

PAPER



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Aluminium(III) dialkyl 2,6-bisimino-4*R*-dihydropyridinates(−1): selective synthesis, structure and controlled dimerization†

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A family of stable and otherwise selectively unachievable 2,6-bisimino-4-*R*-1,4-dihydropyridinate aluminium (III) dialkyl complexes [AlR'₂(4-*R*-ⁱPrHBIPH)] (R = Bn, Allyl; R' = Me, Et, ⁱBu) have been synthesized, taking advantage of a method for the preparation of the corresponding 4-*R*-1,4-dihydropyridine precursors developed in our group. All the dihydropyridinate(−1) dialkyl aluminium complexes have been fully characterized by ¹H-¹³C-NMR, elemental analysis and in the case **2'a**, also by X-ray diffraction studies. Upon heating in toluene solution at 110 °C, the dimethyl derivatives **2a** and **2'a** dimerize selectively through a double cycloaddition. This reaction leads to the formation of two new C–C bonds that involve the both meta positions of the two 4-*R*-1,4-dihydropyridinate fragments, resulting the binuclear aluminium species [Me₂Al(4-*R*-ⁱPrHBIPH)]₂ (R = Bn (**3a**); allyl (**3'a**)). Experimental kinetics showed that the dimerization of **2'a** obeys second order rate with negative activation entropy, which is consistent with a bimolecular rate-determining step. Controlled methanolysis of both **3a** and **3'a** release the metal-free dimeric bases, (4-Bn-ⁱPrHBIPH)₂ and (4-allyl-ⁱPrHBIPH)₂, providing a convenient route to these potentially useful ditopic ligands. When the R' groups are bulkier than Me (**2b**, **2'b** and **2'c**), the dimerization is hindered or fully disabled, favoring the formation of paramagnetic NMR-silent species, which have been identified on the basis of a controlled methanolysis of the final organometallic products. Thus, when a toluene solution of [AlEt₂(4-Bn-ⁱPrHBIPH)] (**2b**) was heated at 110 °C, followed by the addition of methanol in excess, it yields a mixture of the dimer (4-Bn-ⁱPrHBIPH)₂ and the aromatized base 4-Bn-ⁱPrBIP, in ca. 1 : 2 ratio, indicating that the dimerization of **2b** competes with its spontaneous dehydrogenation, yielding a paramagnetic complex containing a AlEt₂ unit and a non-innocent (4-Bn-ⁱPrBIP)^{•−} radical-anion ligand. Similar NMR monitoring experiments on the thermal behavior of [AlEt₂(4-allyl-ⁱPrHBIPH)] (**2'b**) and [AlⁱBu₂(4-allyl-ⁱPrHBIPH)] (**2'c**) showed that these complexes do not dimerize, but afford exclusively NMR silent products. When such thermally treated samples were subjected to methanolysis, they resulted in mixtures of the alkylated 4-allyl-ⁱPrBIP and non-alkylated ⁱPrBIP ligand, suggesting that dehydrogenation and deallylation reactions take place competitively.

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Introduction

More than two decades have passed since the earliest reports on the synthesis of organometallic complexes supported by 2,6-bis(imino)pyridine ligands (BIP).¹ Since then, research on the interaction of such ligands with aluminium(III) alkyls (R₃Al) has attracted the interest of a number of different research groups.^{2–5} The first reports were reported by Gibson and, shortly after, Brookhart and his landmark publications on the discovery of BIP iron and cobalt complexes [MCl₂(BIP)] with methylaluminoxane (MAO) as highly active catalysts for ethylene polymerization.⁶ The extension towards the synthesis of organoaluminium derivatives was envisioned as a straight-

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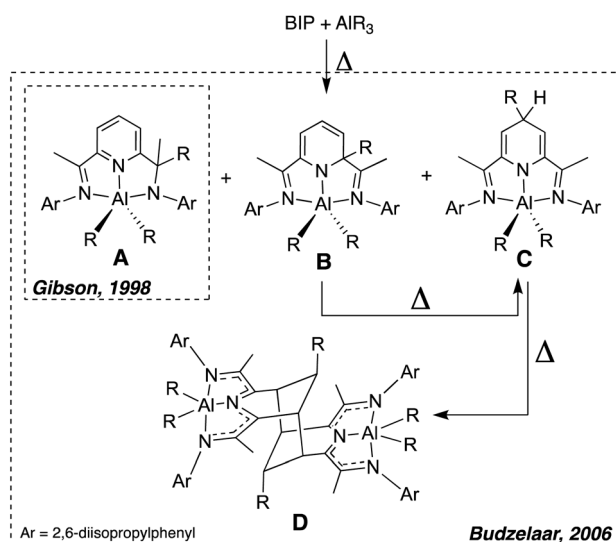
† Electronic supplementary information (ESI) available. CCDC 1898737 for **2'a**, 1898738 for **3a** and 1898739 for **3'a**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/C9DT00847K

forward means to access the corresponding transition metal-free alkyl BIP complexes, which are systems with great potential in such catalytic reactions.² Gibson's initial results, followed by other analogous results reported by Grassi,³ showed that a relatively straightforward reaction ensues when ⁱPrBIP is reacted with an excess of AlMe₃ under rather forced conditions (refluxing toluene). This leads to dialkylaluminum species supported by an imino-amido tridentate ligand arising from the single methylation of one of the imine groups of the ⁱPrBIP ligand. These systems exhibit some olefin polymerization activity when activated with powerful Lewis acids. A few years later, Budzelaar discovered that the reaction of R₃Al with BIP was deceptively simple.⁴ He observed that the treatment of BIP ligands with different aluminum trialkyls under milder reaction conditions, more akin to those applied for polymerization catalysis, invariably led to mixtures of several organometallic species arising from the unselective alkyl transfer from the metal to different positions of the BIP ligand (Scheme 1).^{4b} Whilst type **B** species were invariably the main reaction products, the imine-amide species (**A**) identified by Gibson and Grassi were also formed, along with type **C** species, the products arising from alkyl migration to the remote position 4 in the pyridine ring. Albeit heating the reaction mixtures apparently caused the isomerization of product **B** into **C**, the transformation was never complete, and in addition a fourth binuclear species **D** emerged. These complicated mixtures could not be separated, and the different species were identified on the basis of comparative spectroscopic and computational work, together with the resolution of the structures of the few crystals that grew, among which were a couple of examples of the dimers **D**, whose NMR spectrum could never be adequately recorded. The resolution of the structure of such dimers allowed to establish that the pathway from the initial BIP ligand to these binuclear species **D** crossed through the dihydropyridinate **C**, which is its immediate precursor. Although a

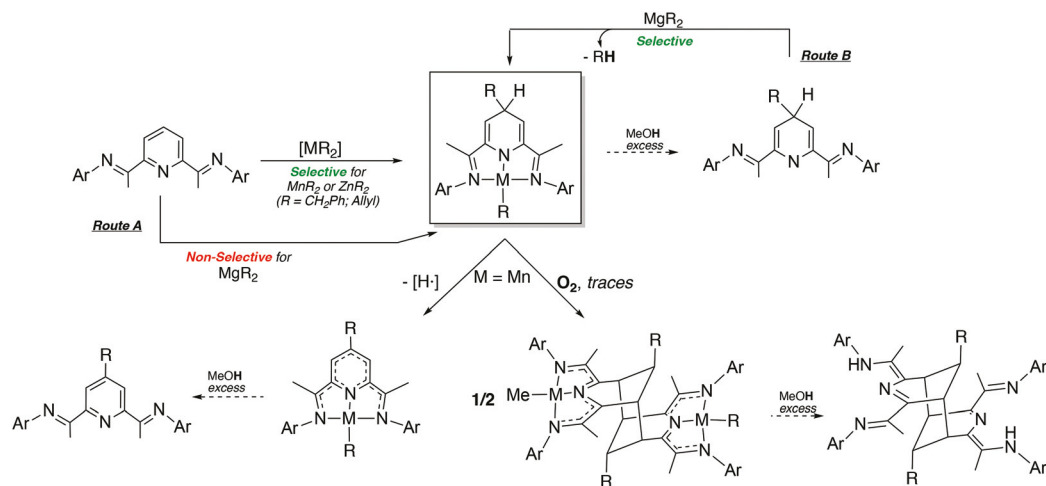
similar process could explain the formation of an analogous binuclear Cr complex as a result of the reaction of [(ⁱPrBIP)CrCl₃] with BnMgCl, the mechanism has remained speculative as the corresponding chromium dihydropyridinate analogue of **C** has not yet been identified.⁷

Even though the complex chemistry disclosed by Budzelaar clarified many details of the peculiar reactivity of ^RBIP ligands in combination with aluminium alkyls, it seemed to have little practical synthetic value. However, different groups, including ours, have investigated the organometallics of ^RBIP ligands, and much progress has been achieved in recent years.^{1c} For example, one of the best-known properties of ^RBIP ligands is their non-innocent character, which plays a critical role in enabling many of the most recent applications of these ligands in catalysis. Whilst this attribute, based on the ability of such ligands to participate in redox transformations, has been well documented for transition metal complexes,⁸ it has even more significance for redox-inactive main-group metal BIP ions.⁹ Non-innocent alkylaluminiums of the type [AlR₂(ⁱPrBIP)], containing an Al(III) fragment and a reduced ⁱPrBIP^{•−} radical-anion ligand, were isolated by Gambarotta¹⁰ and by us,¹¹ whilst a number of derivatives of other non-redox main-group metals have been reported by others.⁸

In particular, we became interested in the aluminium compounds of type **C**, for several reasons. First, these systems are akin to others that we and others have selectively generated with transition metals, such as manganese¹² or iron,¹³ or later with post-transition elements, like zinc,¹⁴ upon straightforward reactions of the corresponding metal dialkyls (MR₂)^{12,14} or monoalkyls (py₂(FeCH₂CMe₃)Cl)¹³ with BIP ligands (Scheme 2, *Route A*, for Mn and Zn). On the other hand, when this direct method did not lead to the expected selective result, like in the case of main group elements such as magnesium,^{14,15} we tackled the problem through an alternative strategy (Scheme 2, *Route B*). This method relied on the demetallation of their Mn or Zn dihydropyridinate complexes with methanol, followed by isolation of the free bases and then reacting them with suitable magnesium dialkyls (MgR₂; R = Bn, Bu).¹⁶ Such reactions were fast and clean, and proved very convenient from a synthetic point of view as they cleanly afforded the expected 4-*R*-1,4-dihydropyridinate(−1) magnesium(II) monoalkyls, which otherwise could not be selectively obtained when *Route A* in Scheme 2 was applied. Furthermore, as we showed a few years ago,¹⁷ manganese dihydropyridinates, although highly sensitive compounds and prone to undergo spontaneous aromatization (Scheme 2, bottom left), can be induced to experience a similar dimerization to that of the aluminium and chromium complexes (Scheme 2, bottom right). Using the above-mentioned ligand-transfer strategy, we demetallated the resulting manganese dimers, and the tricyclic bases were then transferred to different metal complexes (Zn, Pd). Due to the technical difficulties in controlling the oxygen-induced dimerization reaction, the ligand-transfer methodology was restricted to a single BIP ligand.



