

(2,5-Bis{[(2,6-diisopropylphenyl)imino]methyl}pyrrolyl)yttrium and -lutetium Complexes – Synthesis and Structures

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Dedicated to Prof. Dr. Dr. hc. mult. Wolfgang A. Herrmann on the occasion of his 60th birthday

Keywords: Lutetium / N ligands / Potassium / Pyrrole / Yttrium

The reaction of 2,5-bis{[(2,6-diisopropylphenyl)imino]methyl}pyrrole (dip₂-pyr)H with *n*BuLi and KH resulted in the lithium compound [(dip₂-pyr)Li] and the potassium compound [(dip₂-pyr)K], respectively. Transmetalation of [(dip₂-pyr)Li] with YCl₃ in thf afforded the “ate complex” [(dip₂-pyr)YCl₃Li(thf)₃], in which an additional equivalent of LiCl is coordinated as a four-membered Li–Cl–Y–Cl metallacycle. In contrast, treatment of [(dip₂-pyr)K] with anhydrous yttrium and lutetium trichloride resulted in [(dip₂-pyr)LnCl₂(thf)₂] (Ln

= Y, Lu). Obviously, by using the potassium reagent [(dip₂-pyr)K] the formation of “ate complexes” is inhibited. Reaction of NaC₅H₅ with [(dip₂-pyr)YCl₃Li(thf)₃] or [(dip₂-pyr)YCl₂(thf)₂] afforded the metallocene [(dip₂-pyr)Y(η⁵-C₅H₅)₂]. A significant difference in reactivity between the compounds [(dip₂-pyr)YCl₃Li(thf)₃] and [(dip₂-pyr)YCl₂(thf)₂] could not be observed.

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Introduction

In the last 20 years, much progress has been observed in the design and application of (amido)metal chemistry of the early transition metals. In the early stages of this area cyclopentadienyl-analogous amido ligands were studied for comparison with and for further investigations of the well-known cyclopentadienyl moiety. Today, the stable amido–metal bond is utilized in (amido)metal chemistry to produce well-defined reaction centers in transition metal complexes. In this way, the reactivity of the resulting early transition metal compounds can be specifically tailored to allow applications in areas such as the activation of small and poorly reactive molecules, homogeneous catalysis, or organic synthesis.^[1,2] In this context, 2-[(arylimino)methyl]pyrrolyl ligands were recently introduced into aluminum,^[3] group 4,^[4–7] iron,^[4] cobalt,^[4] and nickel^[4] chemistry as nitrogen-based polydentate ancillary ligands. The resulting complexes were used as catalyst precursors for ethylene polymerization. Moreover, some time ago Mashima et al. prepared tridentate bis(iminomethyl)pyrrolyl ligands and investigated their reactions with the homoleptic bis(trimethylsilyl)amide [Y{N(SiMe₃)₂}]₃.^[8] Homoleptic and heteroleptic pyrrolyl complexes of yttrium were obtained by the so called “silylamide route”.^[9] The heteroleptic complexes were used as initiators for the polymerization of ε-caprolactone.

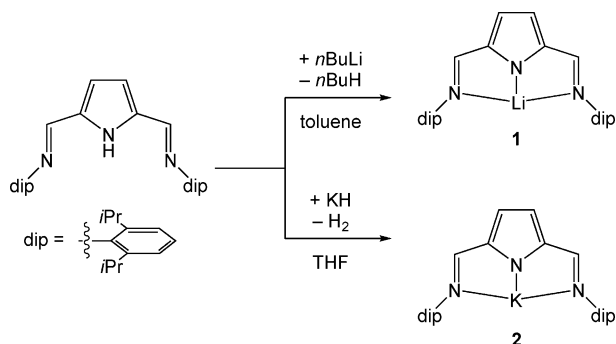
In this contribution, we report on the synthesis of the lithium^[4] and potassium derivative of 2,5-bis{[(2,6-diisopropylphenyl)imino]methyl}pyrrole (dip₂-pyr)H first, followed by the reaction of these compounds with YCl₃ and LuCl₃. Moreover, the yttrium metallocene derivative [(dip₂-pyr)Y(η⁵-C₅H₅)₂] is presented.

