# Lithium and Potassium Amides of Sterically Demanding Aminopyridines

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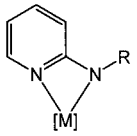
**Keywords:** Amido ligands / Coordination polymers / Lithium / N ligands / Potassium

The reaction of Grignard compounds of 1-bromo-2,4,6-diisopropylbenzene (**1**) or 1-bromo-2,6-dimethylbenzene (**2**), formed in situ, with 2,6-dibromopyridine in the presence of a catalytic amount of [(dme)$NiBr_2$] (dme = 1,2-dimethoxyethane) and tricyclohexylphosphane (1:2 ratio) leads to the corresponding monoarylated bromopyridines. These bromopyridines undergo Pd-catalysed aryl amination (Buchwald–Hartwig amination) with 2,6-diisopropylaniline giving rise to (2,6-diisopropylphenyl)[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]amine (Ap*H) and (2,6-diisopropylphenyl)[6-(2,6-dimethylphenyl)pyridin-2-yl]amine (Ap′H) (Ap = aminopyridinate). Deprotonation of Ap*H in diethyl ether using BuLi results (after workup in hexane) in a colourless crystalline material. X-ray structural analysis reveals it to be a monomeric three-coordinate lithium aminopyridinate. In toluene solution, an equilibrium between [$(Ap^*Li)_2$] (in excess at room temperature) and [$Ap^*Li(OEt_2)$] (prominent at low temperature) is observed. Reaction of Ap′H with BuLi in diethyl ether gives rise to [Ap*LiAp*$Li(OEt_2)$]. Deprotonation of Ap*H and Ap′H using KH leads to $[Ap^*K]_n$ and $[Ap'K]_\infty$, respectively. $[Ap'K]_\infty$ is a rare example of a crystalline organometallic polymer, as determined by X-ray analysis.

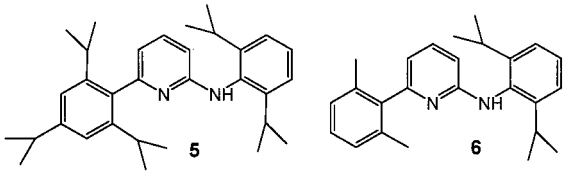

## Introduction

During the renaissance[1] of (amido)metal[2] chemistry, aminopyridinato ligands[3] have been used extensively to stabilise early transition metal and lanthanide ions (Scheme 1).



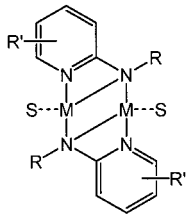

Scheme 1. Aminopyridinato ligand ([M] = early transition metal moiety; R = aryl, silyl or alkyl substituent)

The aminopyridinato ligands used thus far have exhibited a relatively low steric demand, especially in the plane perpendicular to the pyridine moiety. This characteristic has restricted the chemistry of the corresponding metal complexes so far, leading to the formation of "ate" species, for example.[3,4] In order to minimise this feature, we became interested in designing bulkier aminopyridinato ligands by the introduction of 2,6-alkylphenyl (alkyl = methyl or isopropyl) substituents at the amido N atom as well as the 6-position of the pyridine ring. Here, we report on the synthesis and structure of the lithium and potassium amides of Ap*H and Ap′H (Scheme 2).




Scheme 2. Ap*H (**5**) and Ap′H (**6**)

The syntheses and structures of alkali metal aminopyridinates were described first by Clegg and Snaith et al.[5] These compounds are remarkable examples of the diversity metal amides can show in terms of binding and aggregation modes.[6] One of the most common structures observed is a dimer containing two coordinated solvent molecules (Scheme 3).[7]




Scheme 3. The dimeric bis(solvent)-coordinated structure motive (M = alkali metal; R, R′ = alkyl, aryl or silyl substituent; S = mono- or bidentate donor solvent molecule)

Furthermore, structurally diverse alkali metal aminopyridinates have been found in aminopyridinato "ate" complexes[8] and in main group amides.[9]

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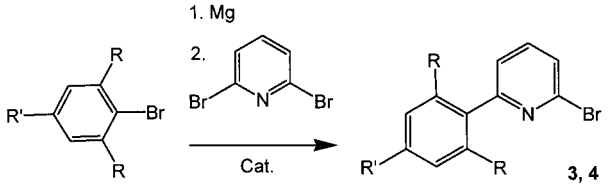
## Results and Discussion

### Synthesis of the Ligands

The reaction of in situ formed Grignard compounds of 1-bromo-2,4,6-diisopropylphenyl or 1-bromo-2,6-dimethylphenyl (**1**, **2**) with 2,6-dibromopyridine in the presence of a catalytic amount of [(dme)$NiBr_2$] and tricyclohexylphosphane (1:2 ratio) leads to the bromopyridines **3** and **4** (Scheme 4). The catalyst system was chosen on the basis of results of parallel screening experiments with various phosphane/group 10 metal combinations. The best combination also turned out to be optimal in terms of material availability (both components can be obtained commercially), selectivity and activity.[10]



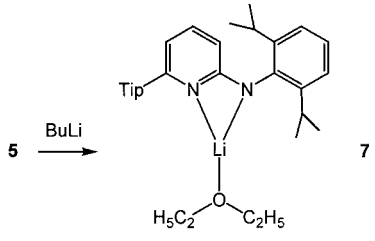

Scheme 4. Synthesis of **3** and **4** (**3** with R, R′ = *i*Pr; **4** with R = $CH_3$, R′ = H)

Compounds **3** and **4** undergo Pd-catalysed aryl amination (Buchwald–Hartwig amination) with 2,6-diisopropylaniline giving rise to **5** and **6**, respectively.[11] Despite the steric demands of the reactants, good yields have been observed for these two reactions.

### Synthesis, Structure and Dynamic Behaviour of the Aminopyridinates

Deprotonation of **5** in diethyl ether using BuLi gave rise (after workup in hexane) to a colourless crystalline material (compound **7**) in about 80% yield (Scheme 5). X-ray crystal structure analysis of **7** revealed it to be a monomeric three-coordinated lithium aminopyridinate in the solid state (Figure 1).

The nearly equivalent Li–N distances [Li–N1 1.987(5), Li–N2 2.020(5) Å] indicate a delocalised binding mode.[12] The coordination of the lithium ion is approximately trigonal-planar (sum of angles = 353°; deviation of Li out of the plane N1–N2–O = 0.26 Å). The steric demand of deprotonated **5** is large. The maximum atom–atom distances of deprotonated **5** in **7** are $a$ = 15 Å (Scheme 6) and, approximately perpendicular to it, $b$ = 8 Å (Scheme 6). Comparison of these distances with those of the bulky, $\eta^5$-coordinated Cp* ligand[13] (Cp* = pentamethylcyclopentadienyl), which has a distance of $a = b$ = 6.2 Å for both directions, indicates that deprotonated **5** should be effective for the protection of large metal ions.




