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# An Unusual N-Bridged (Amido)(hydrido)(phenoxido)aluminium Dinuclear Compound – The Role of Nitrogen Substituents in Determining Nuclearity: A Combined Experimental and Theoretical Study

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The iminophenol 3,5- $tBu_2$ -2-(OH)C<sub>6</sub>H<sub>2</sub>CH=NR and the aminophenol 3,5- $tBu_2$ -2-(OH)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>-NHR (R = tBu, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>F<sub>5</sub>) were prepared in good yields by the appropriate synthetic methods. Reactions of these compounds with AlH<sub>3</sub>·NEtMe<sub>2</sub> in toluene gave the mononuclear [AlH{3,5- $tBu_2$ -2-(O)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>-NR}·NEtMe<sub>2</sub>] [R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**3**), C<sub>6</sub>F<sub>5</sub> (**4**)] or dinuclear [AlH{ $\mu$ -3,5- $tBu_2$ -2-(O)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>-NR]·NEtMe<sub>2</sub>] [R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**3**), C<sub>6</sub>F<sub>5</sub> (**4**)] or dinuclear [AlH{ $\mu$ -3,5- $tBu_2$ -2-(O)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>-NtBu]<sub>2</sub> (**5**) phenoxido–amido aluminium derivatives. All synthesized complexes were characterized by NMR spectroscopic and analytical methods. The X-ray structure of **5** shows a dinuclear molecule in which the aluminium centres

## Introduction

Organoaluminium compounds are known to be important reagents widely employed in organic synthesis<sup>[1,2]</sup> as olefin polymerization cocatalysts<sup>[3,4]</sup> and as initiators in ring-opening polymerization (ROP) processes.<sup>[5]</sup>

A key approach in aluminium chemistry has involved the use of bulky ligands to reduce the degree of aggregation in the metal structures, rendering low-nuclearity derivatives.<sup>[6–10]</sup> In particular, sterically demanding chelating groups have received special attention. For example, neutral diimines give efficient mononuclear transition metal catalysts.<sup>[11–15]</sup> In addition, ligands containing phenoxido groups have been used for the stabilization of catalysts for oxidation,<sup>[16]</sup> epoxidation,<sup>[17]</sup> carbon–carbon bond formation<sup>[18]</sup> and controlled polymerization.<sup>[19]</sup>

Our research interest has been focused on the synthesis and structural study of mononuclear/dinuclear hydride, alkyl and haloalkylaluminium complexes containing N,O bidentate ligands, because such species could show interestare unusually linked by  $\mu_2\text{-}N(amido)$  atoms to form a central planar  $Al_2N_2$  ring in a clearly preferential disposition over the more common  $Al_2O_2$  ring. The experimental work has been assisted by the B3LYP functional and the 6-31G\* basis sets as implemented in Gaussian 03 calculations to determine the role played by the nitrogen substituent group in the structural disposition adopted by the prepared (monohydrido)aluminium compounds, in order to evaluate the factors affecting the coordination modes of the phenoxido–amido ligand on aluminium.

ing catalytic properties. Bidentate N,O-donor ligands<sup>[20–25]</sup> constitute simple nonsymmetric chelating structures that impose control over the metal coordination geometry with a sterically demanding chelating structure. Phenoxido–imido<sup>[26–28]</sup> and the closely related phenoxido–amino bidentate systems<sup>[29–31]</sup> have been widely used for transition metals and to produce alkylaluminium complexes and their cationic derivatives,<sup>[32–34]</sup> which can be utilized as catalysts in ROP processes<sup>[24]</sup> of heterocyclic monomers and in ethylene polymerization reactions.<sup>[21,35]</sup>

Here we report the synthesis and structural analysis of the reaction products from the treatment of iminophenol aminophenol ligand precursors with and alane AlH<sub>3</sub>·NEtMe<sub>2</sub> to prepare derivatives of different nuclearity. Although aluminium hydrides have been widely used in many areas of chemistry since their first isolation in the 1940s,<sup>[36]</sup> there have been few reports on aluminium hydride species stabilized by Schiff base N,O chelate ligands.[37,38] In our research, we have paid considerable attention to the determination of the nuclearity of the aluminium complexes prepared with a combined experimental and theoretical study. We have obtained mononuclear derivatives and the dinuclear species  $[AlH\{\mu-3,5-tBu_2-2-(O)C_6H_2CH_2-NtBu\}]_2$ exhibiting an unusual N-bridged phenoxido-amido structure, which is preferred over the O-bridging arrangement. This structural behaviour contrasts with that found in the literature: O-bridging structures are generally observed in polynuclear aluminium derivatives supported by bridging phenoxido-imino and related ligands.[22,25,39,40]



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#### **Results and Discussion**

Salicylaldimines  $3,5-tBu_2-2-(OH)C_6H_2CH=NR$  (R = tBu, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>F<sub>5</sub>) (1a–c) used as ligand precursor systems were prepared in good yields (80%-95%) as yellow to orange crystalline solids by condensation of 3,5-di-tertbutyl-4-hydroxybenzaldehyde with the appropriate amine in refluxing toluene in the presence of a catalytic amount (0.1%) of *p*-toluenesulfonic acid.<sup>[32,41,42]</sup> Reactions of **1a-c** with LiAlH<sub>4</sub> (4 equiv.) in THF at ambient temperature gave, after work up, the crystalline white to yellow aminophenol compounds 3,5-tBu<sub>2</sub>-2-(OH)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>-NHR (R = tBu, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>F<sub>5</sub>) (**2a**-c).<sup>[29,30]</sup> Spectroscopic data are consistent with the formulation depicted in Scheme 1. The <sup>1</sup>H NMR spectra ( $C_6D_6$ ) of **1a–c** exhibit resonances in the region  $\delta = 7.60-8.13$  ppm for the imine CH protons, with the analogous <sup>13</sup>C NMR signals occurring between  $\delta$ = 161.1 and  $\delta$  = 168.4 ppm. The <sup>1</sup>H NMR spectra (C<sub>6</sub>D<sub>6</sub>) of 2a–c display characteristic doublets ( ${}^{2}J_{\rm HH} \approx 7.0$  Hz) in the range  $\delta = 3.80-3.80$  ppm for the methylene CH<sub>2</sub> protons, with the corresponding <sup>13</sup>C NMR signals between  $\delta$ = 50.0 and 46.0 ppm.

