 Hz, 2H, PhCH*H*'), 4.74 (d, $^3J_{HH}$ = 11.5 Hz, 2H, NH), 6.59 (s, 2H, Mes), 6.65 (s, 2H, Mes), 6.77 (t, $^3J_{HH}$ = 6.5 Hz, 2H, Ph), 6.82 (d, $^3J_{HH}$ = 6.2 Hz, 2H, Ph), 6.95–7.23 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, thf-d^8): δ −10.5 (AlMe), −9.7 (AlMe), 17.6 (br, Mes), 21.3 (Mes), 22.2 (Mes), 55.2 (PhCH$_2$), 123.1 (Ph), 125.2 (Ph), 126.0 (Ph), 127.4 (Ph), 129.3 (Ph), 136.2 (Ph), 136.8 (Ph), 137.1 (Ph), 137.5 (Ph), 139.2 (Ph), 139.9(Ph), 157.2 (Ph).

4.2.6. [μ-η^1,η^1-*N,O*-{2-CH_2NH(Dipp)-C_6H_4O}]$_2Al_2Me_4$ (*2b*)

The dinuclear organoaluminum complex **2b** was synthesized and isolated using an identical procedure to that for the synthesis of complex **2a**, using an equimolar amount of the aminophenol derivative **1b** (700.0 mg, 2.42 mmol) and of $AlMe_3$ (174.5 mg, 2.42 mmol). Compound **2b** (673 mg, 82% yield) was isolated as an analytically pure solid. Anal. Calcd for $C_{42}H_{60}Al_2N_2O_2$: C, 74.30; H, 8.91; N, 4.13. Found: C, 74.78; H, 8.66; N, 4.21. ^1H NMR (300 MHz, thf-d^8): δ −0.78 (s, 6H, $AlMe_2$), −0.62 (s, 6H, $AlMe_2$), 0.91 (d, $^3J_{HH}$ = 7.0 Hz, 6H, Me-^{i}Pr), 1.12 (d, $^3J_{HH}$ = 7.0 Hz, 6H, Me-^{i}Pr), 1.29 (d, $^3J_{HH}$ = 7.0 Hz, 6H, Me-^{i}Pr), 1.37 (d, $^3J_{HH}$ = 7.0 Hz, 6H, Me-^{i}Pr), 2.45 (sept., $^3J_{HH}$ = 6.9 Hz, 2H, CH-^{i}Pr), 2.88 (sept., $^3J_{HH}$ = 6.9 Hz, 2H, CH-^{i}Pr), 3.31 (d, $^3J_{HH}$ = 11.0 Hz, 2H, PhC*H*H'), 4.12 (t, J_{HH} = 11.1 Hz, 2H, PhCH*H*'), 4.85 (d, $^3J_{HH}$ = 11.2 Hz, 2H, N*H*), 6.85 (t, $^3J_{HH}$ = 6.5 Hz, 2H, Ph), 6.92 (d, $^3J_{HH}$ = 6.2 Hz, 2H, Ph), 7.01–7.45 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, thf-d^8): δ −10.1 (br, AlMe), −7.2 (AlMe), 21.4 (Me-^{i}Pr), 22.2 (Me-^{i}Pr), 23.7 (Me-^{i}Pr), 23.8 (Me-^{i}Pr), 29.1 (CH-^{i}Pr), 29.5 (CH-^{i}Pr), 53.3 (PhCH$_2$), 123.5 (Ph), 125.5 (Ph), 126.5 (Ph), 126.9 (Ph), 128.4 (Ph), 129.7(Ph), 135.6 (Ph), 137.1 (Ph), 137.7 (Ph), 138.9 (Ph), 139.4(Ph), 154.7 (Ph).

4.2.7. [η^2-*N,O*-{2–CH_2N(Dipp)–C_6H_4O}AlMe]$_2$ (*3b*)

The dimeric organoaluminum complex **2b** (300.0 mg, 0.442 mmol) and 5 mL of toluene were charged in a Schlenk flask equipped with a Teflon-inside-cover screw cap. The glassware was tightly sealed, immersed in a preheated oil at 80 °C and was vigorously stirred at this temperature for 3 h. After time, the initial colorless suspension had completely yielded a pale yellow solution