Results and Discussion

Alkali Metal Compounds

As reported earlier, (dip₂-pyr)H was synthesized by condensation of pyrrole-2,5-dicarbaldehyde with 2,6-diisopropylaniline.^[5] Treatment of (dip₂-pyr)H with *n*BuLi in toluene resulted in the lithium compound [(dip₂-pyr)Li] (**1**), which was described earlier by Bochmann et al. (Scheme 1).^[4] In contrast, the corresponding potassium compound [(dip₂-pyr)K] (**2**) was not reported previously. Treatment of (dip₂-pyr)H with KH in thf resulted in compound **2** (Scheme 1). The ¹H and ¹³C NMR spectra show the expected set of signals. The observed chemical shifts are in good agreement with the lithium salt **1**. Only one set of each signal is observed at δ(¹H) = 1.13 and 3.19 ppm for the isopropyl groups of compound **2** indicating that the 2,6-diisopropylaniline moieties of the ligand can freely rotate in solution. By recording the NMR spectra in C₆D₆ it clearly can be shown that no thf is coordinated to the potassium atom. This is somewhat surprising because the reaction was performed in thf.

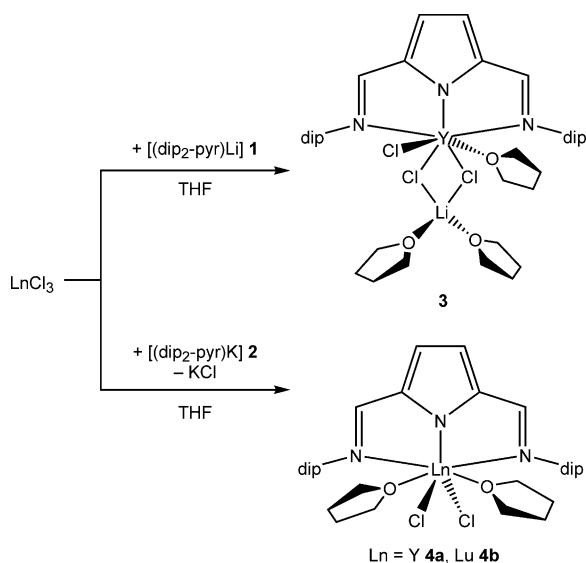
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Scheme 1.

Rare Earth Complexes

Transmetalation of **1** with anhydrous yttrium trichloride in thf afforded the “ate complex” $[(\text{dip}_2\text{-pyr})\text{YCl}_3\text{Li}(\text{thf})_3]$ (**3**) as crystals in good yields (Scheme 2). The new complex has been characterized by standard analytical/spectroscopic techniques, and the solid-state structure was established by single-crystal X-ray diffraction.



Scheme 2.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **3** show the expected sets of signals. In contrast to compounds **1** and **2**, a splitting of the isopropyl CH_3 signals into two sets of doublets is observed, which is interpreted as a consequence of restricted rotation about the $\text{N}-\text{C}_{\text{ipso}}$ bond. Similar observations were made for other 2,6-diisopropylaniline-substituted yttrium complexes, such as $[\text{Y}\{\text{ArN}(\text{CH}_2)_3\text{NAr}\}(\text{thf})_2(\mu\text{-Cl})_2\text{Li}(\text{thf})_2]$ ($\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$).^[10]

Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with two molecules of compound **3** and two thf molecules in the unit cell (Figure 1). In this compound an additional equivalent of LiCl is coordinated as a four-membered $\text{Li}-\text{Cl}-\text{Y}-\text{Cl}$ metallacycle. Additionally, two thf molecules are bound to the lithium atom. This kind of LiCl adduct is well known in lanthanide chemistry. For example, there are

numerous metallocenes and *ansa*-metallocenes known of the general formula $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-Cl})_2\text{Li}(\text{ether})_2]$ and $[\text{Ln}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\}(\mu\text{-Cl})_2\text{Li}(\text{ether})_2]$.^[11] These structures contain two bridging chloride ligands and a lithium atom bound by two solvate molecules. As expected, the $\text{Y}-\text{Cl}$ bonds of compound **3** for the $\mu\text{-Cl}$ atoms [$\text{Y}-\text{Cl}2$ 2.663(9) Å and $\text{Y}-\text{Cl}3$ 2.672(8) Å] are longer than corresponding one for the terminal chlorine atom [$\text{Y}-\text{Cl}1$ 2.554(2) Å].^[12]