Scheme 1



Scheme 2

In this contribution, we report the application of *Route B* in Scheme 2 for the selective synthesis and full characterization of aluminium complexes of type **C**, followed by their treatment to obtain type **D** complexes, both akin (but not identical) to those previously identified by Budzelaar as part of more or less complex mixtures of products. We verified that the aluminium dihydropyridinates, though moderately stable, undergo a well-behaved, clean thermal dimerization. This transformation, followed by a mild demetallation protocol, provides a clean pathway to the corresponding tricyclic bases, allowing for a systematic investigation of these promising molecules as a novel type of ditopic pincer ligands.

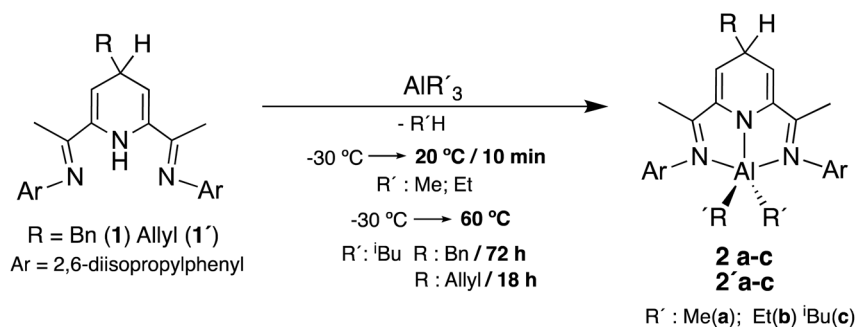
Results and discussion

Reaction of dihydropyridines **1** and **1'** with aluminium alkyls

We initiated our investigation revisiting the synthesis of dihydropyridines 4- R - iPr - H_2 BIP with R = benzyl (**1**) or allyl (**1'**). We had previously reported that these metal-free compounds can be accessed from BIPs using organomanganous chemistry¹² and in addition, we optimized a procedure for the synthesis for R = benzyl, but the allyl derivative was usually obtained

with variable amounts of the aromatized 4- R - iPr BIP.¹⁴ In the same contribution, we also showed that the ZnR_2 -based route was promising, as the Zn dihydropyridinate systems were not prone to undergo spontaneous dehydrogenation. However, the released allyl dihydropyridine was readily oxidized during the work-up. We now describe some practical improvements related to this protocol that allows the syntheses of both 4- R - iPr - H_2 BIP ligands (**1** and **1'**).

Next, we addressed the reaction of **1** and **1'** with aluminium trialkyls derivatives AlR'_3 (R' = Me, Et, iBu , Scheme 3). Upon mixing cold (-30 °C) solutions in toluene- d_8 containing equimolar amounts of both components, intense burgundy (R' = Me, Et) or indigo (R' = iBu) colorations developed. 1H NMR monitoring showed that for R' = Me or Et, the reaction was completed in a short time at room temperature. The spectra were consistent with a clean formation of the corresponding dihydropyridinate complexes with the concomitant elimination of alkane. For example, the 1H NMR spectra of **2a** and **2'a** exhibited two close singlets integrated for 3H each in the highest field region of their spectra (*ca.* -0.69 to -0.71 ppm) for the aluminium-bound methyl groups, which lose their chemical equivalence under the influence of the 4- R -dihydropyridinate ligand. In return, the latter gave rise to signal pat-



Scheme 3

terns very similar to those of the free ligands, except for the absent NH resonance. Likewise, the diethyl derivatives **2b** and **2'b** exhibited similar ^1H -NMR features, excluding the quartets and triplets for the two non-equivalent ethyl groups attached to aluminium. The spectra of these dihydropyridinate complexes were strongly reminiscent of those of the alkyl Zn and -Mg congeners reported by us.^{14,15} An even more pertinent comparison could be established with the partial spectral data reported by Budzelaar for closely related dialkylaluminium dihydropyridinates, and although this was based mostly on the analysis of the spectra of complex reaction mixtures and DFT calculations,⁴ it confirmed our assignments.

NMR samples **2a**, **b** and **2'a**, **b** in toluene or benzene are notoriously stable, and as expected, their spectra showed no visible changes over several days at ambient temperature. This encouraged us to pursue their isolation. These complexes were readily made at preparative scale and were crystallized from hexane, from which they were isolated as dark burgundy crystalline solids and then fully characterized by the usual ensemble of ^1H and ^{13}C NMR, elemental analysis and X-ray diffraction for **2'a**. The relatively low boiling point of both the Me_3Al and Et_3Al used as the dihydropyridinates' precursors is worth noting as this makes the dihydropyridine ligand deprotonation very convenient from a technical point of view, since these reactions do not require an accurate stoichiometric control. We demonstrated that a small excess of trialkylaluminium in the reactor did not affect either the rate or the product yields, while it guaranteed the total consumption of the ligand. Thus, the extra organoaluminium species remaining upon the reaction completion, whether adventitiously or deliberately added, were conveniently removed under reduced pressure.

Fig. 1 shows the crystal structure of **2'a**. The N_3 tridentate ligand features similar bond distances to those found in the

previously reported Zn(II) and Mg(II) dihydropyridinates. As frequently observed in complexes with BIP and BIP-based ligands, the bonds connecting the metal centre with the imine nitrogen atoms N1 and N3 were slightly different (2.235(17) and 2.208(17) Å, respectively), and appreciably longer than the Al–N2 bond involving the heterocyclic N2 atom. The geometry of the pentacoordinated Al centre could be regarded as distorted square pyramidal ($\tau_5 = 0.43$), with the methyl ligands placed in the base and in the apex, respectively. This is in close analogy with Gambarotta's dimethylaluminum complex $[(^i\text{Pr})\text{BIP}]^{-1}(\text{Al}^{\text{III}})\text{Me}_2$, which contained a reduced ^iPr BIP ligand. In contrast, the diethylaluminium analogue $[(^i\text{Pr})\text{BIP}]^{-1}(\text{Al}^{\text{III}})\text{Et}_2$, reported by us, presented a nearly perfect square pyramid geometry with $\tau_5 = 0.04$.

Contrary to the fast reactions of the dihydropyridines **1** and **1'** with AlMe_3 and AlEt_3 , ^1H NMR monitorization of the corresponding reactions with $\text{Al}(\text{tBu})_3$ revealed no signs of products after warming the mixtures to room temperature, in spite of the intense blue indigo colour developed upon mixing the reagents at -30°C . After 2 h at 23°C , the indigo colour of the reaction solutions persisted, and the samples still revealed mostly unaltered signals for the reagents ($\text{Al}(\text{tBu})_3$ and **1** or **1'**), together with small sets of resonances, attributable to the corresponding products **2c** or **2'c**. Full conversions were only attained after prolonged heating at 60°C . At this temperature, the colour of the solutions gradually evolved to burgundy hues, similar to that observed in the reactions with AlMe_3 or AlEt_3 . The reaction was appreciably faster for the allyl ligand **1'** (**2'c** in 18 h) than for the benzyl congener, which required 72 h. As a consequence, we proceeded to isolate **2'c**, but did not pursue the preparation of pure samples of **2c**, which was characterized in solution. Comparison of the spectroscopic features of **2c** with those of **2'c** and the remaining dihydropyridinates **2–2'** allowed its unambiguous identification.

Thermal behaviour of the dihydropyridinate complexes: dimerization vs. aromatization

As mentioned in the Introduction, Budzelaar showed that heating the mixtures resulting from the reaction of ^iPr BIP with aluminium alkyls (in particular, AlClEt_2 ^{4a} and AlH^iBu_2 ^{4b}) allowed to obtain small amounts of tricyclic dimers, arising from the monomeric precursors of type C analogous to complexes **2** or **2'** (Scheme 3). Such dimers were characterized by X-ray diffraction but they seemed to be too insoluble or perhaps contaminated with paramagnetic impurities, which prevented their characterization by NMR. As mentioned, similar dimeric compounds have been isolated in low yields after the reaction of paramagnetic Cr(III) with benzylmagnesium chloride.⁷ Our group previously showed that the dimerization of alkylmanganese(II) dihydropyridinates only takes place if it is triggered by a trace amount of oxygen, as shown in Scheme 2. Otherwise, the monomeric precursors experience spontaneous hydrogen loss, yielding aromatized organomanganese(I) BIP species.^{12b} Due to the difficulty of monitoring the transformation by NMR, either for the paramagnetic Cr or Mn systems or in Budzelaar's work, it was not possible to gather

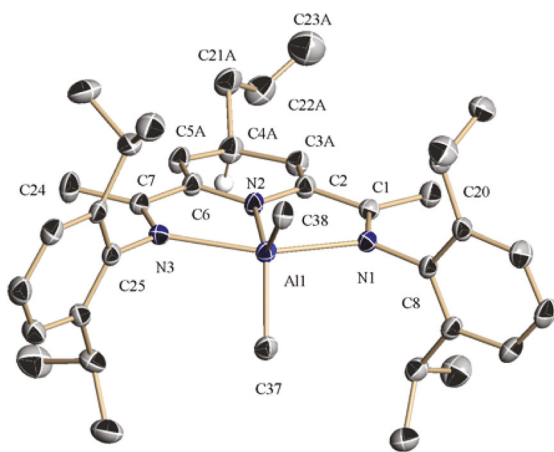
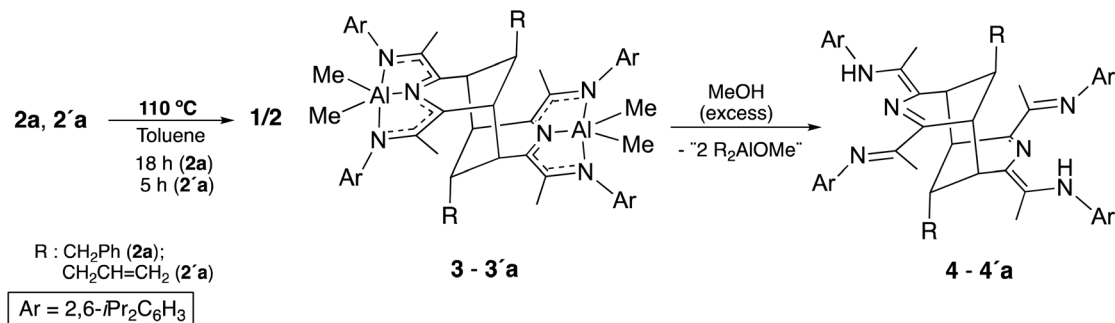


Fig. 1 ORTEP representation of the structure of compound **2'a**. Selected bond lengths (Å) and angles ($^\circ$): Al(1)–C(37), 1.974(2); Al(1)–C(38), 1.975(2); Al(1)–N(1), 2.235(17); Al(1)–N(2), 1.887(17); Al(1)–N(3), 2.208(17); N(2)–C(2), 1.388(3); C(1)–C(2), 1.468(3); C(2)–C(3A), 1.362(5); C(3A)–C(4A), 1.501(5); N(2)–Al(1)–C(38), 126.76(9); N(3)–Al(1)–N(1), 152.63(6); N(2)–Al(1)–C(37), 125.32(9); C(37)–Al(1)–C(38), 107.91(10); N(2)–Al(1)–N(1), 75.92(7); N(2)–Al(1)–N(3), 76.71(7); N(1)–Al(1)–C(38), 98.22(8); N(3)–Al(1)–C(38), 97.67(8).