Scheme 5. Synthesis of **7** (Tip = 2,4,6-triisopropylphenyl)

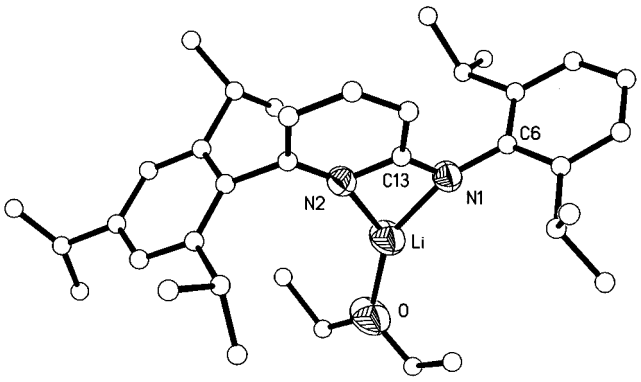
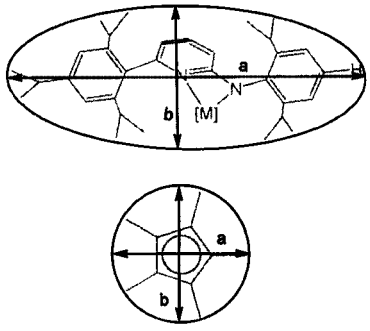



Figure 1. Molecular structure of **7** (ellipsoids correspond to the 50% probability level); selected bond lengths [Å] and angles [°]: Li–O 1.903(5), Li–N1 1.987(5), Li–N2 2.020(5); O–Li–N1 150.4(3), O–Li–N2 132.9(3), N1–Li–N2 69.28(16)




Scheme 6. Description of the steric demand of deprotonated **5**

$^1$H NMR spectroscopy of **7** at room temperature revealed it to be dynamic (Figure 2). One possibility is that the isopropyl groups of the aniline moiety and the pyridine substituent have restricted rotation due to the strained $\eta^2$-coordination mode [angle N1–Li–N2 = 69.28(16)°]. Alternatively, two different compounds (e.g. isomers) could exist in solution. Cooling of the NMR sample resulted in the formation of signals from a second compound (Figure 2). A characteristic of this "room-temperature compound" (**7a**) is that ether coordination is not observed as evidenced by the matching of the well-resolved ether signals to those of "free ether" in $C_7D_8$. In accordance with the structure of **8** (see discussion below) we propose a "solvent-free" dimeric structure for **7a** (Scheme 7)

Cooling down to −30 °C results in a change in the ratio of **7**/**7a** from 2:1 to 3:1. Precipitation of **7** starts at −50 °C (broad signals). Signal resolution occurs with the addition

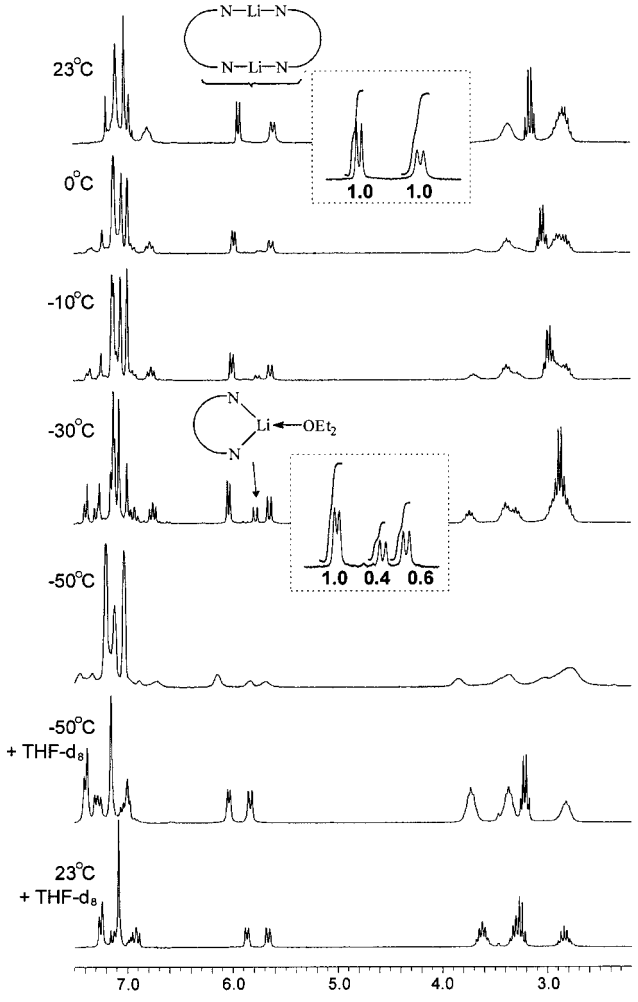
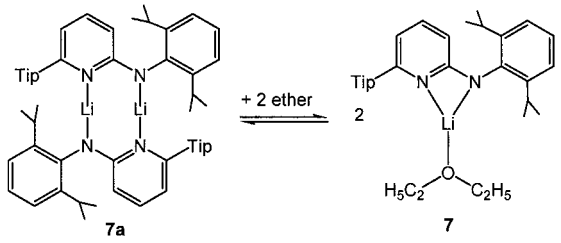


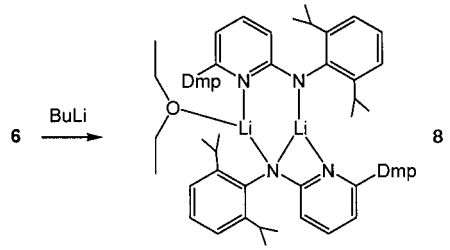

Figure 2. $^1$H NMR of **7** in $C_7D_8$ at different temperatures; the two last spectra show signals after addition of $[D_8]$THF




Scheme 7. Equilibrium between **7a** (dominant at room temperature) and **7** (low-temperature ether adduct)

of an excess of $[D_8]$THF at this temperature with the formation of a THF adduct analogous to **7**. This is indicated by a new, third signal set accompanied by the signals of "free ether". Raising the temperature to 25 °C causes only marginal changes of the signal set, which is in accordance with the expected temperature dependence. Furthermore, the signals observed for the pyridine protons suggest a delocalised binding mode in solution for both **7** and **7a**.[12]

Reaction of **6** with BuLi in diethyl ether gave (after work up in hexane) a crystalline material (**8**) in good yield (Scheme 8).