that was evaporated under reduced pressure to afford a colorless solid residue. As deduced from NMR data, the latter solid consisted of a mixture of **3b** and **4b** in a 3/1 ratio. Subsequent recrystallization of this residue from a 5/1 Et_2O/toluene (3 mL) solution at −40 °C afforded complex **3b** as an analytically pure colorless crystals in 43% yield (121 mg). Anal. Calcd for $C_{40}H_{52}Al_2N_2O_2$: C, 74.28; H, 8.10; N, 4.33. Found: C, 74.52; H, 8.45; N, 4.52. ^{1}H NMR (300 MHz, C_6D_6): δ −0.23 (s, 6H, AlMe), 0.91 (d, $^3J_{HH}$ = 7.0 Hz, 6H, Me-^{i}Pr), 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 6H, Me-^{i}Pr), 1.34 (d, $^3J_{HH}$ = 6.5 Hz, 6H, Me-^{i}Pr), 1.39 (d, $^3J_{HH}$ = 7.0 Hz, 6H, Me-^{i}Pr), 2.86 (d, $^2J_{HH}$ = 13.9 Hz, 2H, PhC*H*H'), 2.71 (sept., $^3J_{HH}$ = 6.9 Hz, 2H, CH-^{i}Pr), 3.26 (sept., $^3J_{HH}$ = 6.9 Hz, 2H, CH-^{i}Pr), 4.23 (d, $^2J_{HH}$ = 14.0 Hz, 2H, PhCH*H*'), 6.68 (t, $^3J_{HH}$ = 6.5 Hz, 2H, Ph), 6.96 (d, $^3J_{HH}$ = 6.2 Hz, 2H, Ph), 7.23–7.72 (m, 10H, Ph). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ −5.2 (br, AlMe), 17.8 (Me-^{i}Pr), 19.2 (Me-^{i}Pr), 21.7 (Me-^{i}Pr), 22.8 (Me-^{i}Pr), 27.1 (CH-^{i}Pr), 28.5 (CH-^{i}Pr), 52.7 ($PhCH_2$), 123.5 (Ph), 124.3 (Ph), 126.5 (Ph), 126.9 (Ph), 128.4 (Ph), 129.7(Ph), 134.2 (Ph), 137.1 (Ph), 137.7 (Ph), 138.9 (Ph), 139.4(Ph), 154.7 (Ph).

4.2.8. Al[η^2-N; μ^2,η^2-O-{2−CH_2N(Mes)−C_6H_4O}](AlMe$_2$) (**4a**)

Dinuclear organoaluminum complex **2a** (400 mg, 0.672 mmol) and 10 mL of toluene were charged in a Schlenk flask equipped with a Teflon-inside-cover screw cap. The reaction flask was tightly sealed, immersed in a preheated oil at 80 °C and kept at this temperature under vigorous stirring for 3 h. Over this period of time, the initial colorless suspension turned to a colorless solution, which was subsequently evaporated under reduced pressure to yield crude **4a** as an off-white solid as deduced from NMR data. Subsequent recrystallization from a cooled Et_2O solution (5 mL, −40 °C) afforded complex **4a** as analytically pure colorless needle-like crystals in 74% yield (280 mg). Anal. Calcd for $C_{34}H_{40}Al_2N_2O_2$: C, 72.58; H, 7.17; N, 4.98. Found: C, 73.01; H, 7.38; N, 5.12. ^{1}H NMR (300 MHz, C_6D_6): δ −0.33 (s, 6H, AlMe$_2$), 1.29 (s, 6H, Mes), 2.14 (s, 6H, Mes), 2.54 (s, 6H, Mes), 3.35 (d, $^2J_{HH}$ = 15.2 Hz, 2H, PhC*H*H'), 4.85 (d, $^2J_{HH}$ = 15.1 Hz, 2H, PhCH*H*'), 6.46–7.15 (m, 12H, Ph). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ −6.8 (AlMe), 18.2 (Mes), 20.7 (Mes), 23.2 (Mes), 51.4 ($PhCH_2$), 123.1 (Ph), 125.7 (Ph), 126.4 (Ph), 127.9 (Ph), 128.8 (Ph), 135.8 (Ph), 136.7 (Ph), 137.5 (Ph), 137.9 (Ph), 139.6 (Ph), 140.1 (Ph), 156.4 (Ph).