Compounds 1a-c and 2a-c react with an equimolar amount of AlH<sub>3</sub>·NEtMe<sub>2</sub> in toluene (from -78 °C to ambient temperature) to afford the mononuclear [AlH{3,5-*t*Bu<sub>2</sub>-2-(O)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>-NR}·NEtMe<sub>2</sub>] (R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **3**; C<sub>6</sub>F<sub>5</sub> **4**) and the white-yellow dinuclear [AlH{ $\mu$ -3,5-*t*Bu<sub>2</sub>-2-(O)-C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>-N*t*Bu}]<sub>2</sub> (**5**) phenoxido-amido complexes (Scheme 1). These compounds are formed with a formal loss of hydrogen by alcoholysis accompanied by a hydroalumination reaction of the imine functionality in the case of **1a-c** or consistent with alcoholysis together with aminolysis in the reactions with **2a-c**. Compounds **3–5** are airsensitive but thermally stable in solution and in the solid state. They must be stored under rigorously dry conditions. Spectroscopic data and elemental analyses concur with the proposed structures.

Hydride aluminium N,O-chelate complexes tend to be mononuclear due to their capacity to form simple adducts with Lewis bases such as amines and normally adopt a mononuclear tetracoordinate tetrahedral geometry around the metal.<sup>[38,43]</sup> In accord with this behaviour, a common feature in the <sup>1</sup>H NMR spectrum ( $C_6D_6$ ) of 3 and 4 is the presence of a neutral NEtMe<sub>2</sub> amine, emanating from the initial aluminium reagent (AlH<sub>3</sub>·NEtMe<sub>2</sub>). Thus, the <sup>1</sup>H NMR ( $C_6D_6$ ) spectra of complexes 3 and 4 have the resonances of the coordinated tertiary amine appearing in the range  $\delta = 0.51$  to  $\delta = 2.20$  ppm. The ethyl group protons and the resonances associated with the "NMe" protons appear, indicating the chiral character of these compounds (see Exp. Sect.). Both compounds exhibit the expected resonances due to the aromatic protons, with corresponding <sup>13</sup>C NMR signals. The diastereotopic benzylic methylene protons are observed as a set of doublets in the range  $\delta = 3.82$ -4.78 ppm in the <sup>1</sup>H NMR spectra. Characteristic Al–H signals and high-field shifted resonances for the tert-butyl groups are also observed. The Al-H stretching absorption in the IR spectra at 1843.6 cm<sup>-1</sup> for 3 and 1861.8 cm<sup>-1</sup> for 4 confirms the terminal hydride bond to the metal centre in both cases. On the basis of these observations, the most likely structures suggested for 3 and 4 are mononuclear chelating compounds, with a terminal hydrido ligand and a coordinated ethyldimethylamine.

However, no signals for an additional Lewis base were observed in the NMR spectrum of **5**, which exhibits characteristic resonances for the aromatic protons of the phenoxido fragment, with diastereotopic AB-type protons of the benzylic methylene group and the expected *tert*-butyl



Scheme 1.

group protons (see Exp. Sect.). The Al–H resonance appears as a broad singlet at  $\delta = 4.42$  ppm. The IR spectrum displays a strong Al–H stretching absorption at 1871.8 cm<sup>-1</sup>, which corresponds to a terminal hydrogen.<sup>[44]</sup> Therefore, these spectroscopic data suggest that only the phenoxido–amido ligand and the hydride groups are bonded to the aluminium; hence, the tetracoordinate aluminium environment should be achieved through a dinuclear disposition.

An NMR spectroscopic study when a small amount of the free amine is added to the solutions of 3–5 rules out the possibility of an equilibrium between mononuclear and dinuclear species in solution.

The nuclearities of compounds **3–5** were verified by diffusion ordered (DOSY) NMR spectroscopy. The diffusion peaks of **3** and **4** are centred at a higher diffusion coefficient value ( $D_3 \approx D_4 \approx 5.7 \pm 0.1 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ ) than that corresponding to **5** ( $D_5 = 4.6 \pm 0.1 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ ), this latter value being smaller by a factor of approximately  $D_3/D_5 =$ 1.24. On the basis of the correlation diffusion coefficients/ molecular radii given by the Stokes–Einstein equation,<sup>[45]</sup> the ratio of the radii ( $r_3/r_4 \approx 1$  and  $r_3/r_5 \approx 0.80$ ) unambiguously demonstrate that the molecular size of **3** is virtually equal to that of **4** and almost half that of **5**.

The solid-state structure of compound **5** has been established by X-ray diffraction studies. Crystals of **5** suitable for X-ray analysis were grown from benzene solution in an NMR tube at room temperature. Figure 1 shows an OR-TEP view of the molecule with selected bond lengths and bond angles. In the asymmetric unit, two chemically equivalent molecules of **5** and one solvent molecule are present.

The X-ray analysis of **5** reveals a centrosymmetric dinuclear structure in which the phenoxido–amido ligands adopt a bidentate and unusual N-bridging disposition. As previously stated, complexes containing Schiff base ligands usually present mononuclear structures.<sup>[32,34,38]</sup> However, dinuclear geometries are also described<sup>[22]</sup> in which the phenolic oxygen atoms of the ligands bridge adjacent aluminium centres.<sup>[40,46]</sup> Surprisingly, in **5** the two aluminium centres are linked by  $\mu_2$ -N(amido) atoms to form a central planar Al<sub>2</sub>N<sub>2</sub> ring in a clearly preferential disposition compared with the most common Al<sub>2</sub>O<sub>2</sub> ring.

For ligands containing both oxygen and nitrogen as potential bridging atoms, it is found that compounds having oxygen bridges between aluminium atoms<sup>[23,24,39,47–50]</sup> predominate over those with nitrogen bridges.<sup>[37,51]</sup> Examples are known with both O and N atoms bridging in hydroxypyridine ligands (in an isolobal disposition to carboxylatebridged ligands)<sup>[25]</sup> or with an amidate group<sup>[52–55]</sup> between two aluminium atoms.