Scheme 8. Synthesis of **8** (Dmp = 2,6-dimethylphenyl)

X-ray crystal structure analysis of **8** revealed a dimeric structure in the solid state (Figure 3). Both Li atoms are coordinated in an almost trigonal-planar manner. The deviations of the lithium atoms out of the coordination planes are 0.43 Å (Li1) and 0.23 Å (Li2). One of the two Ap′ ligands acts as a bridge (bridging binding mode) with a significantly longer $N_{pyridine}-Li$ than $N_{amido}-Li$ bond, indicative of a localisation of the anionic charge of this ligand at the amido nitrogen atom. The second Ap′ ligand binds one of the lithium atoms in the strained $\eta^2$-binding mode [N4−Li2−N3 65.82(14)°] whereas the $N_{amido}$ lone pair acts as a bridge to the second lithium atom. The steric demands of this new ligand can be described as mentioned above for Ap* (Scheme 6). The maximum atom−atom distances are $a$ = 13 Å and, perpendicular to it, $b$ = 8 Å. NMR studies reveal a similar dimeric structure in toluene solution as found in the solid state.

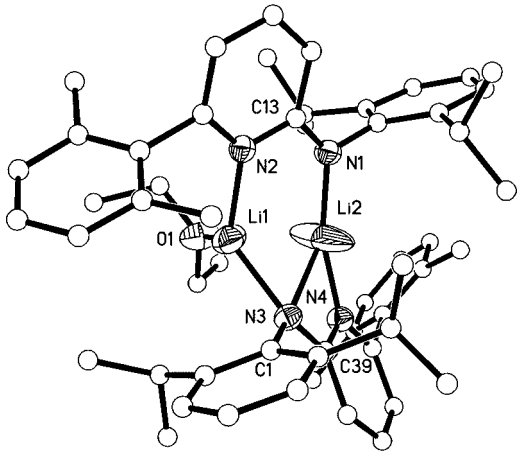
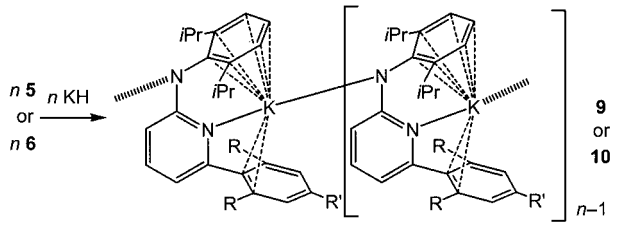



Figure 3. Molecular structure of **8** (ellipsoids correspond to the 50% probability level); selected bond lengths [A] and angles [°]: N4−Li2 1.922(4), N3−Li1 2.023(3), N3−Li2 2.271(5), N2−Li1 2.005(3), O1−Li1 2.013(4), N1−Li2 1.907(4); N2−Li1−O1 112.85(15), N2−Li1−N3 129.09(16), O1−Li1−N3 104.09(14), N1−Li2−N4 164.4(5), N1−Li2−N3 119.1(3), N4−Li2−N3 65.82(14)

The reactions of **5** and **6** with KH lead to crystalline **9** and **10**, respectively, according to Scheme 9. Crystals of **10**




Scheme 9. Synthesis of **9** (R, R′ = *i*Pr) and **10** (R = $CH_3$, R′ = H)

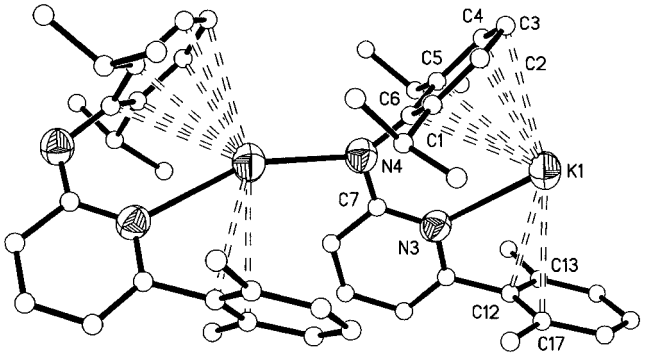
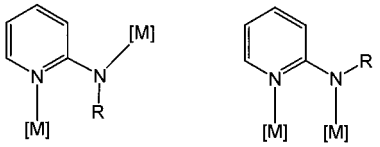



Figure 4. Part of the molecular structure of **10** (ellipsoids correspond to the 50% probability level); selected bond lengths [Å] and angles [°]: C1−K1 3.125(9), C2−K1 3.218(10), C3−K1 3.260(10), C4−K1 3.260(10), C5−K1 3.187(9), C6−K1 3.137(9), C12−K1 3.292(9), C17−K1 3.341(9), N3−K1 2.815(7), N4−K1 2.739(7); N4−K1−N3 157.2(2)

suitable for X-ray analysis were grown from diethyl ether (crystal structure: Figure 4).

The structure of **10** is best described as a coordinative one-dimensional polymer. (The amidoaryl groups appear on the same side in successive "monomer residues" − pseudo-isotactic.) The amido N atom coordinates one potassium atom and the pyridine function binds the next. The coordination thus can be described as a *transoid*-bridging binding mode (Scheme 10).




Scheme 10. *transoid*- (left) and *cisoid*-bridging binding (right) mode of aminopyridinato ligands ([M] metal moiety)

The binding situation observed for **10** might be helpful in explaining the mechanism of polymeric by-product formation found during aminopyridinato early transition metal complex syntheses.[3] The *transoid*-bridging binding mode formed by a two-coordinate potassium ion would be unstable without the π-coordination of the electron-rich phenyl substituents which coordinatively saturate the system. From an alternative viewpoint it could be said that the electron-rich arene functions of **5** and **6** are ideal for coordinatively saturating the potassium atoms and owing to geometric restrictions, the *transoid*-bridging binding mode is favoured. A detailed discussion of bond lengths and angles of **10** is precluded by the high disorder in the X-ray structure and grown-together twinned crystals. Despite the fact that a potassium−arene interaction is a common phenomenon, polymeric structures based on these are rarely observed[14] and homoleptic systems are almost unknown.[15]

## Conclusions

Grignard coupling and palladium-catalysed aryl amination are efficient methods for the preparation of sterically encumbered aminopyridines. The steric coverage of deprotonated aminopyridines (aminopyridinato ligands) approaches the nanometer range and the cover area is about 3.3 and 2.8 times larger for deprotonated **5** and deprotonated **6**, respectively, than for Cp*. The structural and dynamic behaviour of the lithium and potassium amides in solution differ significantly. Compound **10** is a rare example of an Ap complex exhibiting the *transoid*-bridging binding mode.

