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Synthesis of Rare-Earth-Metal Iminopyrrolyl Complexes from Alkyl Precursors: Ln→Al N-Ancillary Ligand Transfer

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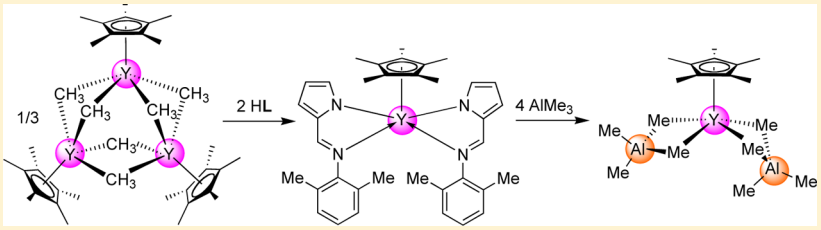
Supporting Information



ABSTRACT: Protonolysis of $[YMe_3]_n$ with 2-{(N-2,6-dialkylphenyl)iminomethyl)}pyrroles (alkyl = *i*Pr (L^1), Me (L^2)) gave homoleptic iminopyrrolyl complexes YL^1_3 and YL^2_3 as well as the complex $[L^2YL^{2,Me}]_2$ containing a dianionic pyrrolaldiminato ligand, formed via methylation of the imino backbone. Treatment of the half-sandwich complex $[(C_5Me_5)YMe_2]_3$ and yttrocene $(C_5Me_5)_2YMe(THF)$ with either 2 or 1 equiv of HL afforded the monomeric complexes $(C_5Me_5)YL_2$ and $(C_5Me_5)_2YL$, respectively. The complex $(C_5Me_5)YL^2_2$ readily underwent Ln→Al iminopyrrolyl ligand transfer in the presence of trimethylaluminum, producing the known $(C_5Me_5)Y(AlMe_4)_2$. Salt metatheses of homoleptic $Ln(AlMe_4)_3$ (Ln = Y, La) with KL gave complicated reaction mixtures from which the $\eta^5/\eta^1{:}\kappa^1$ pyrrolaldiminato-bridged complex $[L^{1,Me}La(AlMe_4)]_2$ and bis(tetramethylaluminate) complex $L^2Y(AlMe_4)_2$ could be isolated and crystallographically characterized. Moreover, the solid-state structures of YL^2_3, $[L^2YL^{2,Me}]_2$, $(C_5Me_5)YL^1_2$, $(C_5Me_5)_2YL^1$, and L^2AlMe_2 are presented.

INTRODUCTION

The pyrrolyl unit features a popular monovalent functional group for designing nitrogen-based (ancillary) ligands.[1,2] Particularly, multidentate variants provide high complex stability, which led to their reputation as versatile spectator ligands in catalytic reactions, especially in so-called post-metallocene catalysts for homogeneous polymerization.[1,3,4] Complexes bearing mono(iminopyrrolyl) ligands were synthesized and structurally characterized for a large variety of metals.[1] Crucially, pyrrolyl ligands can exhibit distinct coordination behavior, as evidenced for η^1 and η^5/κ^1 modes, the latter featuring properties akin to those of Cp ligands.[1] Also in rare-earth-metal chemistry the pyrrolyl motif is found in various multidentate ligand systems,[5,6] including dipyrrolides[7] or porphyrinogenates.[8] A series of yttrium complexes with monovalent iminopyrrolyl and bis(iminopyrrolyl) ligands was initially synthesized by Mashima et al. according to silylamine elimination reactions, utilizing $Y[N(SiMe_3)_2]_3$ as a precursor.[9] The resulting complexes were successfully used as initiators for ε-caprolactone polymerization.[9] Later on, Ln(III) hydrocarbyl derivatives with N,N-bidentate iminopyrrolyl have been exploited for the polymerization of methyl methacrylate (samarium),[10] lactide (yttrium),[11] and isoprene (scandium, yttrium, lanthanum).[12] Salt metathesis[10] and amine[9,13] and alkane elimination,[11,12] as well as a $AlEt_3$-redox addition involving $Ln(CH_2SiMe_3)_3(thf)_2$ and a divalent Sm(II) iminopyrrolyl complex,[14] respectively, have so far been applied as the main synthesis protocols.

We have recently shown that alkylaluminate moieties readily engage in protonolytic[15,16] and salt metathetical ligand exchange reactions.[17] This *aluminate route* emerged in a LLn^{III}bis(tetramethylaluminate)-based post-metallocene library (L = ancillary ligand),[18] which until now was mainly exploited for 1,3-diene polymerization, requiring additional activation by fluorinated boranes/borates.[18−20] Importantly, difficulties of this aluminate route were encountered when nitrogen-based ancillary ligands L^N were employed. The two major drawbacks are ancillary ligand transfer to aluminum, that is formation of complexes L^NAlMe_2,[20b,21,22] as well as ligand backbone (e.g., imine) alkylation, which as a rule leads to divalent ancillary ligands $L^{N,alkyl}$.[23] Since known mono(iminopyrrolyl)-supported post-metallocene catalysts were reported to also require further activation by organoaluminum reagents such as MAO (containing a considerable amount of $AlMe_3$) or $AlEt_3$,[3,4] we

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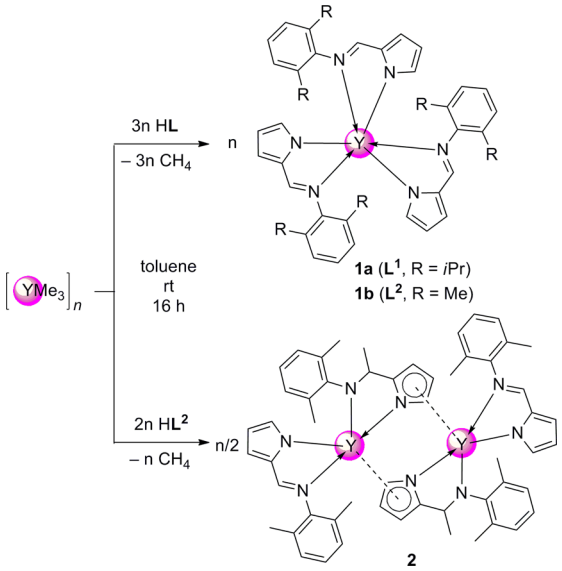
envisaged monoiminopyrrolyl lanthanide tetramethylaluminate complexes as relevant targets for assessing these prominent side reactions.[24]

RESULTS AND DISCUSSION

Yttrium Methyl Complexes as Precursors. Sterically readily accessible Ln–alkyl bonds featuring a donor- and ate-free environment are rare in lanthanide chemistry, especially in homoleptic or half-sandwich complexes.[15b,25] Thus far, tetramethylaluminate derivatives[26] and methyl complexes derived therefrom[27,28] seem to provide the only alternative to the sterically encumbered silylalkyls $Ln[CH(SiMe_3)_2]_3$.[29] To avoid donor contamination and assess the ease of methylation of the imino functionality, we reacted 2-{(N-2,6-dialkylphenyl)-iminomethyl)}pyrrole (alkyl = *i*Pr (HL^1), Me (HL^2)) with $[YMe_3]_n$ (Scheme 1).

Scheme 1. Protonolysis of $[YMe_3]_n$ with Iminopyrroles Affected by the Backbone Phenyl Substituents



The protonolysis reactions with a methyl group/HL ratio of 1/1 proceeded relatively fast in toluene, as indicated by complete dissolution of the yttrium precursors within 45 min. According to NMR spectroscopy, both the dimethyl- and diisopropyl-substituted pyrrolines HL gave homoleptic complexes $Y(L^1)_3$ (**1a**) and $Y(L^2)_3$ (**1b**) in high yields and high purity. Complexes **1** can be efficiently crystallized from *n*-hexane/toluene solutions at −35 °C. The complex $Y[2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CH)C_4H_3N]_3$ (**1a**) was synthesized recently in a similar protonolysis reaction employing the silylalkyl complex $Y(CH_2SiMe_3)_3(THF)_2$ and its solid-state structure determined by X-ray crystallography.[11] In comparison to **1a**, the obtained single crystals of $Y[2\text{-}(2,6\text{-}Me_2C_6H_3N{=}CH)C_4H_3N]_3$ (**1b**) were generally very small, but solvent-free (monoclinic space group $P2_1/c$, Figure 1). Like **1a**, homoleptic complex **1b** features three $\eta^1{:}\kappa^1$-N,N bidentate iminopyrrolyl ligands L^2, resulting in a slightly distorted octahedral coordination geometry. The Y–N distances in **1b** range from 2.323(4) to 2.331(3) Å for the anionic pyrrolyl nitrogen and from 2.448(4) to 2.470(3) Å for the longer imino nitrogen donor bonds (**1a**: 2.315(2)–2.334(2), 2.471(2)–2.493(2) Å).