The aluminium centres in **5** exhibit a typically tetrahedral coordination geometry and are bonded to the terminal hydride atom and the phenoxido–amido ligand, with a N–Al–O chelating bite angle of 104.09(6)°. The terminal Al–H bond length [1.476(19) Å] is within the range observed for terminal hydridoaluminium complexes.<sup>[38,56]</sup> The observed bond lengths Al1–N1 and Al1–N1a#1 [1.9538(14) Å and 1.9593(14) Å, respectively] are much longer than those in



Figure 1. ORTEP view of the structure of **5**. Ellipsoids of 30% of probability. Selected bond lengths [Å]: Al1–Ol 1.7325(12), Al1–Nl 1.9538(14), Al1–N1a#1 1.9593(14), Al1–H1 1.476(19), N1–Cl5 1.520(2), Ol–C2 1.3668(19). Selected angles [°]: N1–Al1–N1a#1 90.01(6), Ol–Al1–N1 104.09(6), Ol–Al1–H1 113.8(7), Ol–Al1–N1a#1 113.54(6), Cl5–N1–Al1 105.36(10), N1–Al1–H1 121.0(7), Cl–Cl5–N1 117.94 (13), N1#–Al1–H1 112.1(7). Hydrogen atoms, except for the hydrido ligands, are omitted for clarity. Symmetry transformations used to generate equivalent atoms: #1 - x, -y + 1, -z + 1.

[AlMe<sub>2</sub>{3,5-*t*Bu<sub>2</sub>-2-(O)C<sub>6</sub>H<sub>2</sub>CH=NR}] (R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> or 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [1.792(3), 1.792(3) Å]<sup>[32]</sup> and in the (monohydrido)aluminium complex [AlH{3-*t*Bu-5-Me-2-(O)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>-N2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·NMe<sub>3</sub>] [1.799(1) Å],<sup>[38]</sup> in which the nitrogen atom does not bridge two metal atoms. The values observed in **5** are in the range observed for other complexes with a bridging N atom<sup>[37,57,58]</sup> and comparable to Al–N dative bond lengths.<sup>[50,59]</sup> The six-membered ring chelate Al metallacycle is significantly twisted, angles between the planes containing the Al<sub>2</sub>N<sub>2</sub> and C<sub>6</sub>H<sub>2</sub> rings ranging from 32.88° to 33.48°.<sup>[32,38]</sup>

In view of these experimental results, we were interested in understanding the factors that determine the tendency to stabilize mononuclear or dinuclear structural dispositions in (amido)(hydrido)(phenoxido) aluminium compounds. The stability of mononuclear or dinuclear aluminium derivatives with analogous N,O-donor ligands depending on electronic and steric factors have been previously studied.<sup>[25,60]</sup> In addition, a discussion of the factors affecting the coordination modes of amidate ligands to aluminium has been reported.<sup>[55]</sup> Thus, we started a computational study in order to clarify and rationalize the structural behaviour observed in the final products obtained in the treatment of AlH<sub>3</sub>·NEtMe<sub>2</sub> with iminophenol and aminophenol compounds, depending on the nitrogen substituents.

The structures were optimized by using the functional B3LYP<sup>[61–63]</sup> and the 6-31G\* basis sets as implemented in the Gaussian 03 program.<sup>[64]</sup> All energy minima were characterized by frequency analysis. The energies reported in this work include zero-point vibrational energy corrections



(ZPVE) and are not scaled. Single-point calculations with the self-consistent reaction field (SCRF) based on the IEF-PCM solvation model (toluene,  $\varepsilon = 2.379$ ) were carried out at the B3LYP/6-31G\* level on the previously optimized structures. The mononuclear and dinuclear phenoxidoamido complexes with different R groups at the nitrogen atom (the experimentally obtained  $R = 2,6-Me_2C_6H_3$  for 3,  $R = C_6F_5$  for 4, R = tBu for 5 and the hypothetical derivatives R = Me for 6 and R = Ph for 7) were computed. The calculated energy values are shown (Table 1) relative to the corresponding mononuclear complexes, which were taken as H, G = 0. Thus, the enthalpy preference for mononuclear (mono) or dinuclear (di) species was computed as exemplified for complex 5:  $\Delta H = [H(5di) + 2H(NEtMe_2)] -$ 2H(5mono). The Gibbs free energy was computed in a similar way:  $\Delta G = [G(5di) + 2G(NEtMe_2)] - 2G(5mono)$ . Negative values indicate preferential formation of the dinuclear species, and positive values indicate formation of mononuclear species.

Table 1. Energy parameters for the computational study.[a]

Entry	Complex	R	$\Delta H$	$\Delta G$	$\Delta G_{ m solv.}$
		Aliphatic R groups			
1	5di-N	<i>t</i> Bu	-2.1	-10.3	-8.9
2	6di-N	Me	-10.1	-20.0	-16.7
3	5di-O	tBu	+8.6	-1.0	+2.5
4	6di-O	Me	+6.6	-4.4	+1.1
		Aromatic R groups			
5	3di-N	Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	+18.2	+9.7	+11.6
6	4di-N	$C_6\overline{F_5}$	+7.9	-1.7	+0.5
7	7di-N	Ph	+9.9	-1.2	+2.4
8	3di-O	$Me_2C_6H_4$	+25.0	+19.5	+24.8
9	4di-O	$C_6F_5$	+8.6	-0.8	+3.2
10	7di-O	Ph	+13.7	+2.4	+13.0

[a] Positive values reflect the preferred formation of mononuclear species, whilst negative values indicate more stable dinuclear complexes.

Two different dinuclear complexes were envisioned, depending on the heteroatom (N or O) that bridges the two aluminium atoms in the central core. For the nitrogenbridged (di-N complexes, Scheme 2), the aluminium and nitrogen atoms form a planar four-membered ( $Al_2N_2$ ) cycle (tetrahedral angle  $\Phi_{AINAIN} = 0.0^{\circ}$ ), presenting four Al–N bonds of similar length (2.0 Å). Each aluminium atom also bonds with a hydrogen (1.6 Å) and an oxygen (1.8 Å) atom in a tetrahedral manner, forming a pentacyclic structure, wherein the *transoid* arrangement of the cycles around the central Al<sub>2</sub>N<sub>2</sub> ring is energetically preferred. Thus, the hydrogen atoms bound to the aluminium centres are arranged in a relative *anti* disposition, pointing towards opposite faces of the Al<sub>2</sub>N<sub>2</sub> four-membered ring. These calculated values for the di-N structural disposition deduced by theoretical calculations correlate well with the observed structural parameters for compound **5** according to the X-ray diffraction studies.