4.2.9. Al[η^2-N; μ^2,η^2-O-{2−CH_2N(Diip)−C_6H_4O}](AlMe$_2$) (**4b**)

Dinuclear organoaluminum complex **3b** (300.0 mg, 0.442 mmol) and 10 mL of toluene were charged in a Schlenk flask equipped with a Teflon-inside-cover screw cap. The reaction flask was tightly sealed, immersed in a preheated oil at 80 °C and kept at this temperature under vigorous stirring for 18 h. Over this period of time, the initial colorless suspension turned to a colorless solution, which was subsequently evaporated under reduced pressure to yield crude **4b** as an off-white solid as deduced from NMR data. Subsequent recrystallization from a cooled Et_2O solution (3 mL, −40 °C) afforded complex **4b** as an analytically pure colorless solid in 61% yield (174 mg). Anal. Calcd for $C_{40}H_{52}Al_2N_2O_2$: C, 74.28; H, 8.10; N, 4.33. Found : C, 74.56; H, 8.21; N, 4.52. ^{1}H NMR (300 MHz, C_6D_6): δ −0.35 (s, 6H, AlMe$_2$), 0.17 (d, $^3J_{HH}$ = 7.0 Hz, 6H, Me-^{i}Pr), 0.91 (d, $^3J_{HH}$ = 6.8 Hz, 6H, Me-^{i}Pr), 1.06 (d, $^3J_{HH}$ = 6.5 Hz, 6H, Me-^{i}Pr), 1.37 (d, $^3J_{HH}$ = 7.0 Hz, 6H, Me-^{i}Pr), 2.98 (sept., $^3J_{HH}$ = 6.9 Hz, 2H, CH-^{i}Pr), 3.36 (d, $^2J_{HH}$ = 14.3 Hz, 2H, PhC*H*H'), 3.74 (sept., $^3J_{HH}$ = 6.9 Hz, 2H, CH-^{i}Pr), 4.97 (d, $^2J_{HH}$ = 13.8 Hz, 2H, PhCH*H*'), 6.78–7.50 (m, 14H, Ph). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ −4.7 (br, AlMe), 16.3 (Me-^{i}Pr), 18.6 (Me-^{i}Pr), 22.7 (Me-^{i}Pr), 22.9 (Me-^{i}Pr), 28.5 (CH-^{i}Pr), 29.4 (CH-^{i}Pr), 55.1 ($PhCH_2$), 123.8 (Ph), 124.7 (Ph), 126.7 (Ph), 127.9 (Ph), 128.8 (Ph), 129.7 (Ph), 135.4 (Ph), 137.8 (Ph), 138.7 (Ph), 139.1 (Ph), 140.4 (Ph), 155.7 (Ph).

4.2.10. η^2-N,O-{2-CH_2NH(Mes)-4,6-^{t}Bu$_2$-C_6H_2O}AlMe$_2$ (**5c**)

To a precooled toluene solution (5 mL) of $AlMe_3$ (100.0 mg, 1.39 mmol) under vigorous stirring, a toluene solution (5 mL) of the aminophenol ligand **1c** (490 mg, 1.39 mmol), also precooled at −40 °C, was added dropwise via a pipette. Upon addition of the aminophenol, the initial colorless solution turned progressively pale yellow. After the addition, the mixture was allowed to warm to room temperature and stirred for 1 h, after which it was evaporated to dryness *in vacuo* to yield crude **5c** as a pale yellow solid residue, as deduced from NMR data. Recrystallization of the latter solid from cold pentane (−40 °C) afforded compound **5c** as analytically pure colorless crystals (313 mg, 55% yield). Anal. Calcd for $C_{26}H_{40}AlNO$: C, 76.24; H, 9.84; N, 3.42. Found: C, 76.56; H, 9.88; N, 3.56. ^{1}H NMR (300 MHz, C_6D_6): δ −0.57 (s, 3H, AlMe), −0.28 (s, 3H, AlMe), 1.38 (s, 9H, ^{t}Bu), 1.65 (s, 3H, Mes), 1.75 (s, 9H, ^{t}Bu), 1.96 (s, 3H, Mes), 2.23 (s, 3H, Mes), 2.98 (d, $^2J_{HH}$ = 11.2 Hz, 1H, PhC*H*H'), 4.52 (t, J_{HH} = 11.5 Hz, 1H, PhCH*H*'), 4.70 (d, $^2J_{HH}$ = 11.5 Hz, 1H, NH), 6.41 (s, 1H, Ph-Mes), 6.55 (s, 1H, Ph-Mes), 6.88 (s, 1H, Ph-O), 7.73 (s, Ph-O). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ −8.9 (br, AlMe), 17.2 (Mes), 20.7 (Mes), 22.2 (Mes), 29.9 (^{t}Bu), 31.5 (^{t}Bu), 34.0 (^{t}Bu), 35.3 (^{t}Bu), 53.9 ($PhCH_2$), 123.1 (Ph), 123.4 (Ph), 124.9 (Ph), 129.5 (Ph), 130.2 (Ph), 130.7 (Ph), 132.0 (Ph), 133.1 (Ph), 135.5 (Ph), 136.3 (Ph), 139.2 (Ph), 157.0 (Ph).