Scheme 4

relevant data to ascertain the mechanism of the dimerization process, though the latter author supported a bimolecular mechanism based on DFT calculations. This involved the consecutive formation of two C–C bonds required to assemble the tricyclic unit, *via* a single-bonded intermediate with a diradical character. This mechanism does not require any activation of the monomers, but the complexity of the overall reaction with aluminium did not allow ruling out the participation of any of the species present in the reaction mixtures.

The selective synthesis of complex **2** or **2'** put us in the position to study whether these complexes were prone to undergo dimerization, or like their organomanganese(II) analogues, they required interacting with an external agent, such as a trace amount of oxygen, to proceed. To clarify this point, we first examined the behaviour of pure (isolated) samples of complexes **2a**, **b** and **2'a–c** dissolved in toluene-*d*₈ under heating in gas-tight NMR tubes, sealed with PTFE valves.

When samples of complexes **2a** and **2'a** were heated in a thermostatic oil bath, their burgundy colour gradually became a deeper hue. The ¹H-NMR spectra showed new sets of signals growing at the expense of the initial ones, consistent with the new dimeric species **3a** and **3'a**, respectively (Scheme 4). The transformation took around three days to complete at 80 °C or 36 h at 110 °C for the 4-benzyl derivative, but proceeded faster for the 4-allyl, being essentially finished in 3 h at 80 °C. For preparative purposes, these reactions were carried out in Teflon-valved glass ampoules also in a thermostatic oil bath, heating the toluene solutions of the monomeric precursors **2a** and **2'a** at 110 °C. A regular work-up provided analytically pure samples of both compounds, which were then subjected to full characterization. For example, Fig. 2 shows a comparison of the ¹H-NMR spectra of **2a** and **3a**. As can be seen, the spectral features of the dimer clearly appear, confirming its identity. As the 3,5 vinyl-type carbons in **2a** became aliphatic bridgehead atoms in **3a**, the characteristic pattern of signals corresponding to the dihydropyridine moiety of **2a**, namely, a doublet at 2.80 ppm for the benzyl CH₂, a multiplet at 4.00 ppm for the heterocyclic 4-CH and a doublet at 5.07 ppm for the neighbouring ring protons, were replaced by a doublet, a multiplet and a singlet, respectively, in the spectrum of the **3a** dimer. The spectrum of **3'a** exhibited a very similar signal pattern for the heterocyclic fragment, and essentially unper-

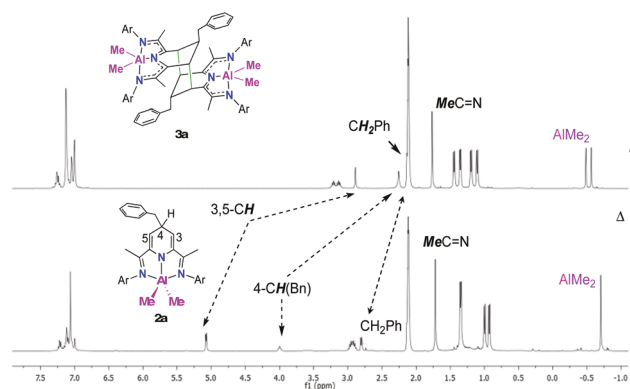


Fig. 2 ¹H NMR (toluene-*d*₈, 25 °C, 400 MHz) spectra showing the transformation of **2a** to **3a** (below, compound **2a**; top, same sample after heating at 80 °C for 72 h).

turbed signals for the pending allyl groups, confirming that the terminal double bond was a mere spectator during the dimerization reaction. As shown also in Scheme 4, the treatment of **3a** or **3'a** with an excess of methanol led to mixtures of the corresponding tricyclic bases **4** and **4'**. We previously applied the same method for analysis of the paramagnetic, NMR-silent complexes formed in the related Mn(II) system. In particular, the signals in the ¹H-NMR spectrum of compound **4'** were undistinguishable from those of a sample containing the product obtained from the Mn route. As noted previously, the NMR spectra of these polyimino bases appeared rather more complex than would be expected because they existed in solution as a mixture of organic tautomers. The ESI-MS analysis of the crude material for **4** showed the expected signal at *m/z* 1146.8 for the protonated molecular ion [M + H]⁺. In addition to their analytic value, the demetallation reactions provide a new and more selective approach to dimers **4** and **4'**, which could not be accessed selectively through the organomanganese route.

Suitable crystals for X-ray diffraction studies of both dimers were grown from cold dichloromethane (**3a**, Fig. 3) or hexane solutions (**3'a**, Fig. 4). These display a tricyclic ditopic ligand symmetrically bridging two AlMe₂ fragments, related by a molecular inversion centre. The pentacoordinated aluminium centres exhibited distorted square pyramidal geometries ($\tau_5 =$

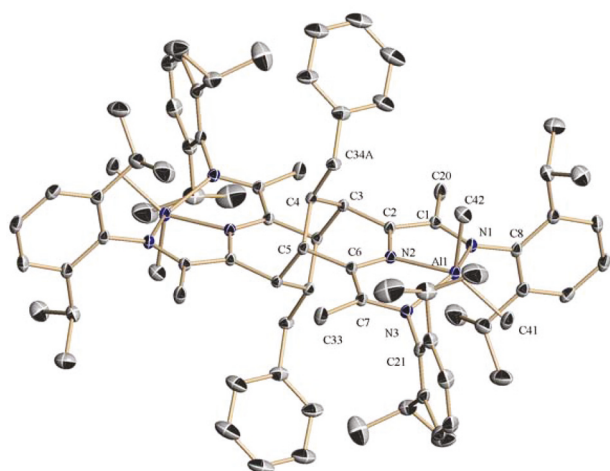


Fig. 3 ORTEP representation of the structure of compound **3a**. Selected bond lengths (Å) and angles (deg): Al–N(1): 2.106(13); Al–N(2): 2.010(13); Al–N(3): 2.120(13); Al–C(41): 1.976(17); Al–C(42): 1.988(13); N(1)–C(1): 1.315(19); N2–C(6): 1.338(19); N(2)–C(2): 1.341(19); N(3)–C(7): 1.310(19); C(1)–C(2): 1.427(2); C(1)–C(20): 1.503(2); C(2)–C(3): 1.511(2); C(3)–C(4): 1.543(2); C(3)–C(5): 1.566(2); C(4)–C(5): 1.543(2); C(5)–C(6): 1.510(2); C(6)–C(7): 1.436(2); C(7)–C(33): 1.504(2); N(2)–Al–N(1): 76.40(5); N(2)–Al–C(41): 143.85(7); N(2)–Al–C(42): 98.56(7); C(41)–Al–C(42): 117.59(9); N(2)–Al–N(3): 76.48(5); N(1)–Al–N(3): 148.01(5).

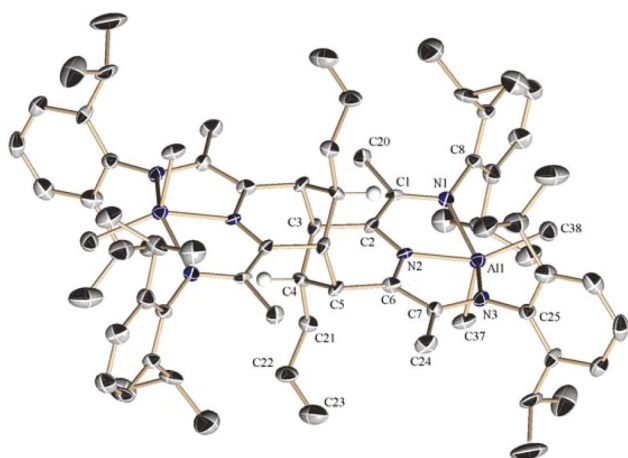


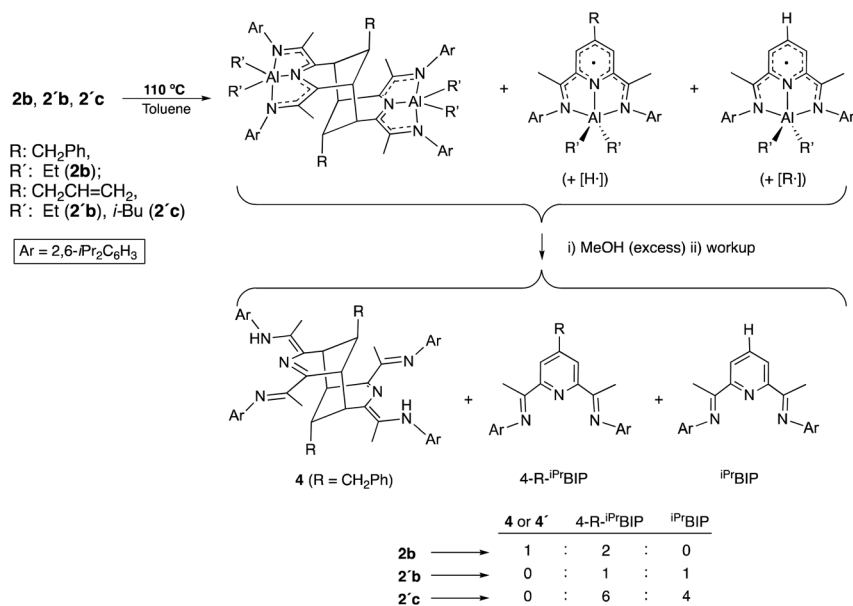
Fig. 4 ORTEP representation of the structure of compound **3'a**. Selected bond lengths (Å) and angles (deg): Al–N(1): 2.106(4); Al–N(2): 2.009(4); Al–N(3): 2.106(4); Al–C(38): 1.975(5); Al–C(37): 1.992(5); N(1)–C(1): 1.329(5); C(1)–C(20): 1.496(6); N2–C(6): 1.327(5); N(2)–C(2): 1.342(5); C(2)–C(3): 1.510(6); C(3)–C(5): 1.541(6); C(3)–C(4): 1.541(6); C(4)–C(5): 1.547(6); C(5)–C(6): 1.518(6); N(3)–C(7): 1.313(5); C(1)–C(2): 1.423(6); C(6)–C(7): 1.436(6); C(7)–C(24): 1.505(6); N(1)–Al–N(2): 76.65(14); N(2)–Al–N(3): 76.10(14); N(2)–Al–C(37): 96.45(18); N(2)–Al–C(38): 143.83(18); C(37)–Al–C(38): 119.7(2); N(1)–Al–N(3): 146.69(15).