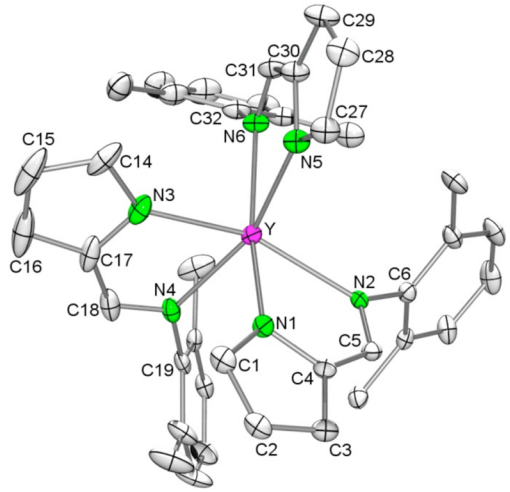


Figure 1. Perspective ORTEP view of the molecular structure of $Y[2\text{-}(2,6\text{-}Me_2C_6H_3N{=}CH)C_4H_3N]_3$ (**1b**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Y–N1 = 2.331(3), Y–N2 = 2.457(3), Y–N3 = 2.323(4), Y–N4 = 2.448(4), Y–N5 = 2.327(4), Y–N6 = 2.470(3); N1–Y–N2 = 71.1(2), N3–Y–N4 = 71.4(2), N5–Y–N6 = 71.3(2), N1–Y–N5 = 91.6(2), N1–Y–N3 = 88.2(2), N1–Y–N4 = 90.1(2), N1–Y–N6 = 162.8(2), N6–Y–N2 = 108.9(2), N6–Y–N3 = 92.4(2), N6–Y–N4 = 106.4(2).

For one reaction run applying the same conditions, dimethyl-substituted HL^2 afforded small amounts of the complex $[L^2YL^{2,Me}]_2$ (**2**), involving imino backbone methylation and formation of the dianionic ligand $L^{2,Me}$. Despite several tries, also using $[YMe_3]/HL^2$ ratios of 1/1 and 1/2, we were not able to isolate larger amounts of this complex. According to NMR spectroscopy and elemental analyses, only pure **1b** could be harvested from crystallizations. Such imino alkylations have been observed previously in metal alkyl promoted protonolysis reactions[23,30,31] and were also shown for the equimolar reaction of $Y(CH_2SiMe_3)_3(THF)_2$ with HL^1.[11] Generally, the steric bulk of the aryl substituents seems to direct the pathway of the competing protonolysis and intramolecular alkyl migration.[30,31] It is noteworthy that ancillary ligand transformation involving a switch from mono- to dianionic coordination often leads to a loss of catalytic activity (when additional activation such as cationization is required), as exemplified for the application of corresponding group 4 salen complexes in ethylene polymerization.[32]

Compound **2** crystallized from a *n*-hexane/toluene/benzene mixture at −35 °C in the monoclinic space group $P2_1/c$ as a dimeric complex (Figure 2). The pyrrolyl ring of the dianionic ligand $L^{2,Me}$ bridges the yttrium centers in a $\eta^5/\eta^1{:}\kappa^1$ fashion. While this coordination mode is a common structural motif of pyrrolyl ligands,[11,12,33−36] for dianionic pyrrolaldiminato ligands it was observed only recently in yttrium and calcium complexes.[11,31b] In complex **2**, the yttrium centers are each surrounded by the monoanionic pyrrolylimine L^2 and the dianionic pyrrolaldiminato $L^{2,Me}$. Since the bridging pyrrolyl moiety of the latter dianionic species coordinates one yttrium center in an η^5 fashion, this amounts to a formal coordination number of 7 for each yttrium center. The pyrrolyl ring is slightly tilted with an Y–N1 distance of 2.647(2) Å and Y–C distances ranging from 2.621(2) to 2.798(3) Å (Y–Ctr(Pyr) = 2.439 Å). For comparison, the Y–C distances in the complex $[YL^{1,CH_2SiMe_3}(CH_2SiMe_3)(THF)]_2$ range from 2.631(6) to

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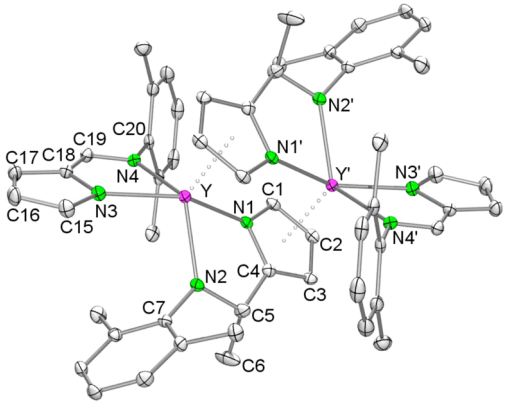
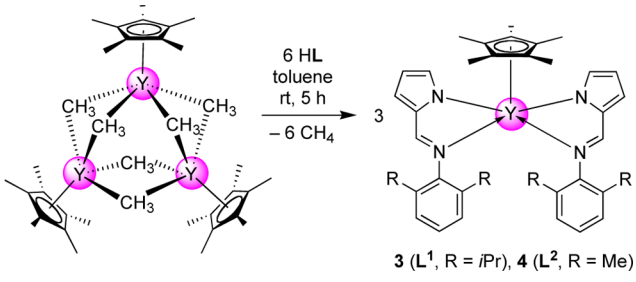


Figure 2. Perspective ORTEP view of the molecular structure of {[2-(2,6-$Me_2C_6H_3N$=CH)C_4H_3N]Y[2-(2,6-$Me_2C_6H_3$NC(H)(Me))-C_4H_3N]}$_2$ (**2**, [$L^2YL^{2,Me}$]$_2$). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Y−N1 = 2.411(2), Y′−N1 = 2.647(2), Y−N2 = 2.194(2), Y−N3 = 2.341(2), Y−N4 = 2.432(2), N2−C5 = 1.463(4), N4−C19 = 1.304(4), Y−Ctr = 2.439; N3−Y−N4 = 100.53(8), N1−Y−N2 = 72.55(8), N2−Y−N3 = 98.02(9), N1−Y−N4 = 89.98(8), N1−Y−Ctr = 103.31, N2−Y−Ctr = 116.31, N3−Y−Ctr = 105.27, N4−Y−Ctr = 121.53.

2.851(6) Å.[11] The Y−N1 bond length of 2.411(2) Å of the bridging pyrrolyl moiety is considerably longer than the Y1−N2 amido bond (2.194(2) Å) of this chelating ligand but equals the Y−N4 imino bond of the second ligand L^2. The Ln−N3 distance of 2.341(2) Å of the latter ligand L^2 is, on the other hand, considerably longer than the Y1−N2 amide bond. Backbone alkylation of $L^{2,Me}$ is also reflected in the N2−C5 single bond showing the expected elongation to 1.463(4) Å in comparison to the N4−C19 double bond (1.304(4) Å) in the monoanionic ligand L^2.

Next, we examined the effects of pentamethylcyclopentadienyl as a monovalent ancillary ligand on this methyl/iminopyrrole ligand exchange reaction. Half-sandwich complexes have gathered great interest in lanthanide chemistry, especially during the past decade.[2,5] The bulky and rigid properties of this archetypal ligand should be ideal for studying these exchange reactions by providing stability, minimizing agglomeration, and yielding traceable products upon subsequent alkylation (vide infra). The trimeric yttrium dimethyl complex [(C_5Me_5)YMe_2]$_3$ is readily obtained according to the aluminate route,[15] and its moderate solubility in aromatic solvents seemed to qualify for the envisaged methane elimination reactions (Scheme 2). As for [YMe_3]$_n$, the half-sandwich complex [(C_5Me_5)YMe_2]$_3$ dissolved quickly upon addition of 2 equiv of pyrrole HL^1 or HL^2 with slight gas

Scheme 2. Generation of Bis(iminopyrrolyl) Yttrium Complexes via Protonolysis from [(C_5Me_5)YMe_2]$_3$



formation. Evaporation of the yellow solutions gave residues of composition [(C_5Me_5)Y(L^1)$_2$] (**3**) and [(C_5Me_5)Y(L^2)$_2$] (**4**), while NMR spectroscopy revealed already a high purity of the crude reaction products. Complexes **3** and **4** can be further purified by recrystallization from toluene/*n*-hexane mixtures at −35 °C.