Closely related structural features are found for the oxygen-bridged complexes (di-O, Scheme 2), wherein the aluminium and oxygen atoms form a planar four-membered (Al<sub>2</sub>O<sub>2</sub>) central core (tetrahedral angle  $\Phi_{AlOAIO} = 0.0^{\circ}$ ) of equal Al–O bond lengths (1.9 Å), with exocyclic distances of 1.8 Å (Al–N) and 1.6 Å (Al–H). As for the di-N complexes, the substituents of the Al atoms are arranged in a relative *anti* disposition. Both systems (di-N and di-O) are achiral and contain a centre of symmetry.

The introduction in the calculation of an external amine in the dinuclear complexes breaks the Al–O–Al or Al–N– Al bridge, generating the mononuclear species, wherein the Al–O (1.8 Å) and Al–N (1.8 Å) bonds are slightly shorter than those corresponding to the internuclear bridges. The new Al–N (external amine) bond has a computed distance of 2.1 Å.

Computational data demonstrate that, among the dinuclear complexes (di-O vs. di-N), the nitrogen bridge exerts a higher stabilization, regardless of the R substituent at the nitrogen position. Indeed, the energetic parameters (H, G and  $G_{solv.}$ ) are always more positive for oxido complexes than for nitrogen complexes (Table 1). The highest difference (ca. 17 kcal/mol) is observed for the more basic methyl group (**6**, R = Me, entries 2 vs. 4, Table 1). In contrast, a small difference of only 1–3 kcal/mol is found for the least basic perfluorophenyl group (**4**, R = C<sub>6</sub>F<sub>5</sub>, entries 6 vs. 9, Table 1). Thus, the basicity of the amine seems to play a crucial role in the preference for the nitrogen bridge in the dinuclear complexes, and the more basic aliphatic amines show a higher preference for di-N over di-O.



Scheme 2.

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More interestingly, the main difference between aliphatic and aromatic substitution is centred on the relative stability of the mono relative to the dinuclear species. The calculated stability decreases in the order di-N > mono > di-O with the aliphatic amines, and mono > di-N > di-O in the aromatic cases, which is in agreement with the crucial observation that only di-N complexes are experimentally obtained when using an aliphatic amine, and only mononuclear complexes are produced when the substituent on the nitrogen is aromatic. Thus, the highest computed preference for di-N is found in the basic methylamine compound 6di-N, 10.1 kcal/mol in  $\Delta H$  over 6 mono (entry 2, Table 1). In contrast, the opposite selectivity was computed for 3mono, which is favoured at 18.2 kcal/mol over 3di-N (entry 5, Table 1) and 25.0 kcal/mol over 3di-O (entry 8, Table 1). Worthy of note, the stoichiometry of the equilibrium between mononuclear and dinuclear species favours the generation of the latter, since two molecules of amine are released upon formation of the oxido or nitrogen bridges, with its logical positive entropy effect, making  $\Delta G$  values of the overall process more negative (or less positive) than  $\Delta H$  in all cases (Table 1). The introduction of the solvent effects by means of the IEF-PCM model (toluene,  $\varepsilon = 2.379$ ) only slightly varies the energy values, and in general increases the Gibbs free energy by 1–3 kcal/mol towards the formation of mononuclear species. Nonetheless, the relevant data is that both  $\Delta H$  and  $\Delta G_{solv.}$  show a similar tendency in all cases, which agrees with the experimental observations.

The different basicity of the amido moiety might be responsible for the preference of mono or dinuclear complexes. Aliphatic substitution induces a higher basicity of the amine, stabilizing more efficiently the dinuclear complexes which possess two Al-N(amido) bonds, whereas aromatic substitution reduces the basic power of the nitrogen(amido) atom, weakening the Al-N interaction and facilitating the bonding of an additional amine to further stabilize the mononuclear species. This effect can also be confirmed by the computed Al-N bond lengths of the different complexes, which slightly vary depending on the R substituent. Thus, Al-N (ethyldimethylamine) is shorter in the aromatic compounds (2.08 Å) than in the aliphatic ones (2.10 Å), whereas the opposite occurs for the Al-N (internal amido moiety), which is shorter in the aliphatic compounds (5, 1.81 Å; 6, 1.80 Å) than in the aromatic ones (3, 1.82 Å; 4, 1.85 Å; 7, 1.84 Å).

Furthermore, a notable steric effect favouring the mononuclear species was also found. Within the aliphatic amines, the 10.1 kcal/mol enthalpy preference for the di-N complex (16.7 kcal/mol in  $G_{solv.}$ , entry 2, Table 1) with methylamine is significantly reduced by approximately 8 kcal/mol relative to *tert*-butylamine (entry 1, Table 1). Similarly, a large difference in the energy values can be found among the different aromatic amines, which must be related to the important steric congestion around the substituents in the phenol and aniline rings, especially in the most hindered 2,6-dimethyl-phenylamine derivative **3**. For example, the forma-



Figure 2. Steric effects in the dinuclear complexes.



tion of 3di-O is hampered by the close contact between the tert-butyl and methyl groups across the borderline of the two monomers, which can be inferred from the very short H····H distances (2.0 and 2.1 Å) between the methyl hydrogen atoms of the phenol and aniline rings (see detail in Figure 2). As a consequence, the phenoxide ring slightly loses its planarity, as can be gauged from the dihedral angle  $\Phi$  $(C^{a}-C^{b}-C^{c}-C^{d}) = 13.0^{\circ}$ . The *tert*-butyl substituent is also slightly out of the plane of the aromatic ring with a dihedral angle  $\Phi$  (C<sup>b</sup>-C<sup>c</sup>-C<sup>d</sup>-C<sup>e</sup>) = 9.1°. Both effects have a tremendous impact on the energy balance of the equilibrium, with an enthalpy preference of approximately 25 kcal/mol for the mononuclear species (3mono), which is enough to prevent the formation of even traces of dinuclear species. The steric repulsion is less important in 3di-N, inducing a lower but still significant energy gap in the equilibrium ( $\Delta H$  = 18.2 kcal/mol, entry 5, Table 1). The corresponding  $\Phi$  dihedral angles of the aromatic ring in 3di-N are smaller than those in 3di-O (6.7° and 2.1°, see detail in Figure 2).