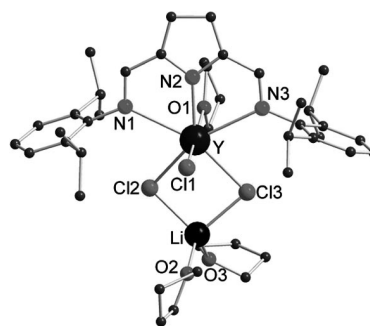


Figure 1. Solid-state structure of **3** with atom-labeling scheme and hydrogen atoms omitted. Selected bond lengths [Å] and angles [°]: $\text{Y}-\text{Cl}1$ 2.554(2), $\text{Y}-\text{Cl}2$ 2.663(9), $\text{Y}-\text{Cl}3$ 2.672(8), $\text{Y}-\text{N}1$ 2.703(9), $\text{Y}-\text{N}2$ 2.306(4), $\text{Y}-\text{N}3$ 2.678(8), $\text{Y}-\text{O}1$ 2.394(4), $\text{Li}-\text{Cl}2$ 2.324(14), $\text{Li}-\text{Cl}3$ 2.229(14), $\text{Li}-\text{O}2$ 1.927(2), $\text{Li}-\text{O}3$ 1.894(15); $\text{N}1-\text{Y}-\text{N}2$ 63.67(14), $\text{N}1-\text{Y}-\text{N}3$ 127.87(13), $\text{N}1-\text{Y}-\text{Cl}1$ 93.14(10), $\text{N}1-\text{Y}-\text{Cl}2$ 74.74(10), $\text{N}1-\text{Y}-\text{Cl}3$ 155.27(10), $\text{N}1-\text{Y}-\text{O}1$ 85.68(14), $\text{N}2-\text{Y}-\text{N}3$ 64.22(12), $\text{N}2-\text{Y}-\text{Cl}1$ 93.60(12), $\text{N}2-\text{Y}-\text{Cl}2$ 137.04(10), $\text{N}2-\text{Y}-\text{Cl}3$ 139.19(10), $\text{N}2-\text{Y}-\text{O}1$ 80.64(14), $\text{N}3-\text{Y}-\text{Cl}1$ 91.6(1), $\text{N}3-\text{Y}-\text{Cl}2$ 154.61(9), $\text{N}3-\text{Y}-\text{Cl}3$ 75.54(9), $\text{N}3-\text{Y}-\text{O}1$ 84.56(14), $\text{Y}-\text{Cl}2-\text{Li}$ 89.66(3), $\text{Y}-\text{Cl}3-\text{Li}$ 89.11(3).

The yttrium atom of compound **3** is heptacoordinated by the $(\text{dip}_2\text{-pyr})^-$ ligand, two thf molecules, and three chlorine atoms. Thus, a distorted pentagonal-bipyramidal coordination polyhedron is formed. In the apices one thf molecule and one chlorine atom are located. The $\text{O}1-\text{Y}-\text{Cl}1$ bond angle is $174.04(10)^\circ$. Even the bonds of the imine nitrogen atoms to the yttrium atom [$\text{Y}-\text{N}1$ 2.671(3) Å and $\text{Y}-\text{N}3$ 2.678(3) Å] are significantly longer than that of the pyrrolyl nitrogen atom to the yttrium atom [$\text{Y}-\text{N}2$ 2.288(3) Å]. We consider the $(\text{dip}_2\text{-pyr})^-$ ligand as tridentate. This is in agreement with the earlier reported compound $[(\text{xyl}_2\text{-pyr})\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_2]$ $\{\text{xyl}_2\text{-pyr} = 2,5\text{-bis}\{[(2,6\text{-dimethylphenyl})\text{imino}]\text{methyl}\}\text{pyrrolyl}; \text{Y}-\text{N}_{\text{pyrrolyl}} 2.288(3) \text{ Å}, \text{Y}-\text{N}_{\text{imine}} 2.707(3) \text{ Å and Y}-\text{N}3 2.776(3) \text{ Å}\}$.^[8]

In contrast to the reaction described above, transmetalation of **2** with anhydrous yttrium and lutetium trichloride in thf at room temperature and crystallization from thf led to the reaction products $[(\text{dip}_2\text{-pyr})\text{LnCl}_2(\text{thf})_2]$ [$\text{Ln} = \text{Y}$ (**4a**), Lu (**4b**)] (Scheme 2). Obviously, by using the potassium reagent **2**, the formation of “ate complexes” is inhibited. The multinuclear NMR spectroscopic data is comparable to that of compound **3**. Most significant again is a splitting of the isopropyl CH_3 signals into two sets of doublets at $\delta(^1\text{H}) = 1.00$ and 1.20 ppm (**4a**), and 1.00 and 1.21 ppm (**4b**); $\delta(^{13}\text{C}\{^1\text{H}\}) = 22.6, 26.7$ ppm (**4a**) and $22.6, 26.8$ ppm (**4b**).