0.07 and 0.05 for **3a** and **3'a**, respectively). Both dimers are similar to the related Cr,⁷ Al⁴ and Pd¹⁷ complexes previously reported in the literature. All of them share in common a central cyclohexane core in a chair conformation, arising from the fusion of the dihydropyridine ring through carbons 3 and 5. In both structures, the 4-R substituents end up as equa-

torial substituents, presumably in order to minimize the unfavourable steric repulsion that would result otherwise. This implies a high level of stereocontrol in the dimerization reaction, as the approach of the monomeric precursors must proceed exclusively *via* the least hindered face of the heterocyclic dihydropyridine ring.

The rate differences observed for the dimerization of **2a** and **2'a** indicate that this process is highly sensitive to steric effects. Thus, it is not completely surprising that dimer formation becomes increasingly more difficult as the size of the metal fragment increases. As we studied the thermal behaviour of the diethylaluminium complexes **2b**, **2'b** and the isobutyl derivative **2'c** at 110 °C in toluene-*d*₈, we found that different processes become significant (Scheme 5). In particular, when a sample of **2b** was heated at the aforementioned temperature for 3 days, a slight colour change denoted that a similar transformation to that undergone by the methyl derivatives had taken place. The ¹H-NMR spectrum apparently confirmed this conclusion, as the signals of the starting material were replaced by a new set of resonances attributable to the corresponding dimer, **3b**, on the basis of their analogy with those of the previously characterized products. However, despite the fact that such signals were the only ones in the final spectrum, their intensity appeared too weak in relation to those residual solvent peaks. Thus, we applied the standard methanol demetallation treatment, resulting in a mixture of organic products with two major components, the expected dimer **4** and the known benzylated diiminopyridine derivative 4-Bn-ⁱPrBIP, identified by comparison of the ¹H-NMR signals with the spectra of these materials.¹² The relative signal intensities indicated that these products were formed in *ca.*1:2 ratio, indicating that only one half of the starting **2b** had undergone dimerization. The remaining was transformed into an NMR-silent species, revealed only after the mixture was subjected to demetallation. We concluded that, as shown in Scheme 5, this compound was probably the paramagnetic compound [AlEt₂(4-Bn-ⁱPrBIP)], similar to other paramagnetic aluminium compounds containing a singly-reduced (4-Bn-ⁱPrBIP)^{•−} radical anion ligand bound to the Al(III)Et₂ fragment. As mentioned before, similar Al species with non-innocent BIP ligands, [AlR₂(ⁱPrBIP)] have been described in the literature, and which, bearing an organic radical character, are virtually undetectable with conventional NMR spectroscopy. The formation of such a product involves aromatization of the dihydropyridine by loss of the hydrogen atom from the benzylated position 4, a process analogous to the spontaneous dehydrogenation that we previously observed in the related organomanganese chemistry.

In addition, Scheme 5 also depicts the thermal transformations undergone by complexes **2'b** and **2'c**. In these cases, heating the samples at 110 °C led to the complete disappearance of any NMR resonances other than the residual peak of the solvent or background impurity traces. The demetallation protocol afforded organic mixtures, whose spectra showed no sign of the tricyclic base **4'**, but mixtures of alkylated (4-allyl-ⁱPrBIP) and non-alkylated ⁱPrBIP, in a gross 1:1



Scheme 5

ratio, although slightly biased to the allyl products in the case of **2'c**. The implication of this finding is that, for **2'b** or **2'c**, spontaneous de-alkylation becomes competitive with dehydrogenation, probably because the elimination of a stabilized allyl radical is a favourable process. In this case, aromatization of the dihydropyridine ring appears to become relatively fast and outcompetes the dimerization reaction.

The clean dimerization reactions experienced by complexes **2a** and **2'a** provide the hitherto only known examples of this process that proceed from well-defined, isolated and diamagnetic starting materials, and hence are amenable to a detailed study by NMR. Therefore, we decided to study the relatively fast dimerization of **2'a** in order to obtain the kinetic parameters of such transformations. Hence, we monitored the evolution of NMR samples in toluene-*d*₈ of a known concentration at five different temperatures evenly distributed over a 50 K range (323–373 K). Each sample was independently prepared and the evolution of selected ¹H resonances of both the reagent and product was monitored over time. Fig. 5 shows the individual second-order kinetic plots (top) and the Eyring graphic of the corresponding reaction rates (below). As can be seen, the experimental data showed good linear fits,¹⁸ consistent with second-order kinetics. The strongly negative activation entropy ($\Delta S^\ddagger = -53 \text{ cal mol}^{-1} \text{ K}^{-1}$) was consistent with the expected restriction of the freedom degrees as the two reactant particles approach in the adequate orientations to reach the transition state. These features support Budzelaar's bimolecular mechanism and rule out that the reaction rate could be controlled by the pre-activation of one of the monomeric molecules, *e.g.* by thermal promotion to an excited diradical state, or by interacting with some reactive intermediate present in a low stationary concentration, as we proposed for the O₂-triggered dimerization of Mn(II) dihydropyridinate species, since such mechanisms would exhibit unimolecular kinetics.

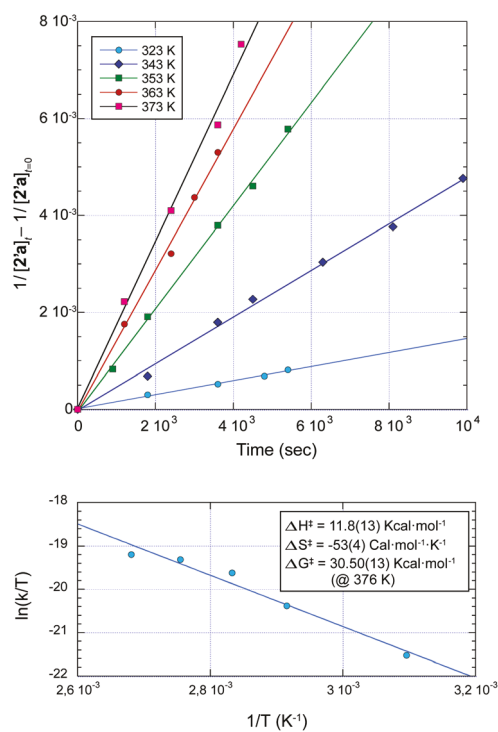


Fig. 5 Second-order kinetic plots for the dimerization of **2'a** at different temperatures (top) and Eyring plot of the reaction rates, showing the activation parameters deduced from the data fit ($\Delta G^\ddagger$ has been interpolated at 376 K, the average of the five temperatures used in the study).

Although the free-energy barrier estimated by Budzelaar's DFT calculation, $13.4 \text{ kcal mol}^{-1}$ at 273 K, was considerably lower than the free activation energy extrapolated from the experimental data for the same conditions ($26.3 \text{ kcal mol}^{-1}$), the

difference could be attributed to the effect of steric hindrance in the real system, which was much smaller in the simplified molecular model. In fact, the experimental activation enthalpy ($\Delta H^\ddagger = 11.8 \text{ kcal mol}^{-1}$) was very close to the computational electronic (SCF) energy barrier ($12.1 \text{ kcal mol}^{-1}$). Thus, our kinetic data can be regarded as being in full agreement with the bimolecular mechanism proposed for the computational model.

Conclusions

Previously developed reactions of $i\text{PrBIP}$ and manganese(II) or zinc(II) alkyls followed by controlled demetallations provide selective access to 2,6-diimino-4-alkyl-1,4-dihydropyridines (4-R- $i\text{PrH}_2\text{BIP}$, R = benzyl or allyl). These ligands can be coordinated to aluminium alkyls AlR'_3 , neutralizing their weakly acidic NH bonds with a concomitant elimination of the corresponding alkane. This represents the first selective route to aluminium dihydropyridinates [$\text{AlR}'_2(4\text{-R-}i\text{PrBIPH})$]. The reactions with trimethylaluminium or triethylaluminium are facile and quantitative, whilst those involving bulkier triisobutylaluminium require more forcing conditions. Although all these dihydropyridinates are thermally stable ($<50^\circ\text{C}$) in the solid state or in solution, at higher temperatures, they change to yield either binuclear complexes that arise from ring fusion at carbons 3,5 of the dihydropyridine ring, or mononuclear aluminium species as a result of spontaneous aromatization of the dihydropyridine with either H' or R' release. The efficiency of the dimerization reaction is very sensitive to steric effects, being the only process detected for $\text{R}' = \text{Me}$, but becomes unfavourable for $\text{R}' = \text{Et}$ or $i\text{Bu}$. Kinetics studies confirmed that such dimerization is a spontaneous bimolecular process with a strongly negative activation entropy, compatible with a previous mechanistic proposal based on DFT calculations. These results pave the way for the investigation of 4-R- H_2BIP and their dimers $(4\text{-R-}\text{H}_2\text{BIP})_2$ as new types of N_3 pincer ligands with many potential applications in coordination and organometallic chemistry, catalysis, or the design of new materials.

Experimental

Most of the compounds included in this contribution were sensitive to traces of oxygen and water. Therefore, all manipulations were carried out under an inert atmosphere using Schlenk techniques and/or a N_2 -filled glove box. The solvents employed (toluene, hexane, dichloromethane, pentane and tetrahydrofuran) were rigorously dried, distilled and degassed prior to use. Anhydrous methanol was obtained after refluxing over carefully dried sodium methoxide, distilled and then stored in a glass ampoule over activated molecular sieves. NMR spectra were recorded on Bruker Avance III-400 and DRX-400 spectrometers (FT 400 MHz, ^1H ; 100 and 125 MHz, ^{13}C). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ resonances of the solvent were used

as the internal standard but the chemical shifts are reported herein with respect to tetramethylsilane (TMS). The assignments were regularly helped with 2D ^1H - ^1H COSY, ^1H - ^{13}C HSQC and HMBC heterocorrelation NMR spectra. NMR-scale reactions (typically in a 0.02 mmol scale) were carried out in NMR tubes sealed with Teflon J. Young-type screw-cap valves. Benzene- d_6 and toluene- d_8 were dried over sodium benzophenone ketyl and vacuum distilled. Mass spectroscopy, elemental analysis and X-ray diffraction measurements were carried out at the Instituto de Investigaciones Químicas. AllylMgBr (1.0 M in Et_2O) was purchased from commercial vendors, being titrated prior to use. Zinc dichloride (ZnCl_2) and the aluminium trialkyls (Me_3Al , Et_3Al 1.0 M in hexane and $i\text{Bu}_3\text{Al}$) were purchased from Sigma-Aldrich. Whilst zinc dichloride was purified by treatment with trimethylsilyl chloride, the aluminium compounds were used without purification or previous treatment. 2,6-[2,6- $i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{C}(\text{Me})_2\text{C}_5\text{H}_3\text{N}$ ($i\text{PrBIP}$) was prepared by the condensation of 2,6-diacetylpyridine with 2,6-diisopropylaniline under azeotropic water-removal conditions and 2,6-[2,6- $i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{C}(\text{Me})_2\text{C}_5\text{H}_3\text{N}$ (4-Bn- $i\text{PrH}_2\text{BIP}$ (**1**)) was obtained according to our own methods, as described in the literature.¹⁴

Preparation of 4-allyl- $i\text{PrH}_2\text{BIP}$ (**1'**)

The method developed for the synthesis of **1**,¹⁴ did not produce satisfactory results when it was applied for the synthesis of 4-allyl- $i\text{PrH}_2\text{BIP}$ (**1'**), since this allylic derivative was routinely obtained with variable amounts of the corresponding aromatized 4-allyl- $i\text{PrBIP}$.^{12,14} The preparation described below, entirely developed in the N_2 -filled glovebox, represents an optimized procedure for the synthesis of **1'a** with respect of that reported by us in the literature.