In summary, both steric effects and basicity seem to influence the arrangement of the different complexes. Under all the reaction conditions experimentally described the dinuclear structure with a N bridge is always predicted to be favoured over the O-bridged disposition. The preference for the dinuclear species increases with the basicity of the nitrogen, whilst the steric repulsion shifts the equilibrium in the opposite direction.

These results permit us to suggest that the nuclearity of the final O,N-chelating hydride aluminium compounds would depend on the nature of the substituents on the nitrogen atom. Electronic and steric effects control the coordination abilities and the degree of association in these derivatives. Thus, the tendency of hydridoaluminium compounds to form adducts with Lewis bases, such as amines, adopting a mononuclear tetracoordinate tetrahedral geometry, may result from both the basicity of the amine functionality and the presence of bulky R groups attached to the nitrogen atom. Higher basicity, as in compound 5, makes the Al-N interaction stronger, stabilizing dinuclear dispositions. On the other hand, when basicity decreases the coordination of an additional Lewis base is easier, which yields mononuclear species. The influence of the nitrogen atom substituents has been observed as well in the behaviour of similar phenoxido-imido aluminium derivatives in ROP processes.[65,66]

#### Conclusions

This work provides mononuclear and dinuclear aluminium complexes bearing phenoxido–amino ligands. Reactions of aminophenol compounds with AlH<sub>3</sub>·NEtMe<sub>2</sub> proceed by a formal loss of hydrogen consistent with alcoholysis and aminolysis, rendering the mononuclear species **3–4** and the dinuclear species **5**. It is possible to achieve the same result by the treatment of the iminophenol derivatives with AlH<sub>3</sub>·NEtMe<sub>2</sub>. In this case, hydrogen migration occurs together with the elimination of H<sub>2</sub> by an alcoholysis reaction accompanied by a hydroalumination process. A computational study by using functional B3LYP and the 6-31G\* basis sets as implemented in Gaussian 03 calculations has permitted us to rationalize the factors that set the most favourable conditions to selectively generate mono or dinuclear species, allowing a quantitative comparison with experimental data. Hence, we have shown that it is possible to access cleanly to mono- or dinuclear chelating hydridoal-uminium compounds by modifying the substituents on the nitrogen atom of the ligand. Although this is a limited study, it is possible to infer the preference of these specific compounds for inter- or intramolecular coordination, and a general trend to predict this effect has emerged for a much wider range of compounds.

### **Experimental Section**

General Considerations: All manipulations were conducted by using Schlenk techniques in conjunction with an inert-atmosphere glovebox. All solvents were rigorously dried prior to use. NMR spectra were recorded at 400.13 (<sup>1</sup>H), 376.00 (<sup>19</sup>F) and 100.60 (<sup>13</sup>C) MHz with a Bruker AV400 instrument. Chemical shifts ( $\delta$ ) are given in ppm in C<sub>6</sub>D<sub>6</sub> as solvent. <sup>1</sup>H and <sup>13</sup>C NMR resonances were measured relative to solvent peaks considering TMS  $\delta$  = 0 ppm, while <sup>19</sup>F NMR resonances were measured relative to external CFCl<sub>3</sub>. Elemental analyses were obtained with a Perkin-Elmer Series II 2400 CHNS/O analyzer. Infrared data were recorded as KBr pellets at room temperature with a Perkin-Elmer Spectrum-2000 FTIR spectrometer and are reported in cm<sup>-1</sup>. All reagents, 3,5-di-tert-butyl-2-hydroxybenzaldehyde, tert-butyl-amine, 2,6-dimethyl-aniline, pentafluoroaniline and the alane aluminium complex solution AlH<sub>3</sub>·NEtMe<sub>2</sub> were commercially obtained and used without further purification.

 $[AIH{3,5-tBu_2-2-(O)C_6H_2CH_2-N(2,6-Me_2C_6H_3)} \cdot NEtMe_2]$  (3): A solution of 1b (0.50 g, 1.48 mmol) in toluene (10 mL) was added dropwise to a solution of AlH<sub>3</sub>·NEtMe<sub>2</sub> (0.5 m, 2.96 mL, 1.48 mmol) in toluene (20 mL) at -78 °C. The solution was stirred during the addition over 10 min, and then the mixture was warmed to room temperature. Volatiles were removed under reduced pressure, and the product was extracted into hexane (10 mL). Filtration followed by cooling at -30 °C afforded 3 as a white solid, which was recrystallized from cold hexane. Yield 83% (0.54 g, 1.24 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 0.51 (t,  $J_{HH}$  = 7.32 Hz, 3 H, NCH<sub>2</sub>CH<sub>3</sub>), 1.36 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.77 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.81 (s, 3 H, NCH<sub>3</sub>), 1.86 (s, 3 H, NCH<sub>3</sub>), 2.20 (m, 2 H, NCH<sub>2</sub>CH<sub>3</sub>), 2.40 (s, 3 H, Ar-CH<sub>3</sub>), 2.48 (s, 3 H, Ar-CH<sub>3</sub>), 3.82 (d,  $J_{\rm HH}$  = 14.6 Hz, 1 H, CH<sub>2</sub>-N), 3.99 (br. s, 1 H, AlH), 4.78 (d,  $J_{\rm HH}$  = 14.7 Hz, 1 H, CH<sub>2</sub>-N), 6.93 (d,  ${}^{4}J_{\rm HH} = 2.5$  Hz, 1 H, OAr-H), 6.96, 7.08, 7.18 (all m 3 H, NAr-H), 7.52 (d,  ${}^{4}J_{HH}$  = 2.5 Hz, 1 H, OAr-*H*) ppm. {}^{13}C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.5 (NCH<sub>2</sub>CH<sub>3</sub>), 20.1 (NAr-CH<sub>3</sub>), 20.9 (NAr-CH<sub>3</sub>), 30.2 [C(CH<sub>3</sub>)<sub>3</sub>], 31.8 [C(CH<sub>3</sub>)<sub>3</sub>], 34.1 [C(CH<sub>3</sub>)<sub>3</sub>], 35.2 [C(CH<sub>3</sub>)<sub>3</sub>], 41.6 (NCH<sub>3</sub>), 42.1 (NCH<sub>3</sub>), 52.1 (NCH<sub>2</sub>CH<sub>3</sub>), 57.9 (CH<sub>2</sub>-N), 121.7, 122.7, 122.8, 128.7, 128.9, 131.9, 135.4, 136.1, 137.4, 139.5, 152.5, 155.5 (all Ar-C) ppm. IR (KBr pellets):  $\tilde{v}_{Al-H} = 1843.6$  (st) cm<sup>-1</sup>. C<sub>27</sub>H<sub>43</sub>AlN<sub>2</sub>O (438.30): calcd. C 74.0, H 9.8, N 6.4; found C 74.08, H 9.5, N 6.2.