The solid-state structure of **4a** was investigated by single-crystal X-ray diffraction (Figure 2). Compound **4a** crystallizes in the orthorhombic space group *Pbca* with eight molecules in the unit cell. The structure reveals a hepta-coordination sphere of the ligands around the yttrium atom resulting in a distorted pentagonal-bipyramidal coordination polyhedron. In contrast to compound **3**, the two chlorine atoms are located in the apices in an almost linear setup forming a Cl1–Y–Cl2 angle of 172.10(3)°, whereas the (dip₂-pyr)[−] ligand and two molecules of thf are located in the plane. The almost planar setup of the latter ligands is revealed by the sum of the corresponding five angles (368.22°). The two phenyl rings are oriented perpendicularly to the plane of the pyrrolyl moiety. As observed in compound **3**, the metal–imine nitrogen bonds [Y–N1 2.671(3) Å and Y–N3 2.679(3) Å] are longer than the Y–N_{pyrrolyl} distance [Y–N2 2.288(3) Å] (Figure 2).

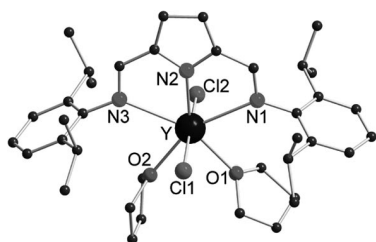
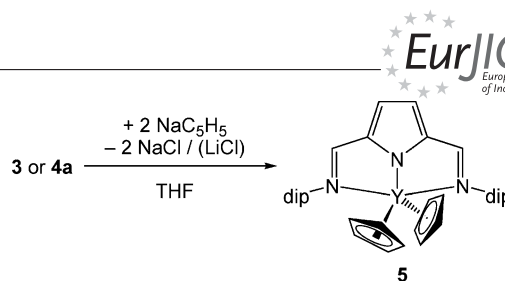


Figure 2. Solid-state structure of **4a** with atom-labeling scheme and hydrogen atoms omitted. Selected bond lengths [Å] and angles [°]: Y–N1 2.671(3), Y–N2 2.288(3), Y–N3 2.679(3), Y–Cl1 2.5915(9), Y–Cl2 2.5826(9), Y–O1 2.389(2), Y–O2 2.409(3); N1–Y–N2 64.71(9), N1–Y–N3 129.15(9), N1–Y–Cl1 91.00(7), N1–Y–Cl2 93.16(7), N1–Y–O1 76.78(9), N1–Y–O2 154.29(9), N2–Y–N3 64.48(9), N2–Y–Cl1 95.20(7), N2–Y–Cl2 92.58(7), N2–Y–O1 141.28(9), N2–Y–O2 141.01(10), N3–Y–Cl1 91.93(6), N3–Y–Cl2 90.65(6), N3–Y–O1 154.00(9), N3–Y–O2 76.53(9).

To learn more about the reactivity of the chlorido complexes, we were interested in synthesizing a cyclopentadienyl derivative. Reaction of NaC₅H₅ with **3** or **4a** in a 2:1 molar ratio in thf at room temperature afforded after crystallization from toluene the metallocene [(dip₂-pyr)Y(η⁵-C₅H₅)₂] (**5**) as yellow crystals. We could not observe a significant difference in reactivity between compounds **3** and **4a** (Scheme 3). As a result of the larger steric bulk of the cyclopentadienyl ligand, no additional solvent is coordinated to the yttrium atom. The new complex has been characterized by standard analytical/spectroscopic techniques. The ¹H and ¹³C{¹H} NMR spectra of **5** are consistent with a C_s symmetry about the yttrium atom. The resonance of the cyclopentadienyl rings in the ¹H NMR spectrum is observed as a sharp singlet (δ = 5.95 ppm). As seen for the compounds described above, a splitting of the isopropyl CH₃ signals into two sets of doublets is observed in the ¹H NMR spectrum, which is consistent with restricted rotation about the N–C_{ipso} bond. This splitting is not well resolved in the ¹³C{¹H} NMR spectrum.