The solid-state structure of **3** revealed the monomeric complex (C_5Me_5)Y[2-(2,6-$iPr_2C_6H_3N$=CH)C_4H_3N]$_2$ (**3**) with a seven-coordinate yttrium center. The four pyrrolyl nitrogen atoms and the cyclopentadienyl centroid adopt a tetragonal-pyramidal geometry (Figure 3). Very recently,

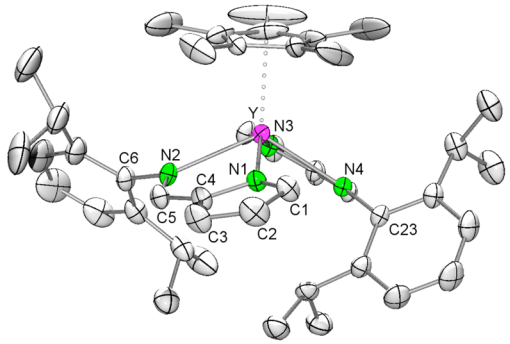


Figure 3. Perspective ORTEP view of the molecular structure of (C_5Me_5)Y[2-(2,6-$iPr_2C_6H_3N$=CH)C_4H_3N]$_2$ (**3**, (C_5Me_5)$YL^1{}_2$). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Y−N1 = 2.377(2), Y−N2 = 2.487(3), Y−N3 = 2.364(2), Y−N4 = 2.457(2), Y−Ctr = 2.344, N4−C22 = 1.303(4), N4−C23 = 1.444(4), N1−Y−N2 = 71.16(8), N3−Y−N4 = 70.89(8), N2−Y−N3 = 98.07(8), N1−Y−N4 = 87.28(8), N1−Y−Ctr = 106.92, N2−Y−Ctr = 114.86, N3−Y−Ctr = 108.01, N4−Y−Ctr = 120.73.

Trifonov et al. reported on the synthesis and characterization of the structurally comparable bis(iminopyrridyl) half-sandwich complex (C_5Me_5)Yb{(2,6-$^iPr_2C_6H_3$NCH(C_5H_5N)$^{\bullet-}$}$_2$.[37] Its formation takes place in a rather unusual oxidation reaction of the divalent ytterbocene (C_5Me_5)$_2$Yb(THF)$_2$ with 2-{[(2,6-diisopropylphenyl)imino]methyl}pyridine. While complex **3** reveals distinct amido (Y−N1 = 2.377(2) Å) and imino donor bonding (Y−N2 = 2.487(3) Å), the aforementioned ytterbium complex displays two almost equidistant Yb−N bonds (Yb1−N1A = 2.356(2) Å, Yb1−N2A = 2.345(2) Å) resulting from charge distribution along the backbone of the radical ligand. The N−Y−Ctr angles in **3** range from 106.92 to 120.73° and the N1−Y−N2 angles at 71.6(8)° lie in the expected range from other yttrium iminopyrrolyl complexes.

In order to complete this series, we examined the reaction of the iminopyrroles HL^1 and HL^2 with yttrocene methyl complexes. Treatment of (C_5Me_5)$_2$YMe(THF) with equimolar amounts of proligand in toluene led to the desired products (C_5Me_5)$_2$YL (**5**, L = L^1; **6**, L = L^2; Scheme 3). The reaction of (C_5Me_5)$_2$Y($AlMe_4$) with 2 equiv of HL^1 or HL^2 also gave complexes **5** and **6**, but isolation of the pure products was hampered by the formation of coproducts Me_2AlL. The yttrocene complexes **5** and **6** exhibit low solubility in aromatic solvents, facilitating recrystallization from benzene at ambient temperature.

The solid-state structure of (C_5Me_5)$_2$Y[2-(2,6-$^iPr_2C_6H_3$N=CH)C_4H_3N] (**5**) revealed a formally eight-coordinate monomeric complex (Figure 4) and a more distinct amido and imino donor bonding (Y−N1 = 2.330(1) Å and Y−N2 = 2.531(1) Å;

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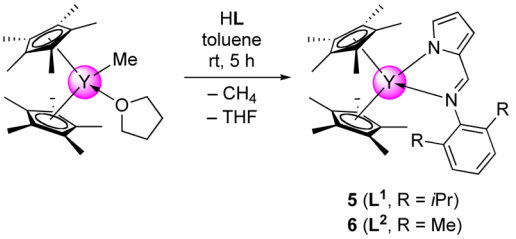
Scheme 3. Preparation of Iminopyrrolyl Yttrocene Complexes from $(C_5Me_5)_2YMe(THF)$ via Protonolysis



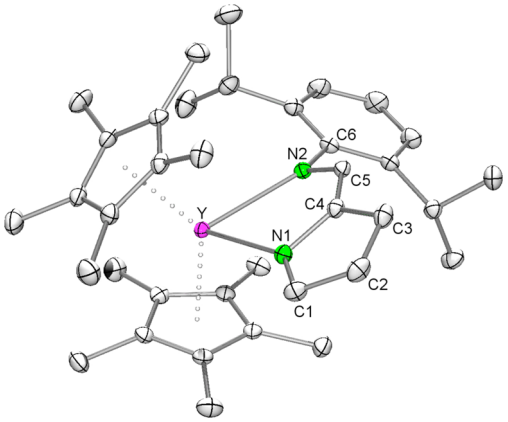
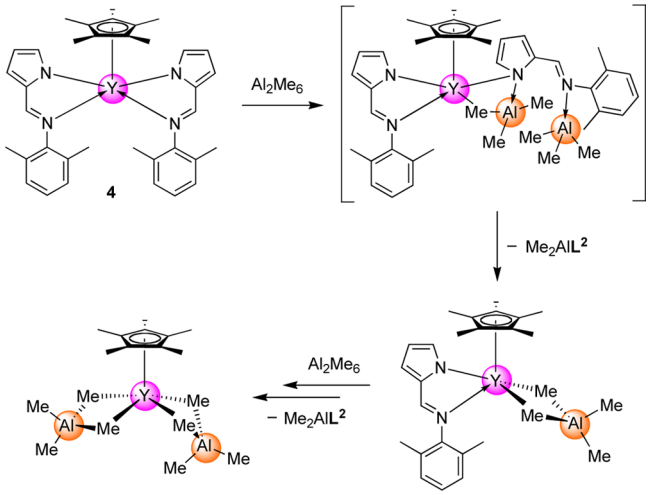


Figure 4. Perspective ORTEP view of the molecular structure of $(C_5Me_5)_2Y[2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CH)C_4H_3N]$ (**5**, $(C_5Me_5)_2YL^1$). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Y1–N1 = 2.330(2), Y1–N2 = 2.531(2), Y1–Ctr1 = 2.405, N2–C5 = 1.318(2), N2–C6 = 1.443(2); N1–Y1–N2 = 73.09(4), N1–Y1–Ctr1 = 101.06, N2–Y1–Ctr2 = 114.82.

Δ_{Y-N} = 0.201 Å) in comparison to half-sandwich complex **3** (Δ_{Y-N} = 0.110 Å). This might originate from enhanced steric repulsion between the diisopropyl substituents of the iminopyrrolyl ligand and the pentamethylcyclopentadienyl ligands. The Ln–N distance is also comparable to those in diazabutadiene lanthanidocene complexes.[38,39]

Reactions with Trimethylaluminum. d-transition-metal-based and f-element-based polymerization catalysis often involves methylalumoxane (MAO) as the most prominent organoaluminum activator.[40] Other routinely employed organoaluminum reagents comprise homoleptic AlR_3 (R = Me, Et, *i*Bu) as well as heteroleptic $HAliBu_2$ or R_2AlCl (R = Me, Et, *i*Bu). It is also noteworthy that commercially available MAO contains a considerable amount of Al_2Me_6. Much effort has been put into the synthesis of new ancillary proligands as alternatives to cyclopentadienyl derivatives (keywords non-cyclopentadienyl or post-metallocene).[3,4] In contrast to the ubiquitous η^5-C_5R_5 ligands, N- and O-donor-based ancillaries L are much more prone to Ln → Al L transfer in the presence of activating organoaluminum reagents, as revealed by studies of the LLn^{III}bis(tetramethylaluminate)-based post-metallocene library (L = ancillary ligand),[18,20–22] Since derivatives $L^1Ln^{III}(AlMe_4)_2$ and $L^2Ln^{III}(AlMe_4)_2$ display potential candidates for this library, we initially studied the proneness of these η^5-coordinating iminopyrrolyl ligands to Ln → Al L transfer. The half-sandwich complex $(C_5Me_5)YL^1_2$ (**4**) seemed to be a good target due to its mononuclearity, the comparatively unsaturated metal environment, and immediate comparability with the cyclopentadienyl ligand. When the reaction of **4** was performed with increasing amounts of trimethylaluminum, an enhanced instability of the Y–L^1 moiety was observed (Scheme 4).