4.2.11. η^2-N,O-{2-CH_2NH(Diip)-4,6-^{t}Bu$_2$-C_6H_2O}AlMe$_2$ (**5d**)

The *N,O*-supported mononuclear Al complex **5d** was synthesized following an identical procedure to that used for **5c** using equimolar amounts of aminophenol **1d** (541.0 mg) and $AlMe_3$ (100. 0 mg, 1.39 mmol). The desired Al complex was isolated in a pure form as a colorless crystalline powder from a concentrated pentane solution stored at −40 °C (320 mg, 51% yield). Anal. Calcd for $C_{29}H_{46}AlNO$: C, 77.12; H, 10.27; N, 3.10. Found: C, 77.56; H, 10.42; N, 2.89. ^{1}H NMR (300 MHz, C_6D_6): δ −0.49 (s, 3H, AlMe), −0.18 (s, 3H, AlMe), 0.79 (d, $^3J_{HH}$ = 7.0 Hz, 3H, Me-^{i}Pr), 0.83 (d, $^3J_{HH}$ = 6.8 Hz, 3H, Me-^{i}Pr), 0.91 (d, $^3J_{HH}$ = 6.5 Hz, 3H, Me-^{i}Pr), 1.19 (d, $^3J_{HH}$ = 7.0 Hz, 3H, Me-^{i}Pr), 1.35 (s, 9H, ^{t}Bu), 1.74 (s, 9H, ^{t}Bu), 2.73 (sept., $^3J_{HH}$ = 6.9 Hz, 1H, CH-^{i}Pr), 3.31 (d, $^2J_{HH}$ = 11.2 Hz, 1H, PhC*H*H'), 3.42 (sept., $^3J_{HH}$ = 6.9 Hz, 1H, CH-^{i}Pr), 4.75 (t, J_{HH} = 11.4 Hz, 1H, PhCH*H*'), 5.18 (d, $^2J_{HH}$ = 11.5 Hz, 1H, NH), 6.80 (s, 1H, Ph-O), 6.80–7.15 (m, 3H, Ph), 6.88 (s, 1H, Ph-O), 7.87 (s, Ph-O). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ −6.7 (br, AlMe), 17.1 (Me-^{i}Pr), 18.3 (Me-^{i}Pr), 22.3 (Me-^{i}Pr), 24.3 (Me-^{i}Pr), 29.5 (CH-^{i}Pr), 29.7 (CH-^{i}Pr), 54.5 ($PhCH_2$), 123.4 (Ph), 124.9 (Ph), 126.8 (Ph), 128.9 (Ph), 129.1 (Ph), 129.9 (Ph), 136.4 (Ph), 137.1 (Ph), 137.6 (Ph), 138.3 (Ph), 139.4 (Ph), 156.6 (Ph).

4.2.12. η^2-N,O-{2-CH_2N(Mes)-4,6-^{t}Bu$_2$-C_6H_2O}Al(Me)(THF) (**6c**)

The η^2-N,O aluminium- coordinated amiphenolate complex **5c** (250. 0 mg, 0.610 mmol) was dissolved in toluene and three equivalent of THF (150.0 μL, 1.830 mmol) were added. The resulting colorless solution was then charged in a Schlenk flask and heated at 80 °C for 18 h affording a pale yellow solution that was allowed to cool to room temperature. Subsequent evaporation under reduced pressure resulted into the formation of an off-white solid residue formulated as crude **6c** on the basis of NMR data. Pure complex **6c** (162 mg, 57% yield) was obtained as a colorless powder by recrystallization of the crude product from an Et_2O solution cooled at −40 °C. Anal. Calcd for $C_{29}H_{44}AlNO_2$: C, 74.80; H, 9.52; N, 3.01. Found: C, 75.02; H, 9.76; N, 3.16. ^{1}H NMR (300 MHz, C_6D_6): δ −0.45 (s, 3H, AlMe), 1.40 (s, 9H, ^{t}Bu), 1.55 (s, 3H, Mes), 1.61 (m, 4H, THF), 1.77 (s, 9H, ^{t}Bu), 2.01 (s, 3H, Mes), 2.13 (s, 3H, Mes), 3.22 (d, $^2J_{HH}$ = 14.1 Hz, 1H, PhC*H*H'), 3.65 (m, 4H, THF), 4.78 (t, J_{HH} = 13.9 Hz, 1H, PhCH*H*'), 6.50 (s, 1H, Ph-Mes), 6.59 (s, 1H, Ph-Mes), 6.79 (s, 1H, Ph-O), 7.72 (s, Ph-O). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ −6.3 (br, AlMe), 16.8 (Mes), 20.5 (Mes), 21.9 (Mes), 25.5 (THF), 28.4 (^{t}Bu), 32.5 (^{t}Bu), 34.1 (^{t}Bu), 36.7 (^{t}Bu), 55.3 ($PhCH_2$), 66.3 (THF), 122.5 (Ph), 124.4 (Ph), 125.5 (Ph), 129.7 (Ph), 130.6 (Ph), 131.4 (Ph), 132.7 (Ph), 133.5 (Ph), 135.9 (Ph), 136.9 (Ph), 140.7 (Ph), 156.2 (Ph).