## Experimental Section

**General Procedures:** All reactions and manipulations with air-sensitive compounds were performed under dry argon, using standard Schlenk and drybox techniques. Solvents were distilled from sodium benzophenone ketyl. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried ($CaH_2$) and distilled prior to use. NMR spectra were obtained using either a Bruker ARX 250 or Bruker DRX 500 spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. *n*BuLi, KH, 1-bromo-2,4,6-triisopropylbenzene, 1-bromo-2,6-dimethylbenzene, $NiBr_2$(dme), tricyclohexylphosphane, 2,6-diisopropylaniline, 3-bis(diphenylphosphanyl)propane, sodium *tert*-butoxide, 1,2-dibromoethane and tris(dibenzylideneacetone)dipalladium(0) were purchased from commercial suppliers. X-ray crystal structure analyses were performed by using a STOE-IPDS I or II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,[16] SHELXL-97[17] and WinGX.[18] Crystallographic details are summarised in Table 1. CCDC-231858 (for **10**), -231859 (for **8**) and -231860 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk]

**Preparation of 1-MgBr-[2,4,6-(*i*Pr)$_3$C$_6$H$_2$] (1):** THF (30 mL) was added to magnesium turnings (0.94 g, 38.7 mmol). 1-Br-2,4,6-(*i*Pr)$_3$C$_6$H$_2$ (35.2 mmol, 9.97 g, 8.86 mL) was then added and the resulting suspension stirred and activated using 1,2-dibromoethane. An exothermic reaction took place and an ice bath was used to cool the reaction mixture when the reaction became too vigorous. After 1 h, the cooled reaction mixture was stirred at 50 °C overnight. The reaction mixture was filtered and the filtrate directly used in the preparation of **3**.

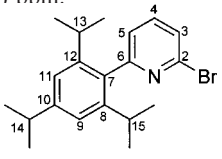
  

Table 1. Details of the X-ray crystal structure analyses

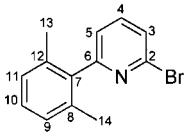
| | **7** | **8** | **10** |
|---|---|---|---|
| Crystal system | monoclinic | monoclinic | orthorhombic |
| Space group | $P2_1/c$ | $P2_1/n$ | *Pbca* |
| *a* [Å] | 18.235(4) | 10.780(5) | 12.669(1) |
| *b* [Å] | 19.007(4) | 17.869(5) | 37.704(5) |
| *c* [Å] | 10.013(2) | 25.205(5) | 18.694(1) |
| β [°] | 95.70(3) | 91.49(5) | – |
| *V* [Å$^3$] | 3453.2(5) | 4854(3) | 8929.6(15) |
| *Z* | 4 | 4 | 8 |
| Crystal size [mm] | 0.18 × 0.16 × 0.08 | 0.5 × 0.4 × 0.3 | 0.4 × 0.2 × 0.2 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.592 | 1.099 | 1.180 |
| μ [mm$^{-1}$] (Mo-$K_\alpha$) | 0.060 | 0.064 | 0.250 |
| *T* [K] | 193(2) | 193(2) | 193(2) |
| θ range [°] | 2.14–26.07 | 1.40–26.03 | 1.08–20.56 |
| No. of unique reflections | 6405 | 9521 | 4511 |
| No. of reflections observed [$I > 2\sigma(I)$] | 3076 | 7740 | 3477 |
| No. of parameters | 361 | 551 | 489 |
| $wR^2$ (all data) | 0.170 | 0.149 | 0.242 |
| *R* value [$I > 2\sigma(I)$] | 0.059 | 0.050 | 0.097 |

**Preparation of 1-MgBr-[2,6-(Me)$_2$C$_6$H$_3$] (2):** THF (30 mL) was added to magnesium turnings (0.94 g, 38.7 mmol). 1-Br-2,6-Me$_2$C$_6$H$_3$ (35.2 mmol, 6.50 g, 4.69 mL) was then added and the resulting suspension stirred. The reaction mixture was activated using 1,2-dibromoethane (approx. 0.4 mL). An exothermic reaction took place and an ice bath was used to cool the reaction mixture when the reaction became too vigorous. After 2 h, the cooled reaction mixture was stirred at 50 °C for 12 h. The reaction mixture was filtered and the filtrate directly used in the preparation of **4**.

**Preparation of 3:** 2,6-Dibromopyridine (7.91 g, 33.4 mmol), dioxane (35 mL), tricyclohexylphosphane [0.075 mmol, 1.5 mL (0.05 M in THF)] and [NiBr$_2$(dme)] (0.012 g, 0.0375 mmol) were added together in a Schlenk flask under argon; **1** was then added to the stirred suspension resulting in a beige precipitate. The reaction mixture was warmed to 50 °C and stirred for 72 h. Water and $CHCl_3$ were added and the resulting suspension transferred to a 2-L separating funnel. The organic phase was collected and the inorganic phase washed with $CHCl_3$ and extracted. The combined organic phases were washed with a saturated sodium chloride solution and dried with $Na_2SO_4$. The solvent was removed to afford a white precipitate. The precipitate was recrystallised from hot *n*-octane and washed with *n*-pentane (20 mL). Yield 7.05 g (58%). M.p. 232–233 °C $C_{20}H_{26}BrN$ (360.3): calcd. C 66.67, H 7.27, N 3.89; found C 67.56, H 7.48, N 3.78. $^1$H NMR (250 MHz, $CDCl_3$, 298 K): δ = 1.00–1.30 [m, 18 H, CH(C*H*$_3$)$_2$], 2.44 [sept, 2 H, C*H*(CH$_3$)$_2$], 2.88 [sept, 1 H, C*H*(CH$_3$)$_2$], 7.02 (s, 2 H, 9,11-H), 7.21 (d, 1 H, 3-H), 7.45 (d, 1 H, 5-H), 7.59 (br. dd, 1 H, 4-H) ppm. $^{13}$C NMR (250 MHz, $CDCl_3$, 298 K): δ = 23.85 [2 CH$_3$, (*C*H$_3$)$_2$CH], 24.06 [2 CH$_3$, (*C*H$_3$)$_2$CH], 24.17 [2 CH$_3$, (*C*H$_3$)$_2$CH], 30.41 [*C*H(CH$_3$)$_2$, C-13,-15], 34.44 [*C*H(CH$_3$)$_2$, C-14], 120.76 (CH, C-9,11), 123.94 (CH, C-3/5), 125.90 (CH, C-3/5), 134.88 (C, C-7), 137.93 (CH, C-4), 141.46 (C, C-2), 146.12 (C, C-8,12), 149.29 (C, C-10), 161.30 (C, C-6) ppm.