Scheme 4. Half-Sandwich Pyrrolyl Complex 4 Displaying Rapid N-Ligand Exchange with Trimethylaluminum



Iminopyrrolyl ligand L^2 was displaced immediately by a tetramethylaluminato moiety. Using 1 equiv of $AlMe_3$ led to a mixture of unreacted **4**, $(C_5Me_5)YL^2(AlMe_4)$, the known bisaluminate $(C_5Me_5)Y(AlMe_4)_2$,[18a] and the byproduct Me_2AlL^2. When 4 equiv of $AlMe_3$ were applied, complete exchange was indicated by the exclusive formation of $(C_5Me_5)Y(AlMe_4)_2$ and Me_2AlL^2. No intermediate trimethylaluminum adducts of the type $[Y(L^2)(AlMe_3)]$ were observed, which could be previously isolated and structurally characterized for several monoanionic amido moieties.[41] This implies that addition of $AlMe_3$ and subsequent displacement of L^2 with a second molecule of trimethylaluminum takes place rather quickly. This can be rationalized on the basis of the dinuclear nature of $(AlMe_3)_2$ approaching the Y–iminopyrrolyl moiety in a way that one $AlMe_3$ unit interacts with the pyrrolyl amido nitrogen, while the second $AlMe_3$ group resides at the reaction site via donor bonding to the imino nitrogen. Thus, the pyrrolyl/aluminato exchange can proceed without the delay of a kinetically controlled subsequent coordination of $AlMe_3$. A similar $(AlMe_3)_2$-based reaction pathway was proposed previously along with a ligand exchange reaction at an organoaluminum-modified thulium 2,3,4,5-tetramethylpyrrolyl complex.[42] We did not observe any methylation of the L^2 imino function. Treatment of both HL^2 and $[KL^2]$ with $AlMe_3$ (even excess) led to L^2AlMe_2 as the only observable product (Scheme 5), which is in accordance with known aluminum chemistry involving similar ligands.[43]

Single crystals of $Me_2Al[2\text{-}(2,6\text{-}Me_2C_6H_3N{=}CH)C_4H_3N]$ (L^2AlMe_2) were gained from concentrated *n*-hexane solutions at −40 °C. Several dimethylaluminum pyrrolylaldiminate complexes were previously structurally characterized, including 5-*tert*-butyl-2-[(2,6-diisopropylphenyl)aldimino]pyrrolyl[44] and 2,5-bis(*N*-aryliminomethyl)pyrrolyl derivatives.[45] Unsurprisingly, the complex L^2AlMe_2 shows a distorted-tetrahedral geometry (Figure 5), originating from a relatively acute N1–Al–N2 angle of 84.68(5)° of the pyrrolaldiminato ligand, which is comparable to those in complex 5-*tert*-butyl-2-[(2,6-diisopropylphenyl)aldimino]pyrrole aluminum dimethyl

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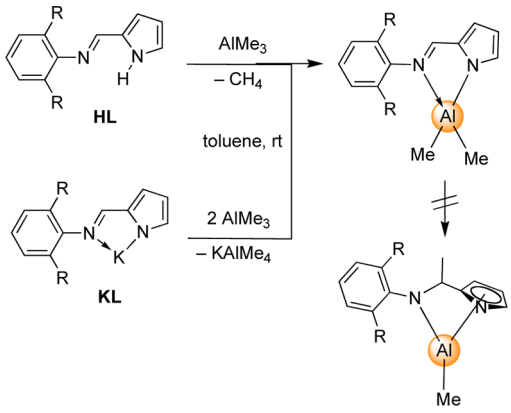
Scheme 5. Synthesis of Iminopyrrolyl Dimethyl Aluminum Complexes via Protonolysis or Salt Metathesis Reactions Utilizing Trimethylaluminum[a]



[a]Backbone methylation was not observed in the absence of rare-earth metals.

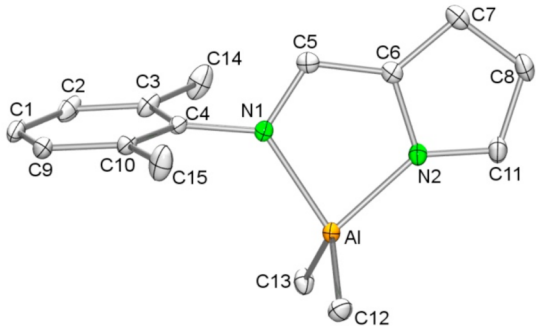
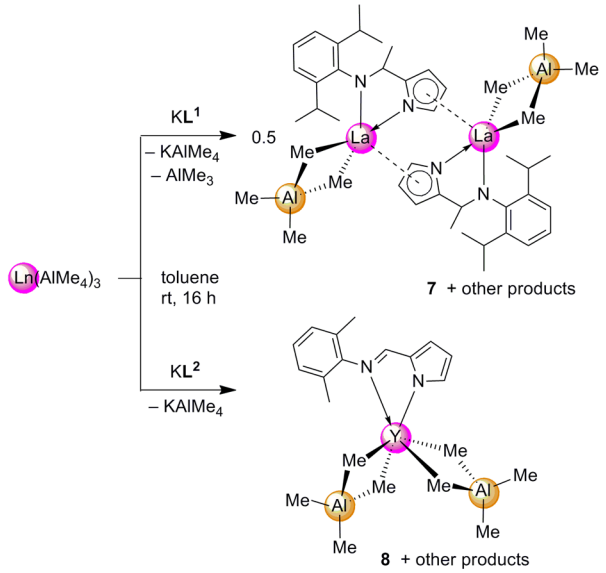


Figure 5. Perspective ORTEP view of the molecular structure of $Me_2Al[2\text{-}(2,6\text{-}Me_2C_6H_3N{=}CH)C_4H_3N]$ (L^2AlMe_2). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Al–N1 = 1.981(2), Al–N2 = 1.911(2), Al–C12 = 1.966(2), Al–C13 = 1.951(2), C4–N1 = 1.440(2), C5–N1 = 1.305(2), C6–N2 = 1.388(2), C11–N2 = 1.352(2); N1–Al–N2 = 84.68(5), N1–Al–C13 = 109.21(6), N1–Al–C12 = 113.81(6), N2–Al–C12 = 110.17(6), N2–Al–C13 = 116.48(7), C12–Al–C13 = 117.90(7).

(85.5(2)°) and its chloride precursor (88.2(2)°).[44] Also, the Al–C12(13) (1.966(2) and 1.951(2) Å) and Al–N1(2) bond lengths (1.981(2) and 1.911(2) Å) lie in the expected range.

Finally, we examined the feasibility of conducting a reverse ligand exchange, meaning the displacement of a tetramethylaluminate moiety by such iminopyrrolyl ligands. We chose homoleptic complexes $Ln(AlMe_4)_3$ (Ln = Y, La) as metal precursors,[26] since that might result in complexes $LLn(AlMe_4)_2$ of relevance for the bis(aluminate) library. Moreover, the large diamagnetic La(III) center might reveal another metal-size effect implied by this multifunctional ligand environment. In order to avoid soluble side products, such as $LAlMe_2$, a salt metathesis route applying KL was chosen over a protonolysis with HL (Scheme 6). The stirring of equimolar reaction mixtures overnight in toluene led to yellow solutions with white precipitates ($KAlMe_4$). The NMR spectra of the obtained yellowish oily solids indicated product mixtures, which is not surprising since complexes $Ln(AlMe_4)_3$ exhibit three equally reactive sites and the iminopyrrolyls under study are not superbulky ancillaries, as evidenced for the formation of even homoleptic complexes (cf. complex **1**).