 $[AlH{3,5-tBu_2-2-(O)C_6H_2CH_2-N(C_6F_5)}NEtMe_2]$  (4): A solution of 1c (0.30 g, 0.70 mmol) in toluene (10 mL) was added dropwise to a solution of AlH<sub>3</sub>·NEtMe<sub>2</sub> (0.5 M, 1.50 mL, 0.70 mmol) in toluene (20 mL) at -78 °C. The solution was stirred during the addition over 10 min, when the mixture was warmed to room temperature.

Volatiles were removed under reduced pressure, and the product was extracted into hexane (10 mL). Filtration followed by cooling at  $-30 \,^{\circ}$ C afforded **4** as a yellow solid. Yield 80% (0.29 g, 0.58 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 0.60$  (t,  ${}^{3}J_{HH} = 7.32$  Hz, 3 H, NCH<sub>2</sub>CH<sub>3</sub>), 1.44 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.66 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.78 [s, 6 H, N(CH<sub>3</sub>)<sub>2</sub>], 2.17 (m, 2 H, NCH<sub>2</sub>CH<sub>3</sub>), 4.00 (br. m, 1 H, CH<sub>2</sub>-N), 4.34 (br. s, 1 H, AlH), 4.50 (br. m, 1 H, CH<sub>2</sub>-N), 7.22 (d,  ${}^{4}J_{HH} = 2.4$  Hz, 1 H, OAr-H), 7.55 (d,  ${}^{4}J_{HH} = 2.4$  Hz, 1 H, OAr-H) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 8.3$  (NCH<sub>2</sub>CH<sub>3</sub>), 30.1 [C(CH<sub>3</sub>)<sub>3</sub>], 31.8 [C(CH<sub>3</sub>)<sub>3</sub>], 34.3 [C(CH<sub>3</sub>)<sub>3</sub>], 35.1 [C(CH<sub>3</sub>)<sub>3</sub>], 42.9 (NCH<sub>3</sub>), 53.0 (NCH<sub>2</sub>CH<sub>3</sub>), 55.0 (CH<sub>2</sub>-N), 122.6, 123.4, 129.9, 130.3, 137.1, 137.6, 139.7, 139.9, 142.5, 154.5 (all Ar-C) ppm. <sup>19</sup>F NMR:  $\delta = -152.8$  (2 F, F<sub>ortho</sub>), -165.6 (2 F, F<sub>meta</sub>), -173.4 (1 F, F<sub>para</sub>) ppm. IR (KBr pellets):  $\tilde{v}_{Al-H} = 1861.8$  (st) cm<sup>-1</sup>. C<sub>25</sub>H<sub>34</sub>AlF<sub>5</sub>N<sub>2</sub>O (500.27): calcd. C 60.0, H 6.8, N 5.6; found C 59.3, H 6.1, N 5.5.

[AlH{µ-3,5-tBu<sub>2</sub>-2-(O)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>-NtBu}]<sub>2</sub> (5): A solution of 1a (0.50 g, 1.73 mmol) in toluene (10 mL) was added dropwise to a solution of AlH<sub>3</sub>·NEtMe<sub>2</sub> (0.5 M, 3.46 mL, 1.73 mmol) in toluene (20 mL) at -78 °C. The solution was stirred during the addition over 10 min, when the mixture was warmed to room temperature. Volatiles were removed under reduced pressure, and the product was extracted into hexane (10 mL). Filtration followed by cooling at -30 °C afforded 5 as a white solid, which was recrystallized from cold hexane. Yield 79% (0.42 g, 1.34 mmol). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta =$ 1.31 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.36 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.69 [s, 9 H, C(CH<sub>3</sub>) <sub>3</sub>], 3.73 (d,  $J_{\rm HH}$  = 16.3 Hz, 1 H,  $CH_2$ -N), 4.42 (br. s, 1 H, AlH), 4.58 (d,  $J_{\rm HH}$  = 16.3 Hz, 1 H,  $CH_2$ -N), 6.97 (d,  ${}^4J_{\rm HH}$  = 2.0 Hz, 1 H, OAr-*H*), 7.51 (d,  ${}^{4}J_{HH}$  = 2.0 Hz, 1 H, OAr-*H*) ppm. {}^{13}C NMR  $(C_6D_6): \delta = 29.9 [C(CH_3)_3], 30.5 [C(CH_3)_3], 31.7 [C(CH_3)_3], 34.1$ [C(CH<sub>3</sub>)<sub>3</sub>], 34.9 [C(CH<sub>3</sub>)<sub>3</sub>], 47.9 [C(CH<sub>3</sub>)<sub>3</sub>], 56.7 (CH<sub>2</sub>-N), 123.4, 124.4, 128.4, 138.3, 140.8, 153.4 (all Ar-C) ppm. IR (KBr pellets):  $\tilde{v}_{Al-H}$  = 1871.8 (st) cm<sup>-1</sup>. C<sub>19</sub>H<sub>32</sub>AlNO (317.20): calcd. C 71.0, H 10.0, N 4.4; found C 70.7, H 9.7, N 4.2.