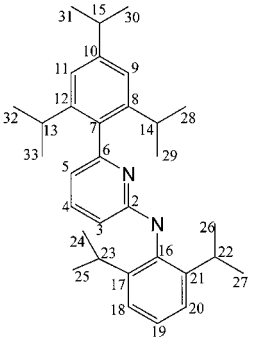

**Preparation of 4:** 2,6-Dibromopyridine (7.91 g, 33.4 mmol), dioxane (35 mL), tricyclohexylphosphane (0.075 mmol, 1.5 mL (0.05 M in THF) and [NiBr$_2$(dme)] (0.012 g, 0.0375 mmol) were combined in a Schlenk flask and cooled to 0 °C. Compound **2** was then slowly added dropwise to the cooled, stirred suspension. A beige precipitate resulted and the resulting mixture was then warmed to room temperature where a moderate exothermic reaction took place. Once the reaction mixture was cooled to room temperature, it was stirred and after 1 h heated to 50 °C for 72 h. Water (50 mL) and $CH_2Cl_2$ (50 mL) were added and the resulting suspension transferred to a 2-L separating funnel. The organic phase was collected and the inorganic phase washed with $CH_2Cl_2$ and extracted. The combined organic phases were washed with a saturated sodium chloride solution and dried with $Na_2SO_4$. The organic phase was concentrated to dryness under vacuum resulting in a red-orange oily product. The reddish oil was purified using silica chromatography (dichloromethane) and then crystallised from pentane at –20 °C. Yield 7.80 g (89%). M.p. 62–63 °C. $C_{13}H_{12}BrN$ (262.1): calcd. C 59.56, H 4.61, N 5.34; found C 60.30, H 4.74, N 5.28. $^1$H NMR (250 MHz, $CDCl_3$, 298 K): δ = 1.91 (s, 6 H, CH$_3$), 6.92 (s, 2 H, 9,11-H), 6.86–7.35 (m, 3 H, Ar, 3,5,10-H), 7.44 (br. dd, 1 H, 4-H) ppm. $^{13}$C NMR (250 MHz, $CDCl_3$, 298 K): δ = 20.17 (2 CH$_3$, C-13,14), 123.41 (CH, C-3/5), 126.03 (CH, C-3/5), 127.52 (CH, C-9,11), 128.21 (C, C-10), 135.64 (C, C-8,12), 138.91 (CH, C-4), 140.73 (C, C-2/7), 141.71 (C, C-2/7), 160.88 (C, C-6) ppm.



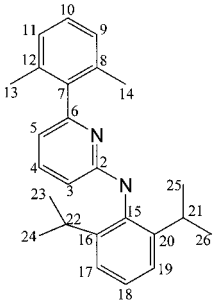

**Preparation of Ap*H (5):** In a drybox the solids **3** (4.00 g, 11.12 mmol), 1,3-bis(diphenylphosphanyl)propane (0.115 g, 0.279 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.126 g, 0.139 mmol) and sodium *tert*-butoxide (0.90 g, 3.10 mmol) were combined in a Schlenk flask. 2,6-Diisopropylaniline (11.12 mmol, 1.97 g, 2.10 mL) and toluene (40 mL) were added to the flask. The

resulting mixture was heated at 95 °C for 48 h. The reaction mixture was cooled to room temperature, and water (50 mL) and diethyl ether (50 mL) were added. The organic phase was extracted and the remaining inorganic phase was washed with diethyl ether (3 × 20 mL). The combined organic phases were washed with a saturated sodium chloride solution and the organic phase was dried with sodium sulfate. The solvent was removed under reduced pressure and the resulting red-orange solid was purified using silica chromatography (dichloromethane). Yield 5.00 g (89%). M.p. 162−163 °C. $C_{32}H_{44}N_2$ (456.7): calcd. C 84.16, H 9.71, N 6.13; found C 83.94, H 9.75, N 5.71. $^1$H NMR (250 MHz, $CDCl_3$, 298 K): δ = 1.00−1.27 [m, 30 H, CH(C$H_3$)$_2$], 2.70 [sept, 2 H, C$H$(CH$_3$)$_2$], 2.90 [sept, 1 H, C$H$(CH$_3$)$_2$], 3.25 [sept, 2 H, C$H$(CH$_3$)$_2$], 3.72 (br. s, 1 H, NH), 5.91 (br. d, $^1J$ = 8.30 Hz, 1 H, 3-H), 5.97 (br. s, 1 H, 4-H), 6.61 (br. d, $^1J$ = 7.2 Hz, 1 H, 5-H), 7.03−7.40 (m, Ar, 5 H, 9,11,18,19,20-H) ppm. $^{13}$C NMR (250 MHz, $CDCl_3$, 298 K): δ = 22.43 [$C$H(CH$_3$)$_2$, C-22,23], 23.95 [2 CH($C$H$_3$)$_2$, C-32,33/28,29/30,31], 24.14 [2 CH($C$H$_3$)$_2$, C-32,33/28,29/30,31], 24.51 [2 CH($C$H$_3$)$_2$, C-32,33/28,29/30,31], 28.47 [CH($C$H$_3$)$_2$, C-24,25,26,27], 30.33 [$C$H(CH$_3$)$_2$, C-13,14], 34.47 [$C$H(CH$_3$)$_2$, C-15], 103.64 (CH, C-3), 114.89 (CH, C-5), 120.74 (CH, C-9,11), 123.92 (CH, C-18,20), 127.90 (CH, C-19), 134.51 (C, C-16), 136.61 (C, C-7), 137.35 (CH, C-4), 146.01 (C, C-8,12), 148.01 (C, C-17,21), 148.45 (C, C-10), 158.54 (C, C-2/6), 159.08 (C, C-2/6) ppm.



**Preparation of Ap′H (6):** In a drybox the solids **4** (2.00 g, 7.63 mmol), 1,3-bis(diphenylphosphanyl)propane (0.115 g, 0.279 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.126 g, 0.139 mmol) and sodium *tert*-butoxide (0.83 g, 8.6 mmol) were combined in a Schlenk flask. 2,6-Diisopropylaniline (7.63 mmol, 1.35 g, 1.43 mL) and toluene (30 mL) were added to the flask. The resulting mixture was heated at 95 °C for 72 h. The reaction mixture was cooled to room temperature, and water (50 mL) and diethyl ether (50 mL) were added. The organic phase was extracted and the remaining inorganic phase washed with diethyl ether (3 × 20 mL). The combined organic phases were washed with a saturated sodium chloride solution and the organic phase was dried with sodium sulfate. The solvent was removed under reduced pressure and the resulting red solid was then purified using column chromatography (dichloromethane) and crystallised at −20 °C from pentane to afford a white crystalline material. Yield 2.10 g (77%). M.p. 106−107 °C. $C_{25}H_{30}N_2$ (358.5): calcd. C 83.75, H 8.43, N 7.81; found C 83.37, H 8.54, N 7.72. $^1$H NMR (250 MHz, $CDCl_3$, 298 K): δ = 0.88−1.20 [m, 12 H, CH(C$H_3$)$_2$], 2.09 (s, 6 H, C$H_3$), 3.25 [sept, 2 H, C$H$(CH$_3$)$_2$], 3.76 (v. br. s, 1 H, NH), 5.86 (br. d, $^1J$ = 8.30 Hz, 1 H, 3-H), 5.98 (br. s, 1 H, 4-H), 6.49 (br. d, $^1J$ = 7.2 Hz, 1 H, 5-H), 7.03−7.35 (m, Ar, 6 H, 9,10,11,17,18,19-H) ppm. $^{13}$C NMR (250 MHz, $CDCl_3$, 298 K): δ = 20.10 (CH$_3$, C-13,14), 23.75 [$C$H(CH$_3$)$_2$, C-21,22], 28.44 [CH($C$H$_3$)$_2$, C-23,24,25,26], 103.73 (CH, C-3), 114.08 (CH, C-5), 124.06 (CH, C-17,19), 127.56 (CH, C-9,11), 127.70 (CH, C-10/18), 128.00 (CH, C-10/18), 134.18 (C, C-15), 135.75 (C, C-8,12), 138.04 (CH, C-4), 140.74 (C, C-7), 148.01 (C, C-16,20), 158.43 (C, C-2/6), 159.37 (C, C-2/6) ppm.