Scheme 6. Synthesis of Iminopyrrolyl Tetramethylaluminate Complexes via Salt Metathesis Utilizing Homoleptic $Ln(AlMe_4)_3$ Featuring Backbone Methylation as a Main Reaction Pathway



In contrast to the case for cyclopentadienyl ligands, this makes the reaction rather unpredictable. Due to complicated NMR spectra not all byproducts could be unambiguously identified. However, we were able to isolate and fully characterize some main products in reasonable yields via fractionate crystallization. From the reaction with KL^1 the dimeric complex $[L^{1,Me}La(AlMe_4)]_2$ (**7**) could be crystallized, revealing methylation of the imino group in the presence of tetraalkylaluminato ligands. Bearing in mind that neither HL nor KL is methylated by free $AlMe_3$ (Scheme 5), it can be speculated about scenarios involving either the migration of transient terminal La–CH_3 groups or imino group methylation via highly mobile La–η^1-$AlMe_4$ moieties.

Complex **7** features a formally seven-cooordinate lanthanum center and a $\eta^5/\eta^1{:}\kappa^1$ bridging coordination mode of the pyrrole moieties, as detected for complex **2** (Figure 6).[11,12] Complex **7** shows an amido and imino donor bonding (La–N1 = 2.560(3) Å and La–N2 = 2.278(3) Å; Δ_{La-N} = 0.282 Å) even more pronounced than in yttrocene **5** (Δ_{Y-N} = 0.201 Å). The tetramethylaluminato ligand is coordinated in an η^2 fashion with an La–C distance of 2.743(4) Å, which is significantly longer than the La–C(η^2-$AlMe_4$) contacts in seven-coordinate homoleptic $La(AlMe_4)_3$ (2.696(3) and 2.701(3) Å).[26] The tetramethylaluminato moiety in **7** shows a torsion angle C19–Al1–C20–La1 of 26.42°, which features a conformation less "bent" than that found in the half-sandwich complex (C_5Me_5)-$La(AlMe_4)_2$ (62.0(2)°)[16a] and homoleptic $La(AlMe_4)_3$ (49.0(1)°).[26b]

The reaction of $Y(AlMe_4)_3$ with 1 equiv of KL^2 led to the isolation of the envisaged mono(iminopyrrolyl) bis(tetramethylaluminate) complex $L^2Y(AlMe_4)_2$ (**8**) (Scheme 6). NMR spectroscopy revealed only one sharp signal for the aluminate methyl group, in accordance with a highly fluxional behavior as reported previously for bis(tetramethylaluminate) complexes such as $(C_5Me_5)Ln(AlMe_4)_2$.[18a] Complex **8** is stable in benzene solution for at least 2 days, showing no sign of a methylation reaction at the imino backbone. However, due to

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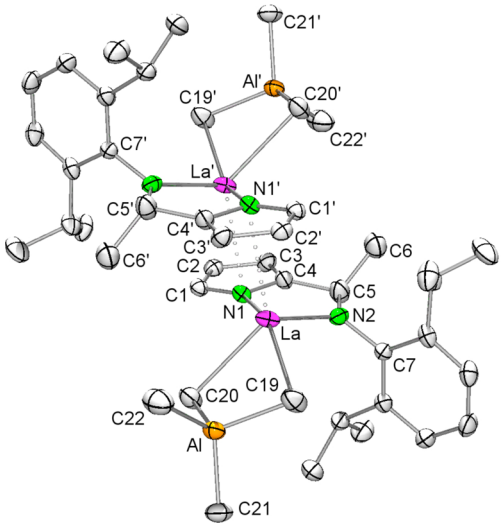

Figure 6. Perspective ORTEP view of the molecular structure of the complex $\{(AlMe_4)La[2\text{-}(2,6\text{-}iPr_2C_6H_3NC(H)(Me))C_4H_3N]\}_2$ (**7**, $L^{1,Me}La(AlMe_4)$). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): La−N1 = 2.560(3), La−N2 = 2.278(3), La−N1′ = 2.822(3), La−C19 = 2.743(4), La−C20 = 2.743(4), La- - -Al = 3.261(2), Al−C19 = 2.074(5), Al−C20 = 2.065(4), Al−C21 = 1.959(4), Al−C22 = 1.994(5), La−Ctr = 2.637; N1−La−N2 = 67.61(10), N1−La−Ctr = 97.40, N2−La−Ctr = 110.72, C19−La−C20 = 76.4(1), C19−La−Ctr = 112.07, C20−La−Ctr = 126.18, C19−A1−C20 = 110.1(2).

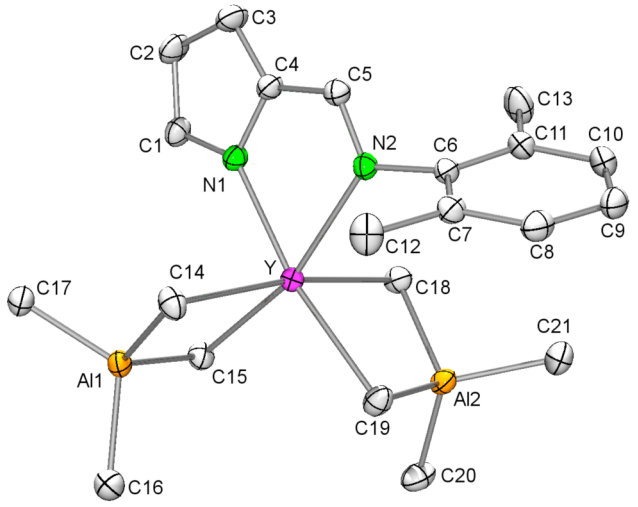

Figure 7. Perspective ORTEP view of the molecular structure of $[2\text{-}(2,6\text{-}Me_2C_6H_3N{=}CH)C_4H_3N]Y(AlMe_4)_2$ (**8**, $L^2Y(AlMe_4)_2$). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Y1−N1 = 2.3024(9), Y1−N2 = 2.4131(9), Y1−C14 = 2.526(1), Y1−C15 = 2.528(1), Y1−C18 = 2.535(1), Y1−C19 = 2.521(1), Y- - -Al1 = 3.0772(4), Y- - -Al2 = 3.1009(3), Al1−C14 = 2.078(1), Al1−C15 = 2.080(1), Al1−C16 = 1.968(1), Al1−C17 = 1.970(1), Al2−C18 = 2.083(1), Al2−C19 = 2.072(1), Al2−C20 = 1.976(1), Al2−C21 = 1.962(1); N1−Y1−N2 = 72.21(3), C14−Y1−C15 = 84.27(4), C18−Y1−C19 = 83.38(4), C15−Y1−C18 = 89.03(4), C14−Y1−C18 = 171.06(4), C15−Y1−N1 = 90.92(4), C19−Y1−N1 = 169.14(4), C19−Y1−N2 = 97.11(9).

rather complicated NMR spectra of the crude product mixture, an initial independent formation of such a methylated species analogue to complex **7** cannot be undoubtedly ruled out. The solid-state structure of complex **8** shows a six-coordinate yttrium center involving two η^2-coordinating alkylaluminato ligands and one bidentate iminopyrrolyl ligand (Δ_{Y-N} = 0.110 Å) (Figure 7). While the iminopyrrolyl bonding is comparable to that in half-sandwich complex **3** showing the same Δ_{Y-N} value of 0.110 Å, the almost planar coordination mode of both tetramethylaluminate ligands (maximum torsion angle 7.40°) was also found in benzamidinate complex $[PhC(NC_6H_4iPr_2\text{-}2,6)_2]Y(AlMe_4)_2$.[20a] Also, the Y−C distances (2.521(1)−2.535(1) Å) and C−Y−C angles (average 84.27(4)°) of **8** match those in the latter benzamidinate complex (2.523(2)−2.542(2) Å, 81.94(8)°). It is noteworthy that complexes of type $[PhC(NC_6H_4iPr_2\text{-}2,6)_2]Y(AlMe_4)_2$ have shown remarkable performance in 1,3-diene polymerization.[20a]

CONCLUSION

Iminopyrrolyl ligands can be easily introduced into organolanthanide complexes via alkane elimination (Ln methyl precursors) or salt metathesis (tetramethylaluminate elimination). Alkylation of the imino backbone, resulting in the formation of a dianionic pyrrolaldiminato ligand, is a major reaction pathway in the presence of reactive Ln−CH_3 or Ln−$AlMe_4$ moieties. Furthermore, the steric bulk of the aryl substituents and the Ln(III) size seem to codirect such intramolecular alkyl migration. Free trimethylaluminum does not alkylate the imino backbone of such iminopyrrolyl ligands but is capable of abstracting these N-ancillary ligands from the rare-earth-metal center. This Ln → Al N-ligand transfer involves the formation of Ln−$AlMe_4$ moieties. Generally, these findings have important implications for the deactivation of polymerization catalysts composed of nitrogen (oxygen)-based ancillary ligands and organoaluminum activators, with ancillary ligand transfer to aluminum and ligand backbone (e.g., imine) alkylation being prominent reaction pathways. The stability of the bis(tetramethylaluminate) complex $[2\text{-}(2,6\text{-}Me_2C_6H_3N{=}CH)C_4H_3N]Y(AlMe_4)_2$ might be further assessed in polymerization reactions.