A 30 mL scintillation vial was charged with 100 mg of ZnCl_2 (0.733 mmol) and 15 mL of THF in the N_2 -filled glovebox. The resultant colourless solution was cooled at -60°C . Then, 1.2 mL of a 1.18 M of allylMgBr (1.750 mmol) in THF was added at -20°C to the ZnCl_2 -containing solution under vigorous stirring. A fine and greyish suspension was instantaneously formed, becoming a slightly grey solution after 5 min. The mixture was stirred for 30 min, cooled again to -20°C and transferred to a suspension of $i\text{PrBIP}$ (282 mg, 0.586 mmol) in 15 mL of THF, cooled at -60°C . The resultant suspension was then stirred for 5 h, during which it turned from yellow to orange and finally to a dark blue-greenish solution. Next, an excess of anhydrous MeOH (3 mL) was added to the later solution. The colour of the mixture changed to dark red, evolving slowly to orange. Then, the solvents and volatiles were evaporated to dryness for 4 h, isolating a brown oily solid. This was extracted in hexane ($2 \times 20 \text{ mL}$) and upon filtration through a PTFE filter and evaporation to dryness, isolating 250 mg (82% yield) of the corresponding 4-allyl- $i\text{PrH}_2\text{BIP}$ (**1'**) as a dark orange foamy solid. Although ^1H -NMR predominantly showed the resonances of the expected product, a set of tiny signals that could be attributed to other derivatives of $i\text{PrBIP}$ were also detected, but according to their relative integration, such species as a whole were in a proportion lower than 5%

with respect of the main product of the process. ^1H NMR (C_6D_6 , 25 °C, 400 MHz) δ 1.10 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, CHMeMe), 1.13 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, CHMeMe), 1.69 (s, 6H, $\text{Me-C}\equiv\text{N-}$), 2.29 (t, 2H, $^3J_{\text{HH}} = 7.4$ Hz, $\text{C}_{4\text{Py}}\text{-CH}_2\text{-CH=CH}_2$), 2.78 (hept, 4H, $^3J_{\text{HH}} = 6.9$ Hz, CHMeMe), 3.50 (m, 1H, 4- CH_{Py}), 5.03 (d, 2H, $^3J_{\text{HH}} = 2.2$ Hz, 3,5- CH_{Py}), 5.08–5.10 (overlapping multiplet, 2H, *cis*, *trans*- $\text{C}_{4\text{Py}}\text{-CH}_2\text{-CH=CH}_2$), 5.81 (m, 1H, $\text{C}_{4\text{Py}}\text{-CH}_2\text{CH=CH}_2$), 7.14 (m, 6H, $\text{CH}_{\text{N-Ar}}$), 8.89 (s, 1H, NH_{Py}).

Synthesis of $[\text{Al}(\text{Me})_2(4\text{-Bn-}^{\text{iPr}}\text{HBIP})]$ (2a)

A cold (−30 °C) colourless toluene solution (15 mL) of Me_3Al (45.9 μL , 0.48 mmol) was added slowly over another toluene yellow solution (15 mL) of **1** (250 mg, 0.43 mmol) at the same temperature and vigorously stirred in a 60 mL scintillation glass vial. The resultant mixture instantaneously changed from yellow to dark purple. The mixture was allowed to gradually reach room temperature and after 1 h stirring, it was evaporated to dryness, leaving a purple oily solid residue. Its ^1H -NMR spectrum showed the signals of complex **2a**. Then, the solid was dissolved in 25 mL of hexane and filtered. The resulting solution was evaporated under reduced pressure to dryness (4 h), yielding 269 mg of a purple microcrystalline solid. Yield: 97%. Next, 100 mg of **2a** were dissolved in hexane (10 mL), filtered and partially evaporated. The concentrated purple solution was stored at −20 °C. After 24 h, dark-pink plate crystals corresponding to compound **2a** had formed, although they were not suitable for X-ray diffraction resolution. ^1H NMR (C_7D_8 , 25 °C, 400 MHz) δ −0.71 (s, 3H, CH_3Al), −0.70 (s, 3H, CH_3Al), 0.93 (d, $^3J_{\text{HH}} = 6.7$ Hz, 6H, CHMeMe), 0.99 (d, $^3J_{\text{HH}} = 6.7$ Hz, 6H, CHMeMe), 1.35 (dd, $^3J_{\text{HH}} = 6.8$, 1.9 Hz, 12H, CHMeMe), 1.72 (s, 6H, $\text{Me-C}\equiv\text{N-}$), 2.80 (d, $^3J_{\text{HH}} = 6.9$ Hz, 2H, CH_2 , Py-Bn), 2.94 (m, $^3J_{\text{HH}} = 6.7$ Hz, 4H, CHMeMe), 4.00 (m, 1H, 4- CH_{Py}), 5.07 (d, $^3J_{\text{HH}} = 3.9$ Hz, 2H, 3,5- CH_{Py}), 7.11 (m, 6H, $\text{CH}_{\text{N-Ar}}$), 7.22 (m, 5H, CH_{Ar} , Py-Bn). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C, 100 MHz) δ −7.0 (MeAl), −6.8 (MeAl), 17.2 ($\text{Me-C}\equiv\text{N-}$), 24.4 (CHMeMe), 25.6 (CHMeMe), 28.4 (CHMeMe), 39.6 (4- CH_{Py}), 47.9 (CH_2 , Py-Bn), 106.7 (3,5- CH_{Py}), 124.5 (*p*- $\text{CH}_{\text{N-Ar}}$), 126.5 (*m*- $\text{CH}_{\text{N-Ar}}$), 126.9 (*p*- CH_{Ar} , Py-Bn), 128.8 (*o*- CH_{Ar} , Py-Bn), 129.9 (*m*- CH_{Ar} , Py-Bn), 139.4 (*i*- C_{Ar} , Py-Bn), 140.6 (2- C_{Py}), 142.2 (*o*- $\text{C}_{\text{N-Ar}}$), 142.5 (*i*- $\text{C}_{\text{N-Ar}}$), 171.0 ($\text{Me-C}\equiv\text{N-}$). Anal. Calcd for $\text{C}_{42}\text{H}_{56}\text{AlN}_3$: C, 80.08; H, 8.96; N, 6.67. Found: C, 80.60; H, 8.40; N, 6.40.

Synthesis of $[\text{Al}(\text{Et})_2(4\text{-Bn-}^{\text{iPr}}\text{HBIP})]$ (2b)

The synthesis of **2b** was performed following the same experimental procedure as the above-described procedure for the synthesis of **2a**. A 15 mL toluene solution containing 0.28 mL of a 1 M hexane solution of Et_3Al (0.280 mmol) was mixed at −30 °C with another 15 mL toluene solution (150 mg, 0.261 mmol) of 4-Bn $^{\text{iPr}}\text{H}_2\text{BIP}$ under stirring, and the mixture was kept for 2 h at room temperature. Upon isolating 157 mg of a dark purple microcrystalline solid (yield: 91%), attempts crystallization were carried out by dissolving the product in 20 mL of hexane, filtering, concentrating the solution and storing it at −20 °C. After 24 h, a significant amount of dark-blue crystals corresponding to **2b**, but unsuitable for X-ray diffraction studies, were isolated. ^1H NMR (C_6D_6 , 25 °C,

400 MHz) δ 0.21 (quart, $^3J_{\text{HH}} = 8.0$ Hz, 2H, $\text{Al-CH}_2\text{CH}_3$), 0.27 (quart, $^3J_{\text{HH}} = 8.0$ Hz, 2H, $\text{Al-CH}_2\text{CH}_3$), 0.99 (d, $^3J_{\text{HH}} = 6.7$ Hz, 6H, CHMeMe), 1.02 (overlapping triplet, 3H, $\text{Al-CH}_2\text{CH}_3$), 1.07 (d, $^3J_{\text{HH}} = 6.7$ Hz, 6H, CHMeMe), 1.15 (t, $^3J_{\text{HH}} = 8.0$ Hz, 3H, $\text{Al-CH}_2\text{CH}_3$), 1.48 (dd, $^3J_{\text{HH}} = 6.8$, 1.9 Hz, 12H, CHMeMe), 1.74 (s, 6H, $\text{Me-C}\equiv\text{N-}$), 2.99 (d, $^3J_{\text{HH}} = 7.1$ Hz, 2H, CH_2 , Py-Bn), 3.08 (m, 4H, CHMeMe), 4.11 (m, 1H, 4- CH_{Py}), 5.15 (d, $^3J_{\text{HH}} = 4.0$ Hz, 2H, 3,5- CH_{Py}), 7.22 (m, 6H, $\text{CH}_{\text{N-Ar}}$), 7.26 (m, 5H, CH_{Ar} , Py-Bn). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C, 100 MHz) δ 0.9 ($\text{Al-CH}_2\text{CH}_3$), 10.3 ($\text{Al-CH}_2\text{CH}_3$), 16.9 ($\text{Me-C}\equiv\text{N-}$), 24.2 (CHMeMe), 25.4 (CHMeMe), 28.3 (CHMeMe), 39.6 (4- CH_{Py}), 48.2 (CH_2 , Py-Bn), 106.4 (3,5- CH_{Py}), 124.4 (*p*- $\text{CH}_{\text{N-Ar}}$), 126.5 (*m*- $\text{CH}_{\text{N-Ar}}$), 126.8 (*p*- CH_{Ar} , Py-Bn), 128.8 (*o*- CH_{Ar} , Py-Bn), 129.9 (*m*- CH_{Ar} , Py-Bn), 139.3 (*i*- C_{Ar} , Py-Bn), 140.5 (2- C_{Py}), 142.6 (*o*- $\text{C}_{\text{N-Ar}}$), 143.1 (*i*- $\text{C}_{\text{N-Ar}}$), 171.8 ($\text{Me-C}\equiv\text{N-}$). Anal. Calcd for $\text{C}_{44}\text{H}_{60}\text{AlN}_3$: C, 80.32; H, 9.19; N, 6.39. Found: C, 80.63; H, 9.14; N, 6.01.