**Preparation of 7:** *n*BuLi (1.38 mL, 1.6 M, 2.20 mmol) was slowly added to a stirred solution of Ap*H (1.00 g, 2.20 mmol) in diethyl ether (40 mL) at 0 °C. After complete addition, the mixture was stirred and warmed to room temperature (ca. 1 h). The reaction mixture was concentrated to dryness and hexane (20 mL) added. The solvent volume was reduced to ca. 2 mL in vacuo, and on standing colourless crystals of the title complex formed. Yield 0.96 g (82%). $C_{36}H_{53}LiN_2O$ (536.8): calcd. C 80.56, H 9.95, N 5.22; found C 79.85, H 9.66, N 4.90. $^1$H NMR (250 MHz, $C_7D_8$, 298 K): δ = 0.89 (br. m, 6 H, CH$_3$, OEt$_2$), 0.98−1.40 [m, 30 H, CH(C$H_3$)$_2$], 2.83 [br. m, 3 H, C$H$(CH$_3$)$_2$] 3.11 (m, 4 H, CH$_2$, OEt$_2$), 3.25 [br. m, 2 H, C$H$(CH$_3$)$_2$], 5.61 (br. d, $^1J$ = 8.05 Hz, 1 H, 3-H), 5.92 (d, $^1J$ = 6.90 Hz, 1 H, 5-H), 6.95 (br. dd, 1 H, 4-H), 6.98−7.32 (m, Ar, 5 H, 9,11,18,19,20-H) ppm. $^{13}$C NMR (250 MHz, $C_7D_8$, 298 K): δ = 14.99 (2 CH$_3$, Et$_2$O), 24.37 [$C$H(CH$_3$)$_2$, C-22,23], 24.47 [CH($C$H$_3$)$_2$, C-28,29,32,33], 24.88 [CH($C$H$_3$)$_2$, C-30,31], 28.42 [CH($C$H$_3$)$_2$, C-24,25,26,27], 30.66 [br., $C$H(CH$_3$)$_2$, C-13,14], 34.94 [br., $C$H($C$H$_3$)$_2$, C-15], 66.17 (2 CH$_2$, Et$_2$O), 107.15 (br. CH, C-3), 108.58 (br., CH, C-5), 120.76, 120.97, 124.47, 137.88, 145.18 (br., $C$H, C-4), 146.70, 148.52, 157.32 (br., C, C-6), 169.56 (br., C, C-2) ppm. $^1$H NMR (250 MHz, $C_7D_8$, 273 K): δ = 0.92 (m, 6 H, CH$_3$, OEt$_2$), 0.98−1.38 [m, 30 H, CH(C$H_3$)$_2$], 2.88 [v. br. m, 3 H, C$H$(CH$_3$)$_2$], 3.05 (m, 4 H, CH$_2$, OEt$_2$), 3.36 [v. br. m, 1 H, C$H$(CH$_3$)$_2$], 3.76 [v. br. m, 1 H, C$H$(CH$_3$)$_2$], 5.62 (br. d, $^1J$ = 8.50 Hz, 1 H, 3-H), 6.69 (v. br. d, 3-H*), 5.98 (d, $^1J$ = 6.80 Hz, 1 H, 5-H), 6.77 (br. dd, 1 H, 4-H), 6.90−7.32 (m, Ar, 5 H, 9,11,18,19,20-H) ppm. $^{13}$C NMR (250 MHz, $C_7D_8$, 273 K): δ = 14.45 (2 CH$_3$, Et$_2$O), 24.43 [$C$H(CH$_3$)$_2$, C-22,23], 24.62 [CH($C$H$_3$)$_2$, C-28,29,32,33], 24.97 [CH($C$H$_3$)$_2$, C-30,31], 28.36 [CH($C$H$_3$)$_2$, C-24,25,26,27], 30.67 [br., $C$H(CH$_3$)$_2$, C-13,14], 37.00 [br., $C$H($C$H$_3$)$_2$, C-15], 66.24 (2 CH$_2$, Et$_2$O), 107.29 (br., CH, C-3), 108.59 (br., CH, C-5), 120.43, 121.06, 123.63, 124.59, 137.25, 137.09, 144.63 (br., CH, C-4), 145.23, 146.64, 148.65, 157.36 (br., C, C-6), 169.51 (br., C, C-2) ppm. $^1$H NMR (250 MHz, $C_7D_8$, 243 K): δ = 0.86 (m, 6 H, CH$_3$, OEt$_2$), 0.95−1.40 [m, 30 H, CH(C$H_3$)$_2$], 2.89 [m, 3 H, C$H$(CH$_3$)$_2$], 3.25 [br. m, 1 H, C$H$(CH$_3$)$_2$], 3.39 (m, 4 H, CH$_2$, OEt$_2$), 3.70 [br. m, 1 H, C$H$(CH$_3$)$_2$], 5.64 (br. d, $^1J$ = 8.50 Hz, 3-H), 5.69 (v. br. d, $^1J$ = 8.30 Hz, 3-H*), 6.04 (d, $^1J$ = 6.90 Hz, 1 H, 5-H), 6.75 (br. dd, 1 H, 4-H), 6.98−7.40 (m, Ar, 5 H, 9,11,18,19,20-H) ppm. $^{13}$C NMR (250 MHz, $C_7D_8$, 243 K): δ = 14.44 (2 CH$_3$, Et$_2$O), 24.53 [$C$H(CH$_3$)$_2$, C-22,23], 24.64 [CH($C$H$_3$)$_2$, C-28,29,32,33], 24.88 [CH($C$H$_3$)$_2$, C-30,31], 28.46 [br., CH($C$H$_3$)$_2$, C-24,25,26,27], 30.86 [br., $C$H(CH$_3$)$_2$, C-13,14], 35.29 [$C$H($C$H$_3$)$_2$, C-15], 66.20 (2 CH$_2$, Et$_2$O), 104.72 (br., CH, C-3*), 104.98 (br., CH, C-5*), 107.29 (br., CH, C-3), 108.59 (br., CH, C-5), 120.53 (br.*), 121.06, 122.47 (br.*), 123.88 (br.*), 124.75, 137.37, 138.36 (*),