EXPERIMENTAL SECTION

All operations were performed with rigorous exclusion of air and water, using standard Schlenk, high-vacuum, and glovebox techniques (MBraun MBLab; <1 ppm O_2, <1 ppm H_2O). *n*-Hexane, THF, and toluene were purified by using Grubbs columns (MBraun SPS, solvent purification system) and stored in a glovebox. C_6H_6 and C_6D_6 were obtained from Aldrich, degassed, dried over Na for 96 h, and filtered. $AlMe_3$ was purchased from Aldrich and used as received. Homoleptic $Ln(AlMe_4)_3$ (Ln = Y (**7a**), La (**7b**)),[26] $[YMe_3]_n$,[27] $[(C_5Me_5)YMe_2]_3$,[28] and $(C_5Me_5)_2YMe(THF)$[28] were synthesized according to literature procedures. Iminopyrroles HL^1 and HL^2 were prepared according to literature procedures[2a] and deprotonated with $KN(SiMe_3)_2$ in *n*-hexane. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 25 °C on a Bruker-BIOSPIN-AV500 (5 mm BBO; ^1H, 500.13 MHz; ^{13}C, 125.77 MHz) and a Bruker-BIOSPIN-AV600 (5 mm cryo probe; ^1H, 600.13 MHz; ^{13}C, 150.91 MHz). ^1H and ^{13}C shifts are referenced to internal solvent resonances and reported in parts per million relative to TMS. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer as Nujol mulls sandwiched between CsI plates or on a Nicolet 6700 FTIR spectrometer as DRIFT measurements of KBr triturations. Elemental analyses were performed on an Elementar Vario EL III instrument. Since the reactions routinely produce hard to separate mixtures, some of the combustion analyses are unsatisfactory (**4**, C value; **5**, N; **8**, H). *Caution*! aluminate compounds and volatiles containing trimethylaluminum react violently when exposed to air.

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Y[2-(2,6-*i*Pr$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N]$_3$ (1a). A toluene solution of 3 equiv of HL[1] (399 mg, 1.567 mmol) and a suspension of freshly prepared [YMe$_3$]$_n$ (70 mg, 0.522 mmol) in toluene were cooled to −35 °C and combined. The mixture cleared up after 1 h to give a yellow solution. After the mixture was stirred for 16 h, the solvent was removed in vacuo to yield the raw product as a pale yellow solid (441 mg, 99%). Two subsequent crystallizations from an *n*-hexane/toluene mixture at −35 °C gave 119 mg (27%) of **1** as colorless crystals. NMR data matched the literature values.[11] IR (Nujol, cm^{-1}): 1593 vs, 1424 vs, 1386 vs, 1342s, 1319 s, 1290 vs, 1259 vs, 1168 vs, 1035 vs, 979 vs, 894 vs, 878 s, 802 s, 786 m.

Y[2-(2,6-Me$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N]$_3$ (1b). Proligand HL[2] (446 mg, 2.25 mmol) was dissolved in 5 mL of toluene and added to a stirred suspension of 100 mg of [YMe$_3$]$_n$ (0.75 mmol) in 5 mL of toluene. After it was stirred at ambient temperature for approximately 45 min, the mixture cleared up but was stirred further overnight (16 h). The solution was filtered, its volume reduced to about 3 mL, 1 mL of hexane added, and the solution cooled to −35 °C. Crystallization of **1b** as small slightly yellow needles was initiated when the vial was taken briefly out of the freezer. Within 2 h at −35 °C, 388 mg (76%) of **1b** crystallized and was isolated by decantation and washing with 1 mL of toluene. DRIFT-IR (KBr, cm^{-1}): 2968 w, 1595 m, 1566 vs, 1486 w, 1465 w, 1436 m, 1388 s, 1299 vs, 1260 m, 1172 s, 1033 vs, 978 m, 893 w, 883 m, 772 m, 750 s, 735 w, 679 w, 535 w. ^{1}H NMR (400 MHz, C$_6$D$_6$, 26 °C): δ 7.16 (m, 1H, 3-pyr), 6.85 (m, 1H, *p*-C$_6$H$_3$), 6.81 (m, 2H, *m*-C$_6$H$_3$), 6.80 (m, 1H, N=CH), 6.58 (br s, 1H, 5-pyr), 6.24 (m, 1H, 4-pyr), 1.78 (s, 6H, C$_6$H$_3$-C*H*$_3$) ppm. ^{13}C {^{1}H} NMR (100 MHz, C$_6$D$_6$, 26 °C): δ 163.9 (N=*C*H), 149.1 (*i*-C$_6$H$_3$), 139.8 (m, 3-pyr), 137.2 (2-pyr), 131.4 (*o*-C$_6$H$_3$), 128.7 (*m*-C$_6$H$_3$), 125.4 (*p*-C$_6$H$_3$), 123.2 (5-pyr), 113.7 (4-pyr), 18.5 (C$_6$H$_3$-*C*H$_3$) ppm. Anal. Calcd for C$_{39}$H$_{39}$N$_6$Y (680.684): C, 68.82; H, 5.78; N, 12.35. Found: C, 68.59; H, 5.50; N, 12.01.

{[2-(2,6-Me$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N]Y[2-(2,6-Me$_2$C$_6$H$_3$NC(H)(Me))-C$_4$H$_3$N]}$_2$ (2). In an experiment similar to the procedure described for the synthesis of **1b**, a toluene solution of 3 equiv of HL[2] (311 mg, 1.567 mmol) and a suspension of freshly prepared [YMe$_3$]$_n$ (70 mg, 0.522 mmol) in toluene were cooled to −35 °C and combined. After 45 min a clear yellow solution was observed. Stirring for another 16 h and subsequent removal of the solvent in vacuo gave a mixture containing the free ligand HL[2], homoleptic complex YL$^2_3$, and **2**, as indicated by NMR spectroscopy. Fractionate crystallization from a toluene/hexane mixture at −35 °C gave complex **2** in form of several small colorless blocks. Collecting these crystals for X-ray structure analysis with a pipet initiated the crystallization of the main product **1b** in large amounts.

(C$_5$Me$_5$)Y[2-(2,6-*i*Pr$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N]$_2$ (3). A toluene solution of 2 equiv of HL[1] (80.1 mg, 0.315 mmol) was cooled to −35 °C and added to a suspension of freshly prepared [(C$_5$Me$_5$)YMe$_2$]$_3$ (40 mg, 0.157 mmol) in toluene likewise precooled to −35 °C. The mixture cleared up totally after 45 min to give a yellow solution. After the mixture was stirred for 5 h, the solvent was removed in vacuo to yield the raw product as a pale yellow solid. Crystallization from an *n*-hexane/toluene/benzene mixture at −35 °C gave 71 mg (62%) of compound **3** as colorless crystals. IR (KBr, cm^{-1}): 2962 s, 2925 s, 2864 s, 1592 s, 1566 vs, 1496 m, 1454 s, 1283 s, 1039 s, 749 s, 690 s, 681 s. ^{1}H NMR (600 MHz, C$_6$D$_6$, 25 °C): δ 7.82 (s, 2H, N=CH), 7.03 (t, 2H, *p*-C$_6$H$_3$), 7.02 (br s, 2H, *m*-C$_6$H$_3$), 6.95 (br s, 2H, *m*-C$_6$H$_3$), 6.70 (d, 2H, 3-pyr), 6.59 (s, 2H, 5-pyr), 6.40 (m, 2H, 4-pyr), 3.44 (h, 2H, C*H*(CH$_3$)$_2$), 2.75 (h, 2H, C*H*(CH$_3$)$_2$), 1.90 (s, 15H, Cp-C*H*$_3$), 1.44 (d, 6H, CH(C*H*$_3$)$_2$), 1.14 (d, 6H, CH(C*H*$_3$)$_2$), 0.92 (d, 6H, CH(C*H*$_3$)$_2$), 0.69 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (151 MHz, C$_6$D$_6$, 25 °C): δ 163.5 (N=CH), 149.4 (*ipso*-C$_6$H$_3$), 139.5 (5-pyr), 129.1 (*o*-C$_6$H$_3$), 128.1 (*o*-C$_6$H$_3$), 126.2 (*m*-C$_6$H$_3$), 125.6 (*m*-C$_6$H$_3$), 123.2 (3-pyr), 123.4 (2-pyr), 119.8 (Cp), 113.2 (4-pyr), 30.2 (CH(CH$_3$)$_2$), 28.0 (CH(CH$_3$)$_2$), 27.2 (CH(*C*H$_3$)$_2$), 26.9 (CH-(CH$_3$)$_2$), 23.2 (CH(CH$_3$)$_2$), 20.3 (CH(CH$_3$)$_2$), 11.5 (Cp-CH$_3$) ppm. Anal. Calcd for C$_{44}$H$_{57}$N$_4$Y (730.868): C, 72.31; H, 7.86; N, 7.67. Found: C, 72.77; H, 7.86; N, 7.32.