Synthesis of $[\text{Al}(\text{Bu}^{\text{i}})_2(4\text{-Bn-}^{\text{iPr}}\text{HBIP})]$ (2c)

This synthesis was carried out at NMR-tube scale. A 0.4 mL C_7D_8 yellow solution of **1** (15.4 mg, 0.026 mmol) was prepared in a 5 mL scintillation vial, which was cooled down to −25 °C. Another 0.3 mL C_7D_8 colorless solution of $^{\text{iBu}}_3\text{Al}$ (6.7 μL , 0.026 mmol) was prepared and stored at the same temperature for 20 min. Then, the organoaluminium solution was slowly added *via* pipette at the above-mentioned temperature and the colour of the resultant mixture changed dramatically to dark blue. Then, the reaction mixture solution was transferred to an NMR tube sealed with a Teflon J. Young-type tap and the ^1H -NMR spectrum was recorded after 5 min at room temperature. After 2 h at 23 °C, the ^1H -NMR did not show significant changes other than the signals of the corresponding compound **2c**, but in a relative ratio of less than 5% with respect to the signals of its precursors (**1** and $^{\text{iBu}}_3\text{Al}$). The blue toluene solution was heated at 60 °C. After 14 h, its colour had changed to burgundy and the ^1H -NMR showed the signals of **2c** and those of both starting materials in a relative ratio of *ca.* 3 : 1 (**1**, for both **1** and $^{\text{iBu}}_3\text{Al}$). The reaction was completed after 72 h at 60 °C. ^1H NMR (C_7D_8 , 25 °C, 400 MHz) δ 0.01 (bs, 2H, $\text{Al-CH}_2\text{CHMe}_2$), 0.13 (bs, 2H, $\text{Al-CH}_2\text{CHMe}_2$), 0.84 (bs, 6H, $\text{Al-CH}_2\text{CHMe}_2$), 0.89, 0.97, 1.05 (d, $^3J_{\text{HH}} = 6.5$ Hz, 18H, $\text{Al-CH}_2\text{CHMe}_2$, CHMeMe , CHMeMe), 1.44 (d, $^3J_{\text{HH}} = 4.1$ Hz, 12H, CHMeMe), 1.63 (m, 2H, $\text{Al-CH}_2\text{CHMe}_2$), 1.70 (s, 6H, $\text{Me-C}\equiv\text{N-}$), 2.93 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2H, CH_2 , Py-Bn), 3.09 (bs, 4H, CHMeMe), 4.01 (m, $^3J_{\text{HH}} = 3.4$ Hz, 1H, 4- CH_{Py}), 5.08 (d, $^3J_{\text{HH}} = 4.0$ Hz, 2H, 3,5- CH_{Py}), 7.01–7.05 (bs, 6H, $\text{CH}_{\text{N-Ar}}$), 7.19 (bs, 5H, CH_{Ar} , Py-Bn). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 25 °C, 100 MHz) δ 16.6 ($\text{Me-C}\equiv\text{N-}$), 21.6 ($\text{Al-CH}_2\text{CHMe}_2$), 23.8 ($\text{Al-CH}_2\text{CHMe}_2$), 23.9 ($\text{Al-CH}_2\text{CHMe}_2$), 25.0 (CHMe_2), 27.8 ($\text{Al-CH}_2\text{CHMe}_2$), 28.0 ($\text{Al-CH}_2\text{CHMe}_2$), 39.3 (4- CH_{Py}), 47.9 (CH_2 , Py-Bn), 106.0 (3,5- CH_{Py}), 123.9 (*p*- $\text{CH}_{\text{N-Ar}}$), 126.0 (*m*- $\text{CH}_{\text{N-Ar}}$), 126.2 (*p*- CH_{Ar} , Py-Bn), 129.3 (*m*- CH_{Ar} , Py-Bn), 138.8 (*i*- C_{Ar} , Py-Bn), 139.9 (2- C_{Py}), 142.1 (*o*- $\text{C}_{\text{N-Ar}}$), 142.6 (*i*- $\text{C}_{\text{N-Ar}}$), 171.5 ($\text{Me-C}\equiv\text{N-}$).

Synthesis of $[\text{Al}(\text{Me})_2(4\text{-allyl-}^{\text{iPr}}\text{HBIP})]$ (2'a)

The same experimental conditions and procedure as above-described for the synthesis of compounds **2a–c** was used for

the synthesis of **2'a**. 20.1 μL (0.210 mmol) of Me_3Al were dissolved in 15 mL of toluene, which was cooled to -30°C and added to another 15 mL toluene solution of 4-allyl^{iPr}BIPH₂ (**1'**, 100 mg, 0.191 mmol) at -30°C . A dark-blue microcrystalline solid was obtained in hexane at -20°C , which upon filtration and drying, yielded 97 mg (82% yield). Proper single crystals for X-ray diffraction studies appeared from a concentrated hexane solution stored at -20°C after 24 h. ^1H NMR (C_6D_6 , 25°C , 400 MHz) δ -0.70 (s, 3H, CH_3Al), -0.69 (s, 3H, CH_3Al), 0.93 (t, $^3J_{\text{HH}} = 4.6$ Hz, 12H, CHMeMe), 1.33 (dd, $^3J_{\text{HH}} = 11.9$, 6.6 Hz, 12H, CHMeMe), 1.75 (s, 6H, $\text{Me-C}\equiv\text{N-}$), 2.29 (t, $^3J_{\text{HH}} = 6.7$ Hz, 2H, $\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 2.93 (m, 4H, CHMeMe), 3.74 (m, 1H, 4-CH_{Py}), 5.09 (overlapping multiplet, 4H, *cis*, *trans*- $\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$ and $3,5\text{-CH}_{\text{Py}}$), 5.83 (m, 1H, $\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 7.09 (m, 6H, $\text{CH}_{\text{N-Ar}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 25°C , 100 MHz) δ -7.2 (*MeAl*), -6.9 (*MeAl*), 17.0 (*Me-C}\equiv\text{N-}*), 24.2 (CHMeMe), 25.4 (CHMeMe), 28.3 (CHMeMe), 37.2 (4-CH_{Py}), 45.9 ($\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 106.5 ($3,5\text{-CH}_{\text{Py}}$), 116.6 ($\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 124.2 (*p-CH*_{N-Ar}), 126.7 (*m-CH*_{N-Ar}), 136.1 ($\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 140.5 (2-C_{Py}), 142.1 (*o-C*_{N-Ar}), 142.3 (*i-C*_{N-Ar}), 170.8 ($\text{Me-C}\equiv\text{N-}$). Anal. Calcd for $\text{C}_{38}\text{H}_{54}\text{AlN}_3$: C, 78.71; H, 9.39; N, 7.25. Found: C, 78.47; H, 9.60; N, 7.30.

Synthesis of $[\text{Al}(\text{Et})_2(4\text{-allyl-}^{i\text{Pr}}\text{HBIP})]$ (**2'b**)

The experimental procedure described above for the synthesis of the analogue system **2b** was developed for the synthesis of the complex **2'b**. 0.20 mL of a 1 M hexane solution of Et_3Al (0.200 mmol) were diluted in 15 mL of toluene and added to another 15 mL toluene solution of **1'** (100 mg, 0.191 mmol). A dark-pink solid (110 mg, 95% yield) corresponding to compound **2'b** was isolated after the solvent and volatiles were removed at reduce pressure. Recrystallization from a hexane concentrated solution produced a microcrystalline solid after 24 h at -20°C . ^1H NMR (C_7D_8 , 25°C , 400 MHz) δ 0.05 (quart, $^3J_{\text{HH}} = 8.0$ Hz, 2H, $\text{Al-CH}_2\text{CH}_3$), 0.14 (quart, $^3J_{\text{HH}} = 8.0$ Hz, 2H, $\text{Al-CH}_2\text{CH}_3$), 0.84 (t, $^3J_{\text{HH}} = 8.0$ Hz, 3H, $\text{Al-CH}_2\text{CH}_3$), 0.98 (dd, $^3J_{\text{HH}} = 8.7$, 6.9 Hz, 12H, CHMeMe), 1.02 (overlapping triplet, 3H, $\text{Al-CH}_2\text{CH}_3$), 1.40 (t, $^3J_{\text{HH}} = 6.4$ Hz, 12H, CHMeMe), 1.77 (s, 6H, $\text{Me-C}\equiv\text{N-}$), 2.34 (t, $^3J_{\text{HH}} = 6.9$ Hz, 2H, $\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 3.00 (m, 4H, CHMeMe), 3.75 (m, 1H, 4-CH_{Py}), 5.09 (d, $^3J_{\text{HH}} = 4.0$ Hz, 2H, $3,5\text{-CH}_{\text{Py}}$), 5.14 (overlapping multiplet, 2H, *cis*, *trans*- $\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 5.90 (m, 1H, $\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 7.04 (m, 6H, $\text{CH}_{\text{N-Ar}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 25°C , 100 MHz) δ 10.2 ($\text{Al-CH}_2\text{CH}_3$), 16.8 ($\text{Me-C}\equiv\text{N-}$), 23.9 (CHMeMe), 24.1 (CHMeMe), 25.2 ($\text{Al-CH}_2\text{CH}_3$), 28.2 (CHMeMe), 37.1 (4-CH_{Py}), 46.0 ($\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 106.2 ($3,5\text{-CH}_{\text{Py}}$), 116.5 ($\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 124.2 (*p-CH*_{N-Ar}), 126.7 (*m-CH*_{N-Ar}), 136.1 ($\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 140.3 (2-C_{Py}), 142.6 (*o-C*_{N-Ar}), 143.0 (*i-C*_{N-Ar}), 171.5 ($\text{Me-C}\equiv\text{N-}$). Anal. Calcd for $\text{C}_{40}\text{H}_{58}\text{AlN}_3$: C, 79.03; H, 9.62; N, 6.91. Found: C, 79.84; H, 9.79; N, 6.80.