The structure of compound **5** was confirmed by single-crystal X-ray diffraction in the solid state. Compound **5** crystallizes in the monoclinic space group *P2₁/c* with four



Scheme 3.

molecules of **5** and four molecules of toluene in the unit cell. As observed in compound **3** and **4a**, the metal–imine nitrogen bonds [Y–N1 2.708(5) Å and Y–N3 2.813(6) Å] of the (dip₂-pyr)[−] ligand are longer than the Y–N_{pyrrolyl} distance [Y–N2 2.302(5) Å]. The cyclopentadienyl rings are bound in the expected η⁵-coordination mode. The Y–ring centroid bond lengths of Y–C_{g1} 2.368(8) Å and Y–C_{g2} 2.383(2) Å fit well into the range of other cyclopentadienyl complexes {e.g. [(η⁵-MeC₅H₄)₂Y(thf){OCN(*i*Pr)₂NPh}]: Y–C_g 2.421(1) Å and 2.391(2) Å;^[13] [(η⁵-C₅H₅)₂Y(C₆H₄-2-CH₂NMe₂): Y–C_g 2.39 Å and 2.38 Å} (Figure 3).^[14]

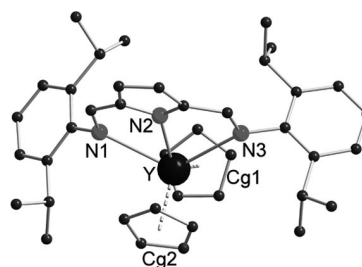


Figure 3. Solid-state structure of **5** with atom-labeling scheme and hydrogen atoms omitted. Selected bond lengths [Å] and angles [°]: Y–N1 2.708(5), Y–N2 2.302(5), Y–N3 2.813(6), Y–C_{g1} 2.368(8), Y–C_{g2} 2.383(2); N1–Y–N2 64.5(2), N1–Y–N3 124.2(2), N1–Y–C_{g1} 99.28(11), N1–Y–C_{g2} 104.60(9), N2–Y–N3 62.4(1), N2–Y–C_{g1} 128.82(13), N2–Y–C_{g2} 103.36(10), N3–Y–C_{g1} 100.62(11), N3–Y–C_{g2} 102.89(13) (C_g = ring center).

Conclusion

We have prepared some new 2,5-bis{[(2,6-diisopropylphenyl)imino]methyl}pyrrolyl compounds of alkaline and rare earth metals. The alkaline metal compounds [(dip₂-pyr)Li] and [(dip₂-pyr)K] could be easily obtained by a deprotonation of (dip₂-pyr)H with the suitable alkaline metal reagents *n*BuLi and KH. By using [(dip₂-pyr)Li] and [(dip₂-pyr)K] in a salt metathesis reaction with YCl₃ different products were obtained. Whereas the reaction of [(dip₂-pyr)Li] resulted in the “ate complex” [(dip₂-pyr)YCl₃Li(thf)₃], a similar reaction of [(dip₂-pyr)K] gave the neutral compound [(dip₂-pyr)YCl₂(thf)₂]. Obviously, by using the potassium reagent the formation of “ate complexes” is inhibited. Both yttrium compounds are different in their structures, but their reactivities are comparable. Thus, treatment of both compounds with NaC₅H₅ afforded the organometallic compound [(dip₂-pyr)Y(η⁵-C₅H₅)₂].

Experimental Section

General Considerations: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual-manifold Schlenk line, interfaced to a high-vacuum (10^{-4} Torr) line, or in an argon-filled MBraun glove box. Tetrahydrofuran was predried with Na wire and distilled under nitrogen from Na/K benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from LiAlH₄. All solvents for vacuum-line manipulations were stored in vacuo over LiAlH₄ in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all ≥ 99 atom-% D) or Euro-iso-Top GmbH (all ≥ 99 atom-% D) and were dried, degassed, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded with a Jeol JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Mass spectra were recorded at 70 eV with a Varian MAT 711 instrument. Elemental analyses were carried out with an Elementar vario EL III. YCl₃,^[15] LuCl₃,^[15] Na(C₅H₅),^[16] and 2,5-bis{[(2,6-diisopropylphenyl)imino]methyl}pyrrol^[17] were prepared according to literature procedures.