139.49 (*), 143.40 (CH, C-4), 144.79 (CH, C-4*), 145.28, 146.64 (*), 146.78 (br.), 147.96 (*), 148.60 (*), 148.84, 157.01 (C, C-6*), 157.47 (C, C-6), 169.64 (C, C-2), 169.92 (C, C-2*) ppm. $^1$H NMR (250 MHz, $C_7D_8$, 223 K): δ = 0.69 (v. br. s, 6 H, $CH_3$, $OEt_2$), 0.95−1.50 [v. br. m, 30 H, CH(C$H_3$)$_2$], 2.77 [v. br. m, 3 H, C$H$(CH$_3$)$_2$], 3.15 [v. br. m, 1 H, C$H$(CH$_3$)$_2$], 3.36 (v. br. m, 4 H, $CH_2$, $OEt_2$), 3.79 [v. br. m, 1 H, C$H$(CH$_3$)$_2$], 5.64 (v. br. d, 3-H), 5.69 (v. br. d, 3-H*), 6.14 (v. br. s, 1 H, 5-H), 6.85 (v. br. s, 1 H, 4-H), 6.98−7.45 (v. br. m, Ar, 5 H, 9,11,18,19,20-H) ppm. $^1$H NMR (250 MHz, $C_7D_8$ {addition of two drops of $C_4D_8O$} 298 K): δ = 1.07 (m, 6 H, $CH_3$, $OEt_2$), 1.20−1.40 [m, 30 H, CH(C$H_3$)$_2$], 2.84 [m, 1 H, C$H$(CH$_3$)$_2$], 3.23 (m, 4 H, $CH_2$, $OEt_2$), 3.35 [m, 2 H, C$H$(CH$_3$)$_2$], 3.65 [m, 2 H, C$H$(CH$_3$)$_2$], 5.66 (br. d, $^1J$ = 8.60 Hz, 1 H, 3-H), 5.86 (d, $^1J$ = 6.90 Hz, 1 H, 5-H), 6.91 (br. dd, 1 H, 4-H), 6.98−7.26 (m, Ar, 5 H, 9,11,18,19,20-H) ppm. $^{13}$C NMR (250 MHz, $C_7D_8$ {addition of two drops of $C_4D_8O$}, 298 K): δ = 15.45 (2 $CH_3$, $Et_2O$), 23.99 [$C$H(CH$_3$)$_2$, C-22*,23*], 24.31 [CH($C$H$_3$)$_2$, C-28*,29*,32*,33*], 24.94 [CH($C$H$_3$)$_2$, C-30*,31*], 28.20 [CH($C$H$_3$)$_2$, C-24*,25*,26*,27*], 30.38 [$C$H(CH$_3$)$_2$, C-13*,14*], 34.88 [$C$H($C$H$_3$)$_2$, C-15*], 65.91 (2 $CH_2$, $Et_2O$), 104.71 (CH, C-3*/5*), 104.82 (CH, C-3*/5*), 120.20 (CH, C-9*,11*), 121.40 (CH, C-19*), 123.44 (CH, C-18*,20*), 136.44 (CH, C-4*), 140.00 (C, C-10*), 143.10 (C, C-8*,12*), 146.61 (C, C-17*,21*), 147.40 (C, C-7*), 149.75 (C, C-16*), 156.95 (C, C-6*), 169.10 (C, C-2*) ppm. $^1$H NMR (250 MHz, $C_7D_8$ {addition of two drops of $C_4D_8O$}, 223 K): δ = 1.06 (m, 6 H, $CH_3$, $OEt_2$), 1.16−1.33 [m, 30 H, CH(C$H_3$)$_2$], 2.84 [br. m, 1 H, C$H$(CH$_3$)$_2$], 3.26 (m, 4 H, $CH_2$, $OEt_2$), 3.35 [br. m, 2 H, C$H$(CH$_3$)$_2$], 3.65 [br. m, 2 H, C$H$(CH$_3$)$_2$], 5.67 (d, $^1J$ = 8.60 Hz, 1 H, 3-H), 5.87 (d, $^1J$ = 6.90 Hz, 1 H, 5-H), 6.91 (br. dd, 1 H, 4-H), 6.98−7.26 (m, Ar, 5 H, 9,11,18,19,20-H) ppm. $^{13}$C NMR (250 MHz, $C_7D_8$ {addition of two drops of $C_4D_8O$}, 223 K): δ = 15.46 (2 $CH_3$, $Et_2O$), 23.99 [$C$H(CH$_3$)$_2$, C-22*,23*], 24.18 [CH($C$H$_3$)$_2$, C-28*,29*,32*,33*], 24.94 [CH($C$H$_3$)$_2$, C-30*,31*], 28.20 [CH($C$H$_3$)$_2$, C-24*,25*,26*,27*], 30.38 [$C$H(CH$_3$)$_2$, C-13*,14*], 34.88 [$C$H($C$H$_3$)$_2$, C-15*], 65.91 (2 $CH_2$, $Et_2O$), 104.18 (CH, C-3*,5*), 120.12 (CH, C-9*,11*), 121.21 (CH, C-19*), 123.36 (CH*, C-18,20*), 136.56 (CH, C-4*), 139.67 (C, C-10*), 142.74 (C, C-8*,12*), 146.24 (C, C-17*,21*), 147.25 (C, C-7*), 149.39 (C, C-16*), 156.78 (C, C-6*), 168.40 (C, C-2*) ppm. * = monomeric isomer.

**Preparation of 8:** *n*BuLi (0.63 mL, 1.6 M, 1.00 mmol) was slowly added to a stirred solution of Ap′H (0.36 g, 1.00 mmol) in diethyl ether (40 mL) at 0 °C. After complete addition, the mixture was stirred and warmed to room temperature (ca. 1 h). The reaction mixture was reduced to dryness and hexane (20 mL) added. The solvent volume was reduced to ca. 10 mL in vacuo, and on standing colourless crystals of the title complex formed. Yield 0.35 g (88%). $C_{54}H_{68}Li_2N_4O$ (803.0): calcd. C 80.76, H 8.53, N 6.98; found C 79.18, H 8.20, N 6.95; the slightly too low C value is due to removal of the coordinated ether during the drying process. $^1$H NMR (500 MHz, $C_7D_8$, 298 K): δ = 0.99 (br. m, 6 H, $CH_3$, $OEt_2$), 0.92−1.10 [m, 24 H, CH(C$H_3$)$_2$], 1.92 (s, 12 H, $CH_3$), 3.19 (m, 4 H, $CH_2$, $OEt_2$), 3.27 [sept, 4 H, C$H$(CH$_3$)$_2$], 5.58 (br. d, $^1J$ = 8.05 Hz, 2 H, 3-H), 5.76 (d, $^1J$ = 6.90 Hz, 2 H, 5-H), 6.83 (br. dd, 2 H, 4-H), 6.98−7.10 (m, Ar, 12 H, 9,10,11,17,18,19-H) ppm. $^{13}$C NMR (250 MHz, $C_7D_8$, 298 K): δ = 15.32 (2 $CH_3$, $Et_2O$), 20.08 (2 $CH_3$, C-13,14), 24.18 [2 $C$H$_3$, CH($C$H$_3$)$_2$, C-23,25/24,26], 24.58 [2 $CH_3$, CH($C$H$_3$)$_2$, C-23,25/24,26], 28.44 [2 $CH_3$, CH($C$H$_3$)$_2$, C-23,25/24,26], 65.88 (2 $CH_2$, $Et_2O$), 106.19 (CH, C-3/5), 107.46 (CH, C-3/5), 124.90 (CH, C-17,19), 127.30−128.40 (CH, C-9,10,11,18), 135.78 (C, C-8,12), 138.53 (CH, C-4), 141.13 (C, C-7), 143.86 (C, C-15), 144.89 (C, C-16,20), 157.16 (C, C-6), 169.19 (C, C-2) ppm.