Synthesis of $[\text{Al}(\text{Bu}^i)_2(4\text{-allyl-}^{i\text{Pr}}\text{HBIP})]$ (**2'c**)

The same experimental procedure used for the synthesis of the previous five complexes was also applied for the synthesis of **2'c**, although in this case, the reaction completion required the aid of heat (60°C) during several hours. A cold (-30°C) color-

less 20 mL toluene solution of 50 μL (0.198 mmol) of $^i\text{Bu}_3\text{Al}$ was added to a yellow 20 mL toluene solution of **1'** (100 mg, 0.191 mmol) at the same temperature. The resultant solution changed instantaneously from yellow to dark violet. The mixture was then transferred into a 100 mL glass ampoule equipped with a Teflon J. Young-type screw-cap valve for sealing. The ampoule containing the reaction mixture was then heated at 60°C inside a silicone oil bath for 36 h. Next, the solvents and volatiles were eliminated under vacuum, isolating a dark purple solid, which was dissolved in hexane, filtered and concentrated prior to storing at -20°C . Upon filtration and drying, a dark-purple solid (112 mg, 88% yield) corresponding to compound **2'c** was isolated. Several attempts at crystallization turned out to be fruitless. ^1H NMR (C_7D_8 , 25°C , 400 MHz) δ 0.03 (bs, 2H, $\text{Al-CH}_2\text{CHMe}_2$), 0.14 (bs, 2H, $\text{Al-CH}_2\text{CHMe}_2$), 0.89 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H, $\text{Al-CH}_2\text{CHMe}_2$), 1.01 (dd, $^3J_{\text{HH}} = 12.6$, 6.7 Hz, 12H, CHMeMe), 1.07 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, $\text{Al-CH}_2\text{CHMe}_2$), 1.43 (t, $^3J_{\text{HH}} = 6.6$ Hz, 12H, CHMeMe), 1.62 (m, 1H, $\text{Al-CH}_2\text{CHMe}_2$), 1.75 (s, 6H, $\text{Me-C}\equiv\text{N-}$), 1.97 (m, 1H, $\text{Al-CH}_2\text{CHMe}_2$), 2.39 (t, $^3J_{\text{HH}} = 6.9$ Hz, 2H, $\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 2.94 (bs, 2H, CHMeMe), 3.09 (bs, 2H, CHMeMe), 3.77 (m, $^3J_{\text{HH}} = 6.9$ Hz, 1H, 4-CH_{Py}), 5.09 (d, $^3J_{\text{HH}} = 3.9$ Hz, 2H, $3,5\text{-CH}_{\text{Py}}$), 5.13 (overlapping multiplet, 2H, *cis*, *trans*- $\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 5.89 (m, 1H, $\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 7.04 (m, 6H, $\text{CH}_{\text{N-Ar}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25°C , 100 MHz) δ 16.8 ($\text{Me-C}\equiv\text{N-}$), 21.4 ($\text{Al-CH}_2\text{CHMe}_2$), 23.9 ($\text{Al-CH}_2\text{CHMe}_2$), 24.1 ($\text{Al-CH}_2\text{CHMe}_2$), 24.6 (CHMeMe), 25.1 (CHMeMe), 27.9 ($\text{Al-CH}_2\text{CHMe}_2$), 28.1 ($\text{Al-CH}_2\text{CHMe}_2$), 37.1 (4-CH_{Py}), 45.9 ($\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 106.3 ($3,5\text{-CH}_{\text{Py}}$), 116.4 ($\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 124.1 (*p-CH*_{N-Ar}), 126.4 (*m-CH*_{N-Ar}), 135.8 ($\text{C}_4\text{Py-CH}_2\text{-CH=CH}_2$), 140.0 (2-C_{Py}), 142.4 (*o-C*_{N-Ar}), 142.7 (*i-C*_{N-Ar}), 171.7 ($\text{Me-C}\equiv\text{N-}$). Anal. Calcd for $\text{C}_{44}\text{H}_{66}\text{AlN}_3$: C, 79.59; H, 10.02; N, 6.33. Found: C, 79.28; H, 10.37; N, 6.10.

Dimerization of **2a**

Synthesis of $[\text{Al}(\text{Me})_2(4\text{-Bn-}^{i\text{Pr}}\text{HBIP})]_2$ (3a**)**. A 30 mL toluene solution of compound **2a** (200 mg, 0.318 mmol) was prepared in a 100 mL Schlenk tube inside a N_2 -filled glovebox. Then, this was taken out, interfaced to a vacuum/argon line and placed into a silicone oil bath heated up to 110°C . The solution was then stirred at such temperature for a period of 36 h. Next, the solvents and volatiles were removed to dryness, isolating 184 mg (yield 92%) of a dark-purple solid, corresponding with the dimer **3a**. Its crystallization was performed by taking a sample of 100 mg of such a powdery solid and dissolving it in 10 mL of hexane. Then, such a solution was concentrated to half its volume and 0.1 mL of dichloromethane was added to it, prior to storing at -25°C . After 48 h, dark-pink plate crystals suitable for X-ray diffraction studies were obtained. ^1H NMR (C_7D_8 , 25°C , 400 MHz): δ -0.57 (s, 6H, CH_3Al), -0.49 (s, 6H, CH_3Al), 1.10 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, CHMeMe), 1.19 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, CHMeMe), 1.35 (d, $^3J_{\text{HH}} = 6.7$ Hz, 12H, CHMeMe), 1.44 (d, $^3J_{\text{HH}} = 6.7$ Hz, 12H, CHMeMe), 1.76 (s, 12H, $\text{Me-C}\equiv\text{N-}$), 2.25 (bs, 4H, $\text{CH}_2\text{Py-Bn}$), 2.88 (s, 4H, $3,5\text{-CH}_{\text{Py}}$), 3.17 (m, 8H, CHMeMe), 7.02 (m, 12H, $\text{CH}_{\text{N-Ar}}$), 7.26 (m, 10H, CH_{Ar} , Py-Bn). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 25°C , 100 MHz) δ 0.7 (*MeAl*), 1.7

(MeAl), 21.8 (Me-C=N-), 29.8 (CHMeMe), 30.0 (CHMeMe), 33.9 (CHMeMe), 37.0 (4-CH_{Py}), 44.4 (CH_{2,Py-Bn}), 48.6 (3,5-CH_{Py}), 129.0 (*p*-CH_{N-Ar}), 131.6 (*m*-CH_{N-Ar}), 131.8 (*p*-CH_{Ar, Py-Bn}), 134.6 (*o*-CH_{Ar, Py-Bn}), 135.1 (*m*-CH_{Ar, Py-Bn}), 145.6 (*i*-C_{Ar, Py-Bn}), 147.5 (2-C_{Py}), 147.8 (*o*-C_{N-Ar}), 148.6 (*i*-C_{N-Ar}), 169.6 (Me-C=N-). Anal. Calcd for C₈₄H₁₁₂Al₂N₆: C, 80.60; H, 8.96; N, 6.67. Found: C, 80.09; H, 9.01; N, 6.56.

Dimerization of 2a and demetallation

In a NMR tube sealed with a Teflon J. Young-type tap, 20 mg (31.8 μmol) of compound **2a** were dissolved in toluene-d₈ and heated up to 110 °C. Once dimerization was completed and the ¹H-NMR showed just the signals of compound **3a** and no resonances of the starting material (**2a**) were left, an excess of dry methanol (2 mL) was added into the tube. The dark-purple solution, which changed quickly to orange, was evaporated off under vacuum to dryness, isolating a reddish orange oily solid. This crude was extracted with 2 × 5 mL of hexane, filtered through a pad of Celite and evaporated to dryness again. The resultant yellow oily-solid, which was completely soluble in benzene-d₆, showed an ¹H-NMR spectrum that included a single set of signals corresponding with those of the metal-free dimer (4-Bn-ⁱPrH₂BIP)₂ as compared with that reported by us in the literature.¹⁸

Dimerization of 2'a

Synthesis of [Al(Me)₂(4-allyl-ⁱPrHBIP)]₂ (3'a). The thermal treatment described above over **2a** was applied to **2'a**, using 95 mg (0.164 mmol) of **2'a** dissolved in 15 mL of toluene with stirring during 5 h at 110 °C. When the solvent and volatiles were removed at reduced pressure, 80 mg (89% yield) of compound **3'a** was isolated. Suitable crystals for X-ray diffraction studies were obtained after dissolving 50 mg of **3'a** in hexane (10 mL), filtering, concentrating to half the volume of such a solution and storing it at -25 °C. ¹H NMR (C₇D₈, 25 °C, 400 MHz): δ -0.73 (s, 6H, CH₃Al), -0.46 (s, 6H, CH₃Al), 1.17 (dd, ³J_{HH} = 6.8, 2.1 Hz, 24H, CHMeMe), 1.34 (dd, ³J_{HH} = 10.9, 6.8 Hz, 24H, CHMeMe), 1.82 (m, 4H, C_{4Py}-CH₂-CH=CH₂), 1.87 (s, 12H, Me-C=N-), 2.02 (m, 2H, 4-CH_{Py}), 3.01 (s, 4H, 3,5-CH_{Py}), 3.12 (m, 4H, CHMeMe), 3.24 (m, 4H, CHMeMe), 5.09 (dd, ³J_{HH} = 16.0, 11.6 Hz, 4H, C_{4Py}-CH₂-CH=CH₂), 5.82 (m, 2H, C_{4Py}-CH₂-CH=CH₂), 7.02 (m, 12H, CH_{N-Ar}). ¹³C{¹H} NMR (C₇D₈, 25 °C, 100 MHz) δ -5.6 (MeAl), -2.5 (MeAl), 16.6 (Me-C=N-), 24.2 (CHMeMe), 24.3 (CHMeMe), 24.8 (4-CH_{Py}), 28.5 (CHMeMe), 29.1 (CHMeMe), 37.3 (C_{4Py}-CH₂-CH=CH₂), 43.6 (3,5-CH_{Py}), 116.6 (C_{4Py}-CH₂-CH=CH₂), 123.9 (*p*-CH_{N-Ar}), 126.4 (*m*-CH_{N-Ar}), 140.5 (C_{4Py}-CH₂-CH=CH₂), 142.2 (2-C_{Py}), 142.6 (*o*-C_{N-Ar}), 143.7 (*i*-C_{N-Ar}), 164.4 (Me-C=N-). Anal. Calcd for C₇₆H₁₀₈Al₂N₆: C, 78.71; H, 9.39; N, 7.25. Found: C, 78.72; H, 9.58; N, 7.28.