X-ray Crystallographic Study of  $[AIH{\mu-3,5-tBu_2-2-(O)C_6H_2CH_2-NtBu}]_2 \cdot C_6D_6$  (5·C<sub>6</sub>D<sub>6</sub>): Crystal data and details of the structure

Table 2.	Crystalle	ographic	data for	compound	5

Empirical formula	$C_{44}H_{64}Al_2D_6N_2O_2$			
Formula wt.	719.02			
Colour/habit	colourless/block			
Crystal dimensions [mm]	$0.35 \times 0.14 \times 0.10$			
Crystal system	monoclinic			
Space group	$P2_1/n$			
a [Å]	14.5912(3)			
b [Å]	11.6599(2)			
c [Å]	25.9184(5)			
	90			
β[°]	97.7702(19)			
δ	90			
$V[Å^3]$	4369.06(14)			
Z	4			
Temperature [K]	100(1)			
Calculated density [g cm <sup>-3</sup> ]	1.093			
$\mu (\text{Mo-}K_a) [\text{mm}^{-1}]$	0.7107			
F(000)	1560			
Min., max. $\theta$ [°]	3.73, 28.80			
Data set $(h; k; l)$	-18 to +17; -15 to +15; -35 to +34			
No. of reflections collected	32603			
No. of indep. reflections, R(int)	10115, 0.0534			
No. of data, restraints, parameters	10115, 0, 477			
$R_1, wR_2, \text{GOF}^{[a]}$	0.0525, 0.1100, 1.025			
Max., av. shift/error	0.001, 0.000			
$\Delta \rho_{\text{max./min.}} [e \text{\AA}^{-3}]$	-0.29, 0.30			
$\overline{[a] w = 1/[\sigma^2(F_0^2) + (0.0399P)^2]}$	+ 2.56 <i>P</i> ]; $P = (F_0^2 + 2F_c^2)/3$ .			

determination are presented in Table 2. Data collection was performed at 100(1) with an Oxford Instruments CryoJet XL nitrogenbased temperature controller, the single-crystal sample being covered in perfluorinated ether oil. All measurements were made by using an Oxford Diffraction Xcalibur S3 four-circle diffractometer equipped with graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda =$ 0.7107 Å). Multiscan<sup>[67]</sup> absorption correction procedures were applied to the data. The structure was solved, with the *SHELTL-97* package, by direct methods (*SHELXS-97*) and refined by using full-matrix least-squares against  $F^2$  (*SHELXL-97*).<sup>[68]</sup> All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms except for those on the Al centres. The final residual electron density maps showed no remarkable features.

CCDC-723507(**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

Supporting Information (see footnote on the first page of this article): Computational details, Cartesian coordinates and final energies for the optimized complexes. DOSY NMR spectra of complexes 3–5.

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- [1] K. Ishihara in *Lewis Acids in Organic Synthesis* (Ed.: H. Yamamoto), Wiley-VCH, Weinheim, Germany, **2000** vol. 1, p. 98.
- T. Ooi, K. Maruoka in *Lewis Acids in Organic Synthesis* (Ed.: H. Yamamoto), Wiley-VCH, Weinheim, Germany, 2000, vol. 1, p. 191.
- [3] E. Y. X. Chen, T. J. Marks, Chem. Rev. 2000, 100, 1391-1434.
- [4] G. Erker, Dalton Trans. 2005, 1883–1890.
- [5] O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* 2004, 104, 6147–6176.
- [6] M. D. Healy, M. R. Mason, P. W. Gravelle, S. G. Bott, A. R. Barron, J. Chem. Soc., Dalton Trans. 1993, 441–454.
- [7] M. D. Healy, M. B. Power, A. R. Barron, Coord. Chem. Rev. 1994, 130, 63–135.
- [8] R. J. Wehmschulte, W. J. Grigsby, B. Schiemenz, R. A. Bartlett, P. P. Power, *Inorg. Chem.* **1996**, *35*, 6694–6702.
- [9] R. J. Wehmschulte, P. P. Power, *Inorg. Chem.* 1996, 35, 3262– 3267.
- [10] K. Knabel, I. Krossing, H. Noth, H. Schwenk-Kircher, M. Schmidt-Amelunxen, T. Seifert, *Eur. J. Inorg. Chem.* 1998, 1095–1114.
- [11] L. K. Johnson, C. M. Killian, M. Brookhart, J. Am. Chem. Soc. 1995, 117, 6414–6415.
- [12] G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. Williams, *Chem. Commun.* **1998**, 849–850.
- [13] B. L. Small, M. Brookhart, J. Am. Chem. Soc. 1998, 120, 7143– 7144.
- [14] B. L. Small, M. Brookhart, A. M. A. Bennett, J. Am. Chem. Soc. 1998, 120, 4049–4050.
- [15] G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Stromberg, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1999**, *121*, 8728–8740.
- [16] N. S. Venkataramanan, G. Kuppuraj, S. Rajagopal, Coord. Chem. Rev. 2005, 249, 1249–1268.