(C$_5$Me$_5$)Y[2-(2,6-Me$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N]$_2$ (4). By a procedure similar to the synthesis of **3**, HL[2] (62.5 mg, 0.315 mmol) was reacted with [(C$_5$Me$_5$)YMe$_2$]$_3$ (40 mg, 0.157 mmol). Crystallization from an *n*-hexane/toluene/benzene mixture at −35 °C gave 76 mg (78%) of compound **4** as colorless crystals. IR (Nujol, cm^{-1}): 1596 vs, 1301 vs, 1258 s, 1172 vs, 1095 m 1087 m, 1038 vs, 977 vs, 892 m, 882 s, 774 s 681 m, 607 m. ^{1}H NMR (600 MHz, C$_6$D$_6$, 25 °C): δ 6.95 (t, 2H, *p*-C$_6$H$_3$), 6.95 (br s, 2H, *m*-C$_6$H$_3$), 6.82 (br s, 2H, *m*-C$_6$H$_3$), 6.72 (d, 2H, 3-pyr), 6.57 (s, 2H, 5-pyr), 6.30 (dd, 2H, 4-pyr), 2.25 (br s, 6H, C$_6$H$_3$-CH$_3$), 1.90 (s, 15H, Cp-C*H*$_3$), 1.49 (br s, 6H, C$_6$H$_3$-CH$_3$) ppm. ^{13}C{^{1}H} NMR (151 MHz, C$_6$D$_6$, 25 °C): δ 163.5 (N=CH) 148.7 (*ipso*-C$_6$H$_3$), 136.3 (*p*-C$_6$H$_3$), 132.8 (*m*-C$_6$H$_3$), 129.7 (*m*-C$_6$H$_3$), 125.1 (2-pyr), 123.0 (3-pyr), 119.5 (5-pyr), 113.3 (4-pyr), 19.3 (C$_6$H$_3$-CH$_3$), 17.7 (C$_6$H$_3$-CH$_3$), 11.4 (Cp-CH$_3$) ppm. Anal. Calcd for C$_{38}$H$_{42}$N$_4$Y (643.683): C, 70.91; H, 6.58; N, 8.70. Found: C, 69.70; H, 6.32; N, 8.85.

(C$_5$Me$_5$)$_2$Y[2-(2,6-*i*Pr$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N] (5). A pentane solution of 1 equiv of HL[1] (17.1 mg, 0.0672 mmol) was cooled to −35 °C and added to a solution of (C$_5$Me$_5$)$_2$YMe(THF) (30.0 mg, 0.0672 mmol) that was likewise precooled to −35 °C. The mixture cleared up after 1 h to give a yellow solution. After the mixture was stirred for 16 h, the solvent was removed in vacuo to yield the raw product as a pale yellow solid (39.5 mg, 96%). IR (KBr, cm^{-1}): 2962 m, 2920 m, 2859 m, 1594 m, 1569 s, 1430 m, 1308 m, 1285 w, 1037 m, 873 w, 749 m, 699 w. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 7.84 (s, 1H, N=C*H*), 7.04 (dd, 1H, $^3J_{HH}$ = 3.4 Hz, $^4J_{HH}$ = 1.6 Hz, 3-pyr), 7.26−7.29 (m, 4H, *m*-C$_6$H$_3$, *p*-C$_6$H$_3$, 5-pyr), 6.69 (dd, 1H, $^3J_{HH}$ = 3.4 Hz, $^4J_{HH}$ = 1.6 Hz, 4-pyr), 3.04 (sept, 2H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 1.97 (s, 30H, Cp(C*H*$_3$)), 1.35 (dd, 12H, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 3.1 Hz, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (151 MHz, C$_6$D$_6$, 25 °C): δ 163.8 (N=CH), 149.8 (*ipso*-C$_6$H$_3$), 140.1 (5-pyr), 129.3 (*o*-C$_6$H$_3$), 128.5 (*m*-C$_6$H$_3$), 125.6 (*p*-C$_6$H$_3$), 125.4 (2-pyr), 125.0 (3-pyr), 118.8 (Cp), 115.1 (4-pyr), 28.8 (CH(CH$_3$)$_2$), 26.9 (CH(CH$_3$)$_2$), 25.7 (CH(CH$_3$)$_2$), 11.3 (Cp-CH$_3$) ppm. Anal. Calcd for C$_{37}$H$_{51}$N$_2$Y (612.720): C, 72.53; H, 8.39; N, 4.57. Found: C, 71.76; H, 8.17; N, 5.58.

(C$_5$Me$_5$)$_2$Y[2-(2,6-Me$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N] (6). Applying a procedure similar to the synthesis of **5**, HL[2] (13.3 mg, 0.0672 mmol) was reacted with (C$_5$Me$_5$)$_2$YMe(THF) (30.0 mg, 0.0672 mmol) in toluene. Yield: 35.5 mg (94% yield). IR (KBr, cm^{-1}): 2903 m, 2855 m, 1595 m, 1562 s, 1566 vs, 1468 m, 1388 m, 1306 m, 765 w, 749 w. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 7.81 (s, 1H, N=CH), 7.50 (m, 1H, 5-pyr), 7.44 (m, 3H, *m*-C$_6$H$_3$, *p*-C$_6$H$_3$), 7.17 (dd, 1H, $^3J_{HH}$ = 3.6 Hz, $^4J_{HH}$ = 1 Hz, 3-pyr), 6.93 (dd, 1H, $^3J_{HH}$ = 3.6 Hz, $^4J_{HH}$ = 1 Hz, 4-pyr), 2.16 (s, 6H, C$_6$H$_3$-C*H*$_3$), 2.15 (s, 30H, Cp(C*H*$_3$)) ppm. ^{13}C{^{1}H} NMR (151 MHz, C$_6$D$_6$, 25 °C): δ 160.8 (N=CH), 150.3 (*ipso*-C$_6$H$_3$), 141.0 (5-pyr), 135.0 (*o*-C$_6$H$_3$), 130.0 (*m*-C$_6$H$_3$), 128.8 (*p*-C$_6$H$_3$), 124.5 (2-pyr), 124.4 (3-pyr), 115.0 (4-pyr), 118.2 (Cp), 21.2 (C$_6$H$_3$-*C*H$_3$), 11.2 (Cp-CH$_3$) ppm. Anal. Calcd for C$_{33}$H$_{43}$N$_2$Y·C$_4$H$_8$O (628.719): C, 70.68; H, 8.18; N, 4.46. Found: C, 70.31; H, 8.64; N, 4.63.

{(AlMe$_4$)La[2-(2,6-*i*Pr$_2$C$_6$H$_3$NC(H)(Me))C$_4$H$_3$N]}$_2$ (7). An *n*-hexane solution of La(AlMe$_4$)$_3$ (100 mg, 0.250 mmol) was combined with a suspension of an equimolar amount of KL[1] (73.07 mg, 0.250 mmol) in *n*-hexane. The suspension turned yellow after 45 min, and the solid part was evenly distributed. After the mixture was stirred for 16 h, the white solid part was separated by centrifugation. The yellow solution was filtered and the solvent removed in vacuo to yield a slightly yellow oily solid. Crystallization from an *n*-hexane/toluene/benzene mixture at −35 °C gave 20.9 mg (17%) of compound **7** as colorless crystals. IR (KBr, cm^{-1}): 2957 s, 2924 s, 2880 s, 1458 m, 1437 m, 1246 s, 1187 s, 912 w, 861 m, 798 m, 695 vs, 667 s. Anal. Calcd for C$_{44}$H$_{72}$Al$_2$N$_4$La$_2$ (988.866): C, 53.44; H, 7.34; N, 5.67. Found: C, 53.04; H, 7.48; N, 4.89.