Dimerization of 2'a and demetallation

The same experimental procedure developed in the case of the thermal treatment of **2a** and subsequent demetallation was applied to **2'a**, obtaining similar results. At the end of process, a benzene-d₆ soluble orange-oily solid was obtained. Its

¹H-NMR showed just a single set of signals, which corresponded with those of the organic ditopic dimer (4-allyl-ⁱPrH₂BIP)₂ as compared with the data reported in the literature.¹⁸

Monitoring the thermal treatment of 2b

Generation of [Al(Et)₂(4-Bn-ⁱPrHBIP)]₂ and [Al(Et)₂(4-Bn-ⁱPrBIP⁻¹)] and demetallation. Compound **2b** (20 mg, 30.4 μmol) was dissolved in toluene-d₈ before being transferred into an NMR tube sealed with a Teflon J. Young-type tap inside a N₂-filled glovebox. The tube was then taken out from the glovebox and placed in a thermostatic bath at 110 °C. After 3 h heating, the tube was removed from the heating bath, cooled down to room temperature and transferred to the NMR probe. The ¹H-NMR spectrum showed the signals of compound **2b** together with another set of resonances attributed to the dimer [Al(Et)₂(4-Bn-ⁱPrHBIP)]₂ (**3b**) ¹H NMR (C₆D₆, 25 °C, 400 MHz) δ 0.07 (quart, ³J_{HH} = 8.0 Hz, 4H, Al-CH₂CH₃), 0.37 (quart, ³J_{HH} = 8.0 Hz, 4H, Al-CH₂CH₃), 0.80 (t, ³J_{HH} = 8.1 Hz, 6H, Al-CH₂CH₃), 0.99 (t, 6H, Al-CH₂CH₃), 1.09 (m, 24H, CHMeMe), 1.40 (dd, 24H, CHMeMe), 1.58 (s, 12H, Me-C=N-), 3.12 (sept, ³J_{HH} = 6.6 Hz, 4H, CHMeMe), 3.24 (sept, ³J_{HH} = 6.7 Hz, 4H, CHMeMe) 7.12 (m, 12H, CH_{N-Ar}). Signals for 3,5-CH_{Py}, 4-CH_{Py} and PhCH₂ could not be assigned with confidence.

Once the reaction was completed (16 h at 110 °C) based on the ¹H-NMR analysis, at the point where it only showed the signals of compound **3b** and no resonances of the starting material (**2b**) were left, an excess of dry methanol (2 mL) was added into the tube. The dark-purple solution changed quickly to orange, then it was evaporated at vacuum to dryness, resulting in a reddish orange oily solid. This crude was extracted with 2 × 5 mL of hexane, filtered through a pad of Celite and evaporated to dryness again. The resultant yellow oily-solid, which was completely soluble in benzene-d₆, showed an ¹H-NMR spectrum that included two sets of signals corresponding with those of the metal-free dimer (4-Bn-ⁱPrH₂BIP)₂ together with the ones of 4-Bn-ⁱPrBIP as compared with the spectra of such compounds reported by us in the literature.¹⁸ The ¹H-NMR showed both species in an approximately relative ratio of 1 : 2.

Monitoring the thermal treatment of 2'b

Generation of [Al(Et)₂(4-allyl-ⁱPrBIP⁻¹)] and [Al(Et)₂(ⁱPrBIP⁻¹)]. The same experimental procedure developed in the case of the thermal treatment of **2b** was applied to **2'b**. After 3 h heating at 110 °C, the ¹H-NMR signals of **2'b** had decreased but new resonances were not detected. The following ¹H-NMR spectra regularly recorded over a period of several hours in which the tube had been kept at 110 °C showed only the signals of **2'b**, until they disappeared after 30 h heating. This left a flat ¹H-NMR spectrum, excluding the peaks attributed to the deuterated solvent. The resultant solution was, however, dark purple. Then, an excess of dry methanol (2 mL) was added into the tube. The colour of the solution changed to orange before being evaporated at vacuum to dryness. The resultant reddish orange oily-solid was extracted with 2 × 5 mL of

hexane, filtered through a pad of Celite and evaporated to dryness. The yellow oily-solid was isolated, which was completely soluble in benzene- d_6 , showed an ^1H -NMR spectrum that included several sets of signals in which we could distinguish those of the known aromatic ligands $^{\text{iPr}}\text{BIP}$ and 4-allyl- $^{\text{iPr}}\text{BIP}^{12}$ as the main products of the process.

Monitoring the thermal treatment 2'c

Generation of $[\text{Al}(\text{Bu})_2(4\text{-allyl-}^{\text{iPr}}\text{BIP}^{-1})]$ and $[\text{Al}(\text{Bu})_2(^{\text{iPr}}\text{BIP}^{-1})]$. The same experimental protocol carried out for the thermal treatment of 2'b followed by demetallation and isolation of the organic residue was applied to 2'c, obtaining comparable results. An orange oily solid, which was completely soluble in benzene- d_6 , was obtained. Its ^1H -NMR spectrum included the signals of the known aromatic ligands $^{\text{iPr}}\text{BIP}$ and 4-allyl- $^{\text{iPr}}\text{BIP}^{12}$ as the main products upon heating 2'c and subsequent demetallation.

Dimerization kinetics of 2'a to 3'a

The dimerization rate of compound 2'a was monitored by performing five NMR-tube scale experiments at five different temperatures distributed over a 50 K range (323, 343, 353, 363 and 373 K). Samples containing 45 μmol of the complex in 0.6 ml of toluene- d_8 were prepared individually. We found operationally convenient to generate the complex directly in the NMR tube. In a nitrogen-filled glove-box, a 5 mL glass vial was charged with 23.7 mg (0.045 mmol) of 4-allyl- $^{\text{iPr}}\text{BIP}$ 1'a and 0.4 mL of toluene- d_8 , storing the yellow clear solution at -30°C for 15 min. In another 5 mL vial, 0.2 mL toluene- d_8 solution of commercial Me_3Al (4.3 μL , 0.045 mmol) was prepared and also placed at -30°C during 10 min. Then, both vials were brought out from the freezer and the aluminum alkyl was slowly transferred *via* pipette to the ligand (1'a)-containing yellow solution, resulting in an instantaneous colour change from yellow to dark burgundy. The reaction mixture was subsequently loaded into a J.-Young NMR tube, gently hand-shaken and taken to the NMR probe, which had been stabilized at the prescribed temperature. The progress of the reaction was monitored every 15 min during 3 h by integration of the selected signals of 2'a (2.92 ppm for the $\text{CH}^{\text{(iPr)}}$ signals; 1.78 ppm for the *Me*-CN signal) and 3'a (centred at 3.24 ppm for the $\text{CH}^{\text{(iPr)}}$ signals; 1.87 ppm for *Me*-CN the signal). The absolute concentration of 2'a in each measurement was calculated by assuming that its conversion was quantitative, and the sum of intensities of the analogous signals of 2'a and 3'a was constant and equal to the initial concentration of 2'a.

X-ray structural analysis for 2'a, 3a and 3'a

Crystals suitable for X-ray diffraction analysis were coated with dry perfluoropolyether, mounted on glass fibres, and fixed in a cold nitrogen stream to the goniometer head. Data collections were performed on a Bruker-Nonius X8 Apex-II CCD diffractometer, using graphite monochromatized Mo radiation ($\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$) and subjected to fine-sliced ω and φ scans (scan widths 0.30° to 0.50°).¹⁹ The data were reduced (SAINT) and corrected for absorption effects by multiscan

method (SADABS).²⁰ The structures were solved by direct methods (SIR2002, SHELXS) and refined against all F^2 data by full-matrix least-squares techniques (SHELXL-2016/6) minimizing $w[F_o^2 - F_c^2]^2$.²¹ All the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the calculated positions and allowed to ride on their carrier atoms with the isotropic temperature factors U_{iso} fixed at 1.2 times (1.5 times for methyl groups) of the U_{eq} values of the respective carrier atoms. In the crystal structure of 2'a, the central ring bearing the allyl group appeared disordered on both sides of the coordination plane forming the pincer ligand with the metal, so this group was modelled in two sets of sites. At the end of the refinement, the occupancy ratio was set at 0.55 : 0.45. Moreover, a search for solvent accessible voids in 2'a using PLATON²² showed some small volumes of potential solvents less than $40 \text{ \AA}^3$, impossible to model even with the most severe restraints. The corresponding CIF data represent SQUEEZE²³-treated structures with the solvent molecules handled as a diffuse contribution to the overall scattering, without specific atom position and excluded from the structural model. The SQUEEZE results were appended to the CIF. The crystal structure of 3a appeared with the benzyl group slightly disordered and was modelled in two sets of sites and the occupancy ratio was set at 0.53 : 0.47. Together with this crystal structure, a dichloromethane molecule was also observed as a crystallization solvent. The crystal structure of 3'a was refined as a two-component TWIN with a 0.533 : 0.467 domain ratio. Next to this crystal structure, a *n*-hexane molecule was also observed as a crystallization solvent. The modelling of the observed disorders described above required some geometric restraints (DFIX instruction), with the ADP restraint SIMU and the rigid bond restraint DELU used in order to obtain more reasonable geometric and ADP values of the disordered atoms. It was also useful to restraint the anisotropic U -values of these atoms to behave more isotropically (ISOR instruction).

Crystal data for 2'a

$\text{C}_{38}\text{H}_{54}\text{AlN}_3$, $M = 579.82$, $a = 32.0061(10) \text{ \AA}$, $b = 32.0061(10) \text{ \AA}$, $c = 13.9450(5) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 14\,285.1(10) \text{ \AA}^3$, $T = 193(2) \text{ K}$, space group $I4_1/a$, $Z = 16$, $\mu = 0.085 \text{ mm}^{-1}$, 80 463 reflections measured, 6454 independent reflections ($R_{\text{int}} = 0.0941$). The final R_1 values were 0.0480 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1228 ($I > 2\sigma(I)$). The final R_1 values were 0.0939 (all data). The final $wR(F^2)$ values were 0.1384 (all data). The goodness of fit on F^2 was 0.975.

Crystal data for 3a

$\text{C}_{84}\text{H}_{112}\text{Al}_2\text{N}_6 \cdot 2(\text{CH}_2\text{Cl}_2)$, $M = 1429.60$, $a = 13.2320(4) \text{ \AA}$, $b = 16.7149(5) \text{ \AA}$, $c = 19.4032(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 102.4510(10)^\circ$, $\gamma = 90^\circ$, $V = 4190.5(2) \text{ \AA}^3$, $T = 193(2) \text{ K}$, space group $P2_1/n$, $Z = 2$, $\mu = 0.208 \text{ mm}^{-1}$, 30 216 reflections measured, 7583 independent reflections ($R_{\text{int}} = 0.0214$). The final R_1 values were 0.0431 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1147 ($I > 2\sigma(I)$). The final R_1 values were 0.0527 (all data). The final $wR(F^2)$ values were 0.1204 (all data). The goodness of fit on F^2 was 1.084.

Crystal data for 3'a

$C_{76}H_{108}Al_2N_6 \cdot C_6H_{14}$, $M = 1245.81$, $a = 10.5741(14)$ Å, $b = 12.4548(16)$ Å, $c = 16.270(2)$ Å, $\alpha = 74.182(3)^\circ$, $\beta = 76.401(3)^\circ$, $\gamma = 75.500(4)^\circ$, $V = 1963.7(5)$ Å³, $T = 193(2)$ K, space group $P\bar{1}$, $Z = 1$, $\mu = 0.081$ mm⁻¹, 5872 reflections measured, 5872 independent reflections. The final R_1 values were 0.0690 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1571 ($I > 2\sigma(I)$). The final R_1 values were 0.1224 (all data). The final $wR(F^2)$ values were 0.1784 (all data). The goodness of fit on F^2 was 1.062.

Conflicts of interest

There are no conflicts of interest.

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