**Preparation of 9:** Diethyl ether (50 mL) was added to the solids KH (0.09 g 2.19 mmol) and Ap*H (1.00 g, 2.19 mmol) and the reaction mixture stirred for 12 h. The mixture was filtered and the filtrate concentrated to dryness under vacuum. The resulting off-white residue was washed with hexane (30 mL) and the resulting white precipitate dried under vacuum. Yield 0.86 g (79%). $[C_{32}H_{43}KN_2]_n$: calcd. C 77.68, H 8.76, N 5.66; found C 77.39, H 8.94, N 5.34. $^1$H NMR (250 MHz, $C_6D_6$, 298 K): δ = 1.10−1.30 [m, 30 H, CH(C$H_3$)$_2$], 2.85 [sept, 1 H, C$H$(CH$_3$)$_2$], 3.18 [sept, 2 H, C$H$(CH$_3$)$_2$], 3.33 [sept, 2 H, C$H$(CH$_3$)$_2$], 5.76 (v. br. d, 1 H, 3-H), 5.92 (br. d, $^1J$ = 6.80 Hz, 1 H, 5-H), 6.93 (br. dd, 1 H, 4-H), 6.90−7.21 (m, Ar, 5 H, 9,11,18,19,20-H) ppm. $^{13}$C NMR (250 MHz, $C_6D_6$, 298 K): δ = 24.15 [CH($C$H$_3$)$_2$, C-28,29,32,33], 24.46 [CH($C$H$_3$)$_2$, C-30,31], 25.11 [$C$H(CH$_3$)$_2$, C-22,23], 28.38 [$C$H(CH$_3$)$_2$, C-13,14], 30.44 [CH($C$H$_3$)$_2$, C-24,25,26,27], 34.93 [$C$H(CH$_3$)$_2$, C-15], 106.58 (CH, C-3), 120.73 (CH, C-9,11), 121.93 (CH, C-5), 123.82 (CH, C-18,20), 125.84 (CH, C-19), 136.26 (CH, C-4), 139.96 (C, C-7), 143.49 (C, C-16), 146.54 (C, C-8,12), 146.77 (C, C-10), 147.99 (C, C-17,21), 154.05 (C, C-6), 157.81 (C, C-2) ppm.

**Preparation of 10:** Diethyl ether (50 mL) was added to the solids KH (0.09 g 2.19 mmol) and Ap′H (1.00 g, 2.19 mmol) and the reaction mixture stirred for 12 h. The mixture was filtered and the filtrate concentrated to dryness under vacuum. The resulting off-white residue was washed with hexane (30 mL) and the resulting white precipitate dried under vacuum. Yield 0.86 (79%). Crystals of **6** were grown from diethyl ether. $C_{25}H_{29}KN_2$ (396.6): calcd. C 75.71, H 7.37, N 7.06; found C 75.45, H 7.63, N 6.63. $^1$H NMR (250 MHz, $C_6D_6$, 298 K): δ = 1.11−1.16 [m, 12 H, CH(C$H_3$)$_2$], 2.25 (s, 6 H, $CH_3$), 3.32 [m, 2 H, C$H$(CH$_3$)$_2$], 5.85 (v. br. d, 1 H, 3-H), 6.23 (br. d, 1 H, 5-H), 7.00−7.45 (m, Ar, 7 H, 4,9,10,11,17,18,19-H) ppm. $^{13}$C NMR (250 MHz, $C_6D_6$, 298 K): δ = 20.47 ($CH_3$, C-13,14), 24.11 [$C$H(CH$_3$)$_2$, C-23,24,25,26], 28.53 [CH, $C$H(CH$_3$)$_2$, C-21,22], 121.42 (1 CH, C-3/4/5), 123.09, 123.97 (CH, C-17,19), 124.40, 127.26 (CH, C-9,11), 135.65, 135.83 (C, C-8,12), 137.07 (1 CH, C-3/4/5), 150.07 (C, C-16,20) ppm. $^1$H NMR (250 MHz, $C_4D_8O$, 298 K): δ = 1.08−1.12 [m, 12 H, CH(C$H_3$)$_2$], 2.20 (s, 6 H, $CH_3$), 3.39 [m, 2 H, C$H$(CH$_3$)$_2$], 5.34 (v. br. d, 1 H, 3-H), 5.51 (br. d, 1 H, 5-H), 6.76 (br. dd, 1 H, 4-H), 6.95−7.02 (m, Ar, 6 H, 9,10,11,17,18,19-H) ppm. $^{13}$C NMR (250 MHz, $C_4D_8O$, 298 K): δ = 20.45 ($CH_3$, C-13,14), 24.51 [$C$H(CH$_3$)$_2$, C-23,24,25,26], 28.90 [CH, $C$H(CH$_3$)$_2$, C-21,22,], 101.92 (v. br., 1 CH, C-3/4/5), 104.21 (1 CH, C-3/4/5), 119.77 (v. br., 1 CH, C-3/4/5), 122.58 (CH, C-17,19), 126.29 (CH, C-10), 126.79 (CH, C-9,11), 135.03 (CH, C-18), 135.50 (C, C-8,12), 142.82 (v. br., C, C-16,20), 144.82 (br., C, C-7), 157.74 (C, C-6), 165.71 (v. br., C, C-2) ppm; C-15 signal could not be observed.

## Acknowledgments

We thank Wolfgang Milius for his support in the X-ray laboratory and Elena Klimkina for her help with the assignment of the NMR spectroscopic data. Financial support from the Alexander von Humboldt Stiftung (N. M. S.), the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm 1166 "Lanthanoidspezifische Funktionalitäten in Molekül und Material") and the Fonds der Chemischen Industrie is gratefully acknowledged.

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Received March 22, 2004
Early View Article
Published Online June 1, 2004

  