*4.2.13. η^2-N,O-{2-CH_2N(Diip)-4,6-^{t}Bu$_2$-C_6H_2O}Al(Me)(THF) (**6d**)*

Compound **6d** was synthesized following an identical procedure to that for **6c** but using complex **5d** (250.0 mg, 0.553 mmol) and THF (3 equiv., 135.0 μL) as reagents. Pure complex **6d** (118 mg, 42% yield) was isolated as colorless needle-shape crystals by recrystallization of the crude product from a 1/1 Et_2O/pentane solution cooled at −40 °C. Anal. Calcd for $C_{32}H_{50}AlNO_2$: C, 75.70; H, 9.93; N, 2.76. Found: C, 75.96; H, 9.99; N, 3.01. ^{1}H NMR (300 MHz, CD_2Cl_2): δ −0.83 (s, 3H, AlMe), 0.86 (d, $^3J_{HH}$ = 7.0 Hz, 3H, Me-^{i}Pr), 1.05 (d, $^3J_{HH}$ = 6.8 Hz, 3H, Me-^{i}Pr), 1.24 (d, $^3J_{HH}$ = 6.5 Hz, 3H, Me-^{i}Pr), 1.26 (s, 9H, ^{t}Bu), 1.32 (d, $^3J_{HH}$ = 7.0 Hz, 3H, Me-^{i}Pr), 1.51 (s, 9H, ^{t}Bu), 2.19 (m, 4H, THF), 3.36 (sept., $^3J_{HH}$ = 6.9 Hz, 1H, CH-^{i}Pr), 3.50 (d, $^2J_{HH}$ = 11.2 Hz, 1H, PhC*H*H'), 3.71 (sept., $^3J_{HH}$ = 6.9 Hz, 2H, CH-^{i}Pr), 4.38 (m, 4H, THF), 4.77 (t, J_{HH} = 11.4 Hz, 1H, PhCH*H*'), 6.74 (s, 1H, Ph-O), 7.06–7.12 (m, 3H, Ph), 7.16 (s, 1H, Ph-O). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ −9.4 (br, AlMe), 19.1 (Me-^{i}Pr), 20.3 (Me-^{i}Pr), 23.6 (Me-^{i}Pr), 25.7 (Me-^{i}Pr), 29.5 (CH-^{i}Pr), 30.7 (CH-^{i}Pr), 57.1 ($PhCH_2$), 121.7 (Ph), 123.8 (Ph), 126.7 (Ph), 127.9 (Ph), 129.4 (Ph), 130.2 (Ph), 135.4 (Ph), 136.1 (Ph), 137.3 (Ph), 138.8 (Ph), 139.4 (Ph), 152.3 (Ph).

5. X-ray determination

Single crystals of complexes **2a**, **3b**, **4a-b**, and **6d** were mounted on a Nonius Kappa-CCD area detector diffractometer Mo Kα radiation (λ = 0.71073 Å) by using ω−2θ scan at 173 K. The complete conditions of data collection (Denzo software) [17] and structure refinements are given in tables RX1 and RX2. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 and CRYSTALBUILDER softwares [18,19]. All non-hydrogen atoms were refined anisotropically. Excepted in specific cases (see the corresponding .cif files), hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97. The absorption was not corrected. Tables S1 and S2 (see Supporting Information) summarize the crystal data, experimental conditions and final refinement parameters for both compounds. Selected bond lengths and angles are gathered in figure captions. Crystallographic calculations were carried out with PLATON software and the figures were made with the use of ATOMS software (commercially available).

X-Ray diffraction data collection for complex **5d** was carried out on a Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 36 mm. The cell parameters were determined (Denzo software) [17] from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved by Direct methods using the program SHELXS-97 [18a] The refinement and all further calculations were carried out using SHELXL-97 [18b]. The H atom of the NH group was located from Fourier difference maps and refined isotropically. The other H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. One t-butyl group is disordered over two positions.

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Appendix A. Supplementary material

CCDC 833219–833224; contains the supplementary crystallographic data for compounds **2a**, **3b**, **4a-b**, **5d** and **6d**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary information

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.09.020.

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