[(dip₂-pyr)Li] (1):^[4] To a solution of 2,5-bis{[(2,6-diisopropylphenyl)imino]methyl}pyrrole (2.00 g, 4.5 mmol) in toluene (40 mL) a solution of *n*BuLi in *n*-hexane (2.5 M, 1.80 mL, 4.6 mmol) was slowly added. After stirring at ambient temperature for 2 h, the solution was concentrated to obtain the analytically pure product as a yellow powder. Yield: 2.00 g, 4.4 mmol, 98%. ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ = 1.05 [d, $J_{\text{H,H}}$ = 6.4 Hz, 24 H, CH(CH₃)₂], 3.16 [sept, $J_{\text{H,H}}$ = 6.4 Hz, 4 H, CH(CH₃)₂], 6.90 (s, 2 H, 3,4-pyr), 7.31 (m, 6 H, Ph), 8.18 (s, 2 H, N=CH) ppm. ¹³C{¹H} NMR (C₆D₆, 100.4 MHz, 25 °C): δ = 24.0 [CH(CH₃)₂], 28.4 [CH(CH₃)₂], 120.6 (3,4-pyr), 123.8 (Ph), 125.3 (Ph), 140.6 (2,5-pyr), 145.1 (Ph), 147.5 (Ph), 163.0 (N=CH) ppm.

[(dip₂-pyr)K] (2): To a mixture of KH (2.06 g, 4.6 mmol) and 2,5-bis{[(2,6-diisopropylphenyl)imino]methyl}pyrrole (0.23 g, 5.8 mmol) was added thf (50 mL). After gas evolution had stopped, the suspension was heated to 60 °C for 12 h. Remaining KH was filtered off, and the thf solution was concentrated, layered with pentane and cooled to -24 °C to obtain the product as yellow microcrystalline needles. Yield: 2.13 g, 4.4 mmol, 95%. ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ = 1.13 [d, $J_{\text{H,H}}$ = 6.8 Hz, 24 H, CH(CH₃)₂], 3.18 [sept, $J_{\text{H,H}}$ = 6.8 Hz, 4 H, CH(CH₃)₂], 6.92 (s, 2 H, 3,4-pyr), 7.09–7.17 (m, 6 H, Ph), 8.14 (s, 2 H, N=CH) ppm. ¹³C{¹H} NMR (C₆D₆, 100.4 MHz, 25 °C): δ = 24.2 [CH(CH₃)₂], 28.2 [CH(CH₃)₂], 120.2 (3,4-pyr), 123.5 (Ph), 124.1 (Ph), 139.3 (2,5-pyr), 144.0 (Ph), 151.4 (Ph), 161.1 (N=CH) ppm.

[(dip₂-pyr)YCl₃Li(thf)₃] (3): thf (10 mL) was condensed at -78 °C onto a mixture of YCl₃ (0.12 g, 0.6 mmol) and [Li(dip₂-pyr)] (1) (0.22 g, 0.5 mmol), and the mixture was stirred at ambient temperature for 18 h. The solution was concentrated, and the remaining residue was extracted with toluene (10 mL). The product was obtained as yellow crystals from an oversaturated thf solution. Crystals suitable for X-ray diffraction were collected directly from this crop. Yield: 0.23 g, 0.3 mmol, 60%. ¹H NMR ([D₈]thf, 400 MHz, 25 °C): δ = 1.00 [d, $J_{\text{H,H}}$ = 6.7 Hz, 12 H, CH(CH₃)₂], 1.21 [d, $J_{\text{H,H}}$ = 6.7 Hz, 12 H, CH(CH₃)₂], 3.71 [sept, $J_{\text{H,H}}$ = 6.7 Hz, 4 H, CH(CH₃)₂], 6.61 (s, 2 H, 3,4-pyr), 7.07–7.14 (m, 6 H, Ph), 8.08 (s, 2 H, N=CH) ppm. ¹³C{¹H} NMR ([D₈]thf, 100.4 MHz, 25 °C): δ = 22.6 [CH(CH₃)₂], 24.0 [CH(CH₃)₂], 28.1 [CH(CH₃)₂], 117.5 (3,4-pyr), 123.8 (Ph), 126.4 (Ph), 138.5 (Ph), 142.6 (2,5-pyr), 142.7 (Ph), 164.6 (N=CH) ppm. C₄₆H₇₀Cl₃LiN₃O₄Y (3·thf) (931.28): C 59.31, H 7.59, N 4.51; found C 60.01, H 7.05, N 4.63.