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1528



- [18] R. B. Bedford, D. W. Bruce, R. M. Frost, J. W. Goodby, M. Hird, *Chem. Commun.* 2004, 2822–2823.
- [19] V. C. Gibson, S. K. Spitzmesser, Chem. Rev. 2003, 103, 283– 315.
- [20] D. A. Atwood, J. A. Jegier, D. Rutherford, J. Am. Chem. Soc. 1995, 117, 6779–6780.
- [21] P. A. Cameron, V. C. Gibson, C. Redshaw, J. A. Segal, M. D. Bruce, A. J. P. White, D. J. Williams, *Chem. Commun.* 1999, 1883–1884.
- [22] P. A. Cameron, V. C. Gibson, C. Redshaw, J. A. Segal, A. J. P. White, D. J. Williams, J. Chem. Soc., Dalton Trans. 2002, 415– 422.
- [23] V. C. Gibson, D. Nienhuis, C. Redshaw, A. J. P. White, D. J. Williams, *Dalton Trans.* 2004, 1761–1765.
- [24] J. Liu, N. Iwasa, K. Nomura, *Dalton Trans.* 2008, 3978–3988.
- [25] J. A. Francis, S. G. Bott, A. R. Barron, J. Chem. Soc., Dalton Trans. 1998, 3305–3310.
- [26] T. Fujita, Y. Tohi, M. Mitani, S. Matsui, J. Saito, M. Nitabaru, K. Sugi, H. Makio, T. Tsutsui, Mitsui Chemicals Inc., EP-0874005, 1998.
- [27] T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science* 2000, 460–461.
- [28] D. J. Jones, V. C. Gibson, S. M. Green, P. J. Maddox, *Chem. Commun.* 2002, 1038–1039.
- [29] V. C. Gibson, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White, D. J. Williams, J. Chem. Soc., Dalton Trans. 1999, 827– 829.
- [30] D. C. H. Oakes, V. C. Gibson, A. J. P. White, D. J. Williams, *Inorg. Chem.* 2006, 45, 3476–3477.
- [31] A. R. F. Cox, V. C. Gibson, E. L. Marshall, A. J. P. White, D. Yeldon, *Dalton Trans.* 2006, 5014–5023.
- [32] P. A. Cameron, V. C. Gibson, C. Redshaw, J. A. Segal, G. A. Solan, A. J. P. White, D. J. Williams, J. Chem. Soc., Dalton Trans. 2001, 1472–1476.
- [33] M. S. Hill, A. R. Hutchison, T. S. Keizer, S. Parkin, M. A. VanAelstyn, D. A. Atwood, *J. Organomet. Chem.* 2001, 628, 71–75.
- [34] S. Dagorne, I. Janowska, R. Welter, J. Zakrzewski, G. Jaouen, Organometallics 2004, 23, 4706–4710.
- [35] D. Pappalardo, C. Tedesco, C. Pellecchia, *Eur. J. Inorg. Chem.* 2002, 621–628.
- [36] O. Stecher, E. Wiberg, Ber. Dtsch. Chem. Ges. 1942, 75, 2003– 2012.
- [37] M. J. Harvey, M. Proffitt, P. R. Wei, D. A. Atwood, *Chem. Commun.* 2001, 2094–2095.
- [38] Y. Peng, H. J. Hao, V. Jancik, H. W. Roesky, R. Herbst-Irmer, J. Magull, *Dalton Trans.* 2004, 3548–3551.
- [39] M. A. Muñoz-Hernández, B. Sannigrahi, D. A. Atwood, J. Am. Chem. Soc. 1999, 121, 6747–6748.
- [40] S. Dagorne, L. Lavanant, R. Welter, C. Chassenieux, P. Haquette, G. Jaouen, Organometallics 2003, 22, 3732–3741.
- [41] M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 2002, 124, 3327–3336.
- [42] M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, T. Nakano, H. Tanaka, T. Fujita, J. Am. Chem. Soc. 2003, 125, 4293–4305.
- [43] T. Mole, A. Jefrey, Organoaluminium Chemistry, Elsevier, New York, 1972.
- [44] A. J. Downs, C. R. Pulham, Adv. Inorg. Chem. 1994, 41, 171– 232.

- [45] Y. Cohen, L. Avram, L. Frish, Angew. Chem. Int. Ed. 2005, 44, 520–554.
- [46] M. S. Hill, D. A. Atwood, *Main Group Chem.* 1998, 2, 285–292.
- [47] H. Nöth, A. Schlegel, B. Singaram, J. Knizek, P. Mayer, T. Seifert, *Eur. J. Inorg. Chem.* 2001, 173–180.
- [48] J. Qiao, L. D. Wang, J. F. Xie, G. T. Lei, G. S. Wu, Y. Qiu, *Chem. Commun.* 2005, 4560–4562.
- [49] A. Willner, A. Hepp, N. W. Mitzel, *Dalton Trans.* 2008, 6832– 6842.
- [50] S. Dagorne, F. Le Bideau, R. Welter, S. Bellemin-Laponnaz, A. Maisse-Francois, *Chem. Eur. J.* 2007, 13, 3202–3217.
- [51] S. Dagorne, I. A. Guzei, M. P. Coles, R. F. Jordan, J. Am. Chem. Soc. 2000, 122, 274–289.
- [52] J. R. Horder, M. F. Lappert, J. Chem. Soc. A 1968, 2004–2006.
- [53] J. R. Jennings, K. Wade, B. K. Wyatt, J. Chem. Soc. A 1968, 2535–2538
- [54] Y. L. Huang, B. H. Huang, B. T. Ko, C. C. Lin, J. Chem. Soc., Dalton Trans. 2001, 1359–1365.
- [55] B. H. Huang, T. L. Yu, Y. L. Huang, B. T. Ko, C. C. Lin, *Inorg. Chem.* 2002, 41, 2987–2994.
- [56] H. P. Zhu, J. F. Chai, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, D. Vidovic, J. Magull, *Eur. J. Inorg. Chem.* 2003, 3113–3119.
- [57] D. A. Atwood, D. Rutherford, Inorg. Chem. 1995, 34, 4008– 4010.
- [58] D. A. Atwood, M. P. Remington, D. Rutherford, Organometallics 1996, 15, 4763–4769.
- [59] A. Haaland, *Coordination Chemistry of Aluminium* (Ed.: G. H. Robinson), VCH Publishers, New York, **1993**.
- [60] J. A. Francis, C. N. McMahon, S. G. Bott, A. R. Barron, Organometallics 1999, 18, 4399–4416.
- [61] C. T. Lee, W. T. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785–789.
- [62] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.
- [63] W. Kohn, A. D. Becke, R. G. Parr, J. Phys. Chem. 1996, 100, 12974–12980.
- [64] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. J. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, A. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, A. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, A. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, A. Johnson, W. Chen, M. W. Wong, A. Gonzalez, J. A. Pople, Gaussian 03, Revision E.01, Gaussian Inc., Wallingford CT, 2004.
- [65] N. Iwasa, J. Y. Liu, K. Nomura, *Catal. Commun.* **2008**, *9*, 1148–1152.
- [66] N. Iwasa, M. Fujiki, K. Nomura, J. Mol. Catal. A 2008, 292, 67–75.
- [67] SORTAV. R. H. Blessing, Acta Crystallogr., Sect. A 1995, 51, 33–38.
- [68] G. M. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112–122. Received: November 20, 2009 Published Online: February 19, 2010