(AlMe$_4$)$_2$Y[2-(2,6-Me$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N] (8). In a procedure similar to the synthesis of **7**, KL[2] (67.5 mg, 0.286 mmol) was reacted with Y(AlMe$_4$)$_3$ (100 mg, 0.286 mmol). Crystallization from an *n*-hexane/toluene/benzene mixture at −35 °C gave 53.5 mg (41%) of **8** as colorless crystals. IR (KBr, cm^{-1}): 2915 s, 2880 m, 1587 w, 1454 m, 1302 w, 1250 m, 1189 m, 793 m, 768 m, 693 s, 573 m. ^{1}H NMR (600 MHz, C$_6$D$_6$, 25 °C): δ 7.16 (s, 1H, 5-pyr), 6.86 (s, 2H, *m*-C$_6$H$_3$), 6.83 (m, 1H, *p*-C$_6$H$_3$), 6.69 (d, 1H, 3-pyr), 6.33 (dd, 1H, 4-pyr), 1.93 (s, 6H, C$_6$H$_3$-C*H*$_3$), −0.17 (d, 24H, Al-CH$_3$) ppm. ^{13}C{^{1}H} NMR (151

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Table 1. Crystallographic Data for Complexes 1b, 2, 3, 5, 7, 8, and L^2AlMe_2

	1b	2	3	5	7	8	L^2AlMe_2
formula	$C_{39}H_{39}N_6Y$	$C_{78}H_{82}N_8Y_2$	$C_{47}H_{64}N_4Y$	$C_{43}H_{57}N_2Y$	$C_{44}H_{72}N_4Al_2La_2$	$C_{21}H_{37}N_2AlY_2$	$C_{15}H_{19}N_2Al$
M_r	680.67	1309.34	773.93	690.82	988.84	460.40	254.30
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	9.7346(5)	11.9605(4)	15.4304(7)	9.9779(4)	11.0471(5)	9.2848(3)	8.5714(16)
b/Å	17.5172(11)	23.4161(8)	13.3008(6)	16.8309(6)	18.7061(9)	11.5466(4)	8.6724(16)
c/Å	20.4851(13)	12.3163(4)	20.858(1)	21.9970(8)	13.7101(6)	12.5982(5)	19.893(4)
α/deg						105.821(1)	
β/deg	95.894(4)	107.273(1)	93.685(1)	92.770(1)	109.152(1)	106.197(1)	96.567(5)
γ/deg						93.899(1)	
V/Å^3	3474.7(4)	3293.8(2)	4272.0(3)	3689.8(2)	2676.4(2)	1232.62(8)	1469.0(5)
Z	4	2	4	4	2	2	4
F(000)	1416	1368	1652	1472	1008	484	544
T/K	100(2)	100(2)	100(2)	120(2)	120(2)	120(2)	100(2)
ρ_{calcd}/g cm^{-3}	1.301	1.320	1.203	1.244	1.227	1.240	1.150
μ/mm^{-1}	2.633	1.804	1.401	1.612	1.636	2.444	0.123
R1(obsd)[a]	0.0459	0.0395	0.0481	0.0318	0.0503	0.0198	0.0397
wR2(all)[b]	0.1170	0.0943	0.1118	0.0492	0.1294	0.0520	0.0931
S[c]	1.305	1.082	1.094	1.045	1.244	1.081	1.077

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $F_o > 4\sigma(F_o)$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)^2/(n_o - n_p)]^{1/2}$.

MHz, C_6D_6, 25 °C): δ 164.3 (N=CH), 147.3 (*ipso*-C_6H_3), 140.3 (5-pyr), 136.0 (*p*-C_6H_3), 130.5 (*m*-C_6H_3), 126.3 (2-pyr), 125.2 (3-pyr), 114.6 (4-pyr), 19.3 (C_6H_3-CH_3), 2.1 (Al-CH_3) ppm. Anal. Calcd for $C_{21}H_{37}Al_2N_2Y$ (460.406): C, 54.78; H, 8.10; N, 6.08. Found: C, 55.47; H, 7.18; N, 6.57.

$Me_2Al[2\text{-}(2,6\text{-}Me_2C_6H_3N{=}CH)C_4H_3N]$. In addition to its occurrence as a byproduct in alkylation reactions of e.g. $(C_5Me_5)Y[2\text{-}(2,6\text{-}Me_2C_6H_3N{=}CH)C_4H_3N]_2$ (**4**) with $AlMe_3$, this dimethylaluminum pyrrolylaldiminate complex can be synthesized in high yield and purity as follows: HL^2 (200 mg, 1.01 mmol) was dissolved in 3 mL of toluene, and 146 mg (2.02 equiv) of $AlMe_3$ in 2 mL of toluene was added with rigorous stirring. The mixture was stirred for 3 h at ambient temperature and subsequently its volume reduced under vacuum. The resulting oil was dissolved in 2 mL of *n*-hexane and evaporated to dryness to give a crystalline solid. Recrystallization from small amounts (1−2 mL) of *n*-hexane at −40 °C yielded 235 mg (91%) of colorless crystals. IR (KBr, cm^{-1}): 2932 m, 2890 w, 1593 s, 1567 vs, 1503 m, 1452 m, 1393 vs, 1288 vs, 1183, vs, 1096 w, 1040 vs, 993 m, 904 m, 793 m, 771 m, 755 m, 739 w, 689 s, 679 vs, 603 w, 574 w. ^{1}H NMR (400 MHz, C_6D_6, 26 °C): δ 7.20 (m, 1H, 3-pyr), 6.99 (m, 1H, *p*-C_6H_3), 6.96 (m, 2H, *m*-C_6H_3), 6.86 (m, 1H, N=CH), 6.86 (m, 1H, 5-pyr), 6.50 (m, 1H, 4-pyr), 1.99 (s, 6H, C_6H_3-CH_3), −0.35 (s, 6H, Al-CH_3) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 26 °C): δ 161.9 (N=CH), 143.9 (*i*-C_6H_3), 136.9 (m, 3-pyr), 136.1 (2-pyr), 132.4 (*o*-C_6H_3), 128.8 (*m*-C_6H_3), 126.8 (*p*-C_6H_3), 121.2 (5-pyr), 115.9 (4-pyr), 18.5 (C_6H_3-CH_3), −9.0 (br, Al-CH_3) ppm. Anal. Calcd for $C_{15}H_{19}AlN_2$ (254.311): C, 70.84; H, 7.53; N, 11.02. Found: C, 70.79; H, 7.96; N, 11.12.

Crystallographic Data Collection and Refinement. Crystals were grown by standard techniques from saturated solutions using toluene at −35 °C (**1b**, **2**, **3**, **5**, **7**, and **8**) or *n*-hexane at −35 °C (L^2AlMe_2). Suitable single crystals were selected in a glovebox and coated with Paratone-N (Hampton Research) and fixed in a nylon loop. Data collection was done on a Bruker SMART 2K CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) performing 182° ω scans in four orthogonal ϕ positions (**2**, **3**, **5**, **7**, and **8**) and on a Bruker APEX DUO diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) (L^2AlMe_2) or Cu Kα radiation (λ = 1.54178 Å) (**1b**) performing ω and ϕ scans. Raw data were collected using the program SMART,[46] integrated, and reduced with the program SAINT.[47] Numerical corrections for absorption effects were applied using SHELXTL.[48] The structures were solved by direct or Patterson methods using SHELXS and SHELXL for structure solution and refinement, respectively.[49] Further details of the refinement and crystallographic data are given in Table 1 and in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving full crystallographic data for complexes **1b**, **2**, **3**, **5**, **7**, **8**, and L^2AlMe_2. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have also been deposited at the Cambridge Crystallographic Data Centre under CCDC reference numbers 907091 (**2**), 907092 (**3**), 907093 (**5**), 907094 (**7**), 907095 (**8**), 920027 (L^2AlMe_2), and 922387 (**1b**) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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