[(dip₂-pyr)LnCl₂(thf)₂] [Ln = Y (4a), Lu (4b)]. General Procedure: thf (10 mL) was condensed at -78 °C onto a mixture of LnCl₃ and [(dip₂-pyr)K] (2), and the mixture was stirred at ambient temperature for 18 h. The solution was filtered off and concentrated until a white residue appeared. The residue was dissolved by heating and the remaining yellow solution was allowed to stand at ambient temperature. After 1 d, the product crystallized as yellow crystals. The crystals were isolated and washed with *n*-pentane. **4a:** YCl₃: 0.23 g, 1.2 mmol; [(dip₂-pyr)K]: 0.48 g, 1 mmol. X-ray quality crystals were obtained from hot thf. Yield: 0.48 g, 0.6 mmol, 60%. ¹H NMR ([D₈]thf, 400 MHz, 25 °C): δ = 1.00 [d, $J_{\text{H,H}}$ = 6.7 Hz, 12 H, CH(CH₃)₂], 1.20 [d, $J_{\text{H,H}}$ = 6.7 Hz, 12 H, CH(CH₃)₂], 3.71 [sept, $J_{\text{H,H}}$ = 6.7 Hz, 4 H, CH(CH₃)₂], 6.57 (s, 2 H, 3,4-pyr), 6.95–7.13 (m, 6 H, Ph), 8.07 (s, 2 H, N=CH) ppm. ¹³C{¹H} NMR ([D₈]thf, 100.4 MHz, 25 °C): δ = 22.6 [CH(CH₃)₂], 26.7 [CH(CH₃)₂], 28.1 [CH(CH₃)₂], 117.5 (3,4-pyr), 123.9 (Ph), 126.4 (Ph), 142.3 (2,5-pyr), 142.7 (Ph), 150.1 (Ph), 164.7 (N=CH) ppm. C₃₈H₅₄Cl₂N₃O₂Y (744.67): calcd. C 61.29, H 7.31, N 5.6; found C 61.57, H 7.44, N 5.57. **4b:** LuCl₃: 0.42 g, 1.5 mmol; [(dip₂-pyr)K]: 0.67 g, 1.4 mmol. ¹H NMR ([D₈]thf, 400 MHz, 25 °C): δ = 1.00 [d, $J_{\text{H,H}}$ = 6.7 Hz, 12 H, CH(CH₃)₂], 1.21 [d, $J_{\text{H,H}}$ = 6.7 Hz, 12 H, CH(CH₃)₂], 3.75 [sept, $J_{\text{H,H}}$ = 6.7 Hz, 4 H, CH(CH₃)₂], 6.61 (s, 2 H, 3,4-pyr), 7.09–7.14 (m, 6 H, Ph), 8.11 (s, 2 H, N=CH) ppm. ¹³C{¹H} NMR ([D₈]thf, 100.4 MHz, 25 °C): δ = 22.6 [CH(CH₃)₂], 26.8 [CH(CH₃)₂], 28.0 [CH(CH₃)₂], 117.4 (3,4-pyr), 123.9 (Ph), 126.4 (Ph), 142.3 (2,5-pyr), 142.8 (Ph), 150.3 (Ph), 164.3 (N=CH) ppm. C₃₈H₅₄Cl₂LuN₃O₂ (830.73): calcd. C 54.94, H 6.55, N 5.06; found C 54.74, H 6.38, N 5.03.

[(dip₂-pyr)Y(η⁵-C₅H₅)₂] (5). Route A: thf (10 mL) was condensed at -78 °C onto a mixture of **3** (0.43 g, 0.5 mmol) and Na(C₅H₅) (0.09 g, 1 mmol), and the mixture was stirred at ambient temperature for 18 h. The solution was then concentrated, and the remaining residue was extracted with toluene (10 mL). The solution was concentrated and the remaining residue washed with *n*-pentane. **Route B:** thf (10 mL) was condensed at -78 °C onto a mixture of **4a** (0.37 g, 0.5 mmol) and Na(C₅H₅) (0.09 g, 1 mmol), and the mixture was stirred at ambient temperature for 18 h. The solution was then concentrated, and the remaining residue was extracted with toluene (10 mL). The solution was then filtered and concentrated until a white residue appeared. The residue was dissolved by heating, and the remaining yellow solution was allowed to stand at ambient temperature. Yellow crystals appeared after several hours. X-ray quality crystals were collected directly from this crop. Yield: 0.17 g, 0.3 mmol, 60%. ¹H NMR ([D₈]thf, 400 MHz, 25 °C): δ = 1.09 [d, $J_{\text{H,H}}$ = 6.8 Hz, 12 H, CH(CH₃)₂], 1.21 [d, $J_{\text{H,H}}$ = 6.8 Hz, 12 H, CH(CH₃)₂], 3.29 [sept, $J_{\text{H,H}}$ = 6.8 Hz, 4 H, CH(CH₃)₂], 5.95 (s, 10 H, C₅H₅), 6.76 (s, 2 H, 3,4-pyr), 7.09–7.25 (m, 6 H, Ph), 8.06 (s, 2 H, N=CH) ppm. ¹³C{¹H} NMR ([D₈]thf, 100.4 MHz, 25 °C): δ = 23.1 [CH(CH₃)₂], 27.8 [CH(CH₃)₂], 110.9 (C₅H₅), 118.9 (3,4-pyr), 123.5 (Ph), 125.5 (Ph), 140.5 (2,5-pyr), 142.8 (Ph), 149.1 (Ph), 162.5 (N=CH) ppm. C₄₀H₄₈N₃Y (659.74): calcd. C 72.82, H 7.33, N 6.37; found C 72.80, H 7.72, N 6.32.

X-ray Crystallographic Studies of 3–5: Crystals of **3–5** were coated in mineral oil (Aldrich) and mounted on glass fibers. They were transferred directly to the -73 °C cold stream of a STOE IPDS 2T diffractometer with Mo-*K*_α radiation. Structures were solved using SHELXS-97^[18] and refined against *F*² using SHELXL-97.^[19] **3:** C₄₆H₇₀Cl₃LiN₃O₄Y (3·thf), triclinic, *P* $\bar{1}$ (no. 2); lattice constants *a* = 10.7803(6), *b* = 14.7469(9), *c* = 17.7228(12) Å, *a* = 83.424(5), β = 85.672(5), *V* = 70.525(5) Å³, *Z* = 2; μ (Mo-*K*_α) = 1.297 mm⁻¹; θ_{max} = 25.0; 9210 (*R*_{int}) = 0.0469 independent reflections measured, of which 7271 were considered observed with *I* > 2σ(*I*); max./min. residual electron density 1.098/-0.547 e/Å⁻³;

464 parameters, $R_1 [I > 2\sigma(I)] = 0.0672$; wR_2 (all data) = 0.1919. **4a**: $C_{38}H_{54}Cl_2N_3O_2Y$, orthorhombic, *Pbca* (no. 61); lattice constants $a = 19.8426(9)$, $b = 16.2320(8)$, $c = 24.170(2)$ Å, $V = 7784.7(7)$ Å³, $Z = 8$; $\mu(\text{Mo-K}\alpha) = 1.670$ mm⁻¹; $\theta_{\text{max.}} = 25.0$; 6864 ($R_{\text{int}} = 0.0713$) independent reflections measured, of which 12788 were considered observed with $I > 2\sigma(I)$; max./min. residual electron density 0.302/−0.385 e/Å⁻³; 422 parameters, $R_1 [I > 2\sigma(I)] = 0.0514$; wR_2 (all data) = 0.0906. **5**: $C_{47}H_{56}N_3Y$ (**5**-toluene), monoclinic, *P2₁/n* (no. 14); lattice constants $a = 10.6172(7)$, $b = 18.8255(12)$, $c = 20.5107(14)$ Å, $\beta = 93.443(5)^\circ$, $V = 4092.2(5)$ Å³, $Z = 4$; $\mu(\text{Mo-K}\alpha) = 1.460$ mm⁻¹; $\theta_{\text{max.}} = 25.0$; 7197 ($R_{\text{int}} = 0.1090$) independent reflections measured, of which 4869 were considered observed with $I > 2\sigma(I)$; max./min. residual electron density 1.216/−1.009 e/Å⁻³; 419 parameters, $R_1 [I > 2\sigma(I)] = 0.0850$; wR_2 (all data) = 0.2318. CCDC-668003 (**3**), -668004 (**4a**), and -668005 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) (“Schwerpunktprogramm Lanthanoidspezifische Funktionalitäten in Molekül und Material”) (SPP 1166) and the Fonds der Chemischen Industrie.

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Received: November 19, 2007

Published Online: February 5, 2008