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(Amidomethyl)pyridine zirconium and hafnium complexes: Synthesis and structural characterization

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In memoriam Professor F. Albert Cotton

Abstract

A series of 2-formyl and 2-acetylpyridines was condensed with 2,6-diisopropylaniline to yield the corresponding imines. Their reaction with sodium borohydride gave the respective *N*-arylaminomethylpyridines. Treatment of the *N*-arylformimino- or -acetiminopyridines with trimethylaluminum followed by hydrolysis furnished a series of the respective substituted *N*-arylaminoethylpyridine derivatives. Their reaction with tetrabenzylzirconium or tetrakis(dimethylamido)zirconium or -hafnium gave the corresponding (chelate ligand)MX_3 systems in a variety of cases. Some of these gave very active ethene polymerization catalysts upon activation with methylalumoxane. Six of the neutral aminoalkylpyridines were characterized by X-ray diffraction, as were eight of the zirconium or hafnium complexes and two aluminum chelate complex systems.

Keywords: Chelate ligands; Pyridine derivatives; Iminopyridines; Amido ligands; Zirconium; Hafnium

1. Introduction

Use of the 2,6-bisiminopyridine ligand family has been of great importance for the development of the "post-metallocene" homogeneous Ziegler–Natta olefin polymerization catalysts [1]. Such complexes (**1**) of the late transition metals, notably of iron, cobalt or palladium, have been valuable substrates for the generation of very active catalysts [2,3].

The adoption of such ligand types for applications in related early metal complex chemistry and catalysis has resulted in the change and conversion of such systems into mono- or dianionic derivatives, such as e.g. **2** or **3** (and many related systems) [4,5]. It turned out that the special coordination features of the Group 4 metals did not necessarily require the presence of tridentate stabilizing and controlling ligands but that bidentate analogues served their purpose as well quite efficiently.

In the recent years a series of patents has appeared describing the use of the bidentate zirconium complexes **4** and **5** and derivatives thereof, mostly generated in situ, for use in polymerization catalysis [6,7]. This prompted us to now disclose and describe our work carried out in the recent years on the synthesis of a series of closely related complexes and their detailed spectroscopic and structural characterization.

2. Results and discussion

2.1. Syntheses of the chelate ligands

The syntheses of three series of 2-aminomethylpyridines were carried out. They all featured the 2,6-diisopropylphenyl substituent at the nitrogen atom. The synthetic series started from the respective substituted 2-formyl- or 2-acetylpyridine precursors, which were first converted to the respective imines by condensation with 2,6-diisopropylaniline followed by either reduction ($NaBH_4$) or reductive

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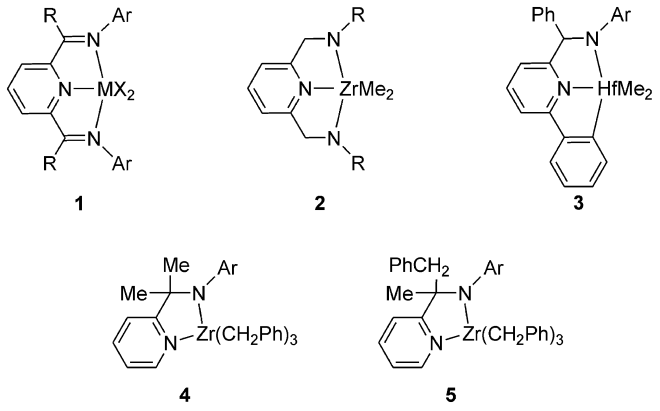
methylation ($AlMe_3$), both followed by hydrolysis. The carbonylpyridine precursors were prepared by variations or adaptations of literature procedures (see Scheme 1).

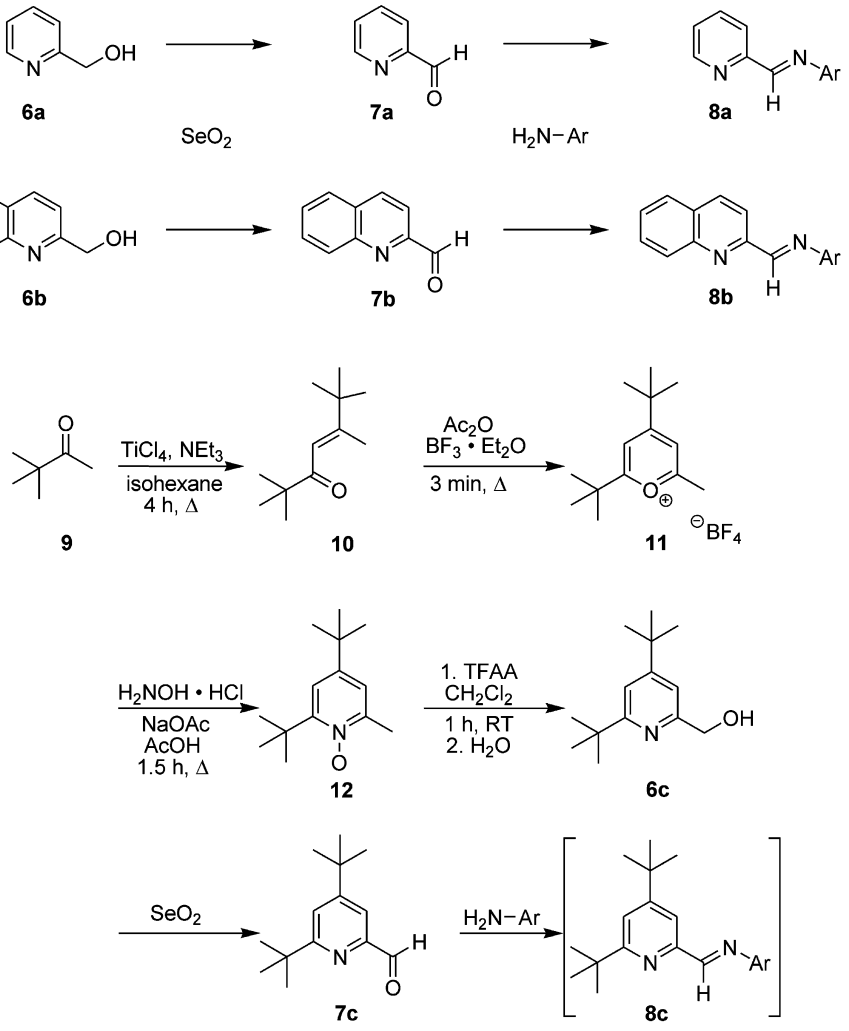


Scheme 1.

2-Formylpyridine (**7a**) was prepared by SeO_2 oxidation of commercially available 2-hydroxymethylpyridine (**6a**). Similarly, 2-formylquinoline (**7b**) was obtained by the analogous oxidation (SeO_2) of the 2-hydroxymethylquinoline precursor (**6b**) (see Scheme 2). The synthesis of 2-formyl-4,6-di-*tert*-butylpyridine (**7c**) was effected by a pyrylium route (see Scheme 2) starting from methyl-*tert*-butylketone (**9**) [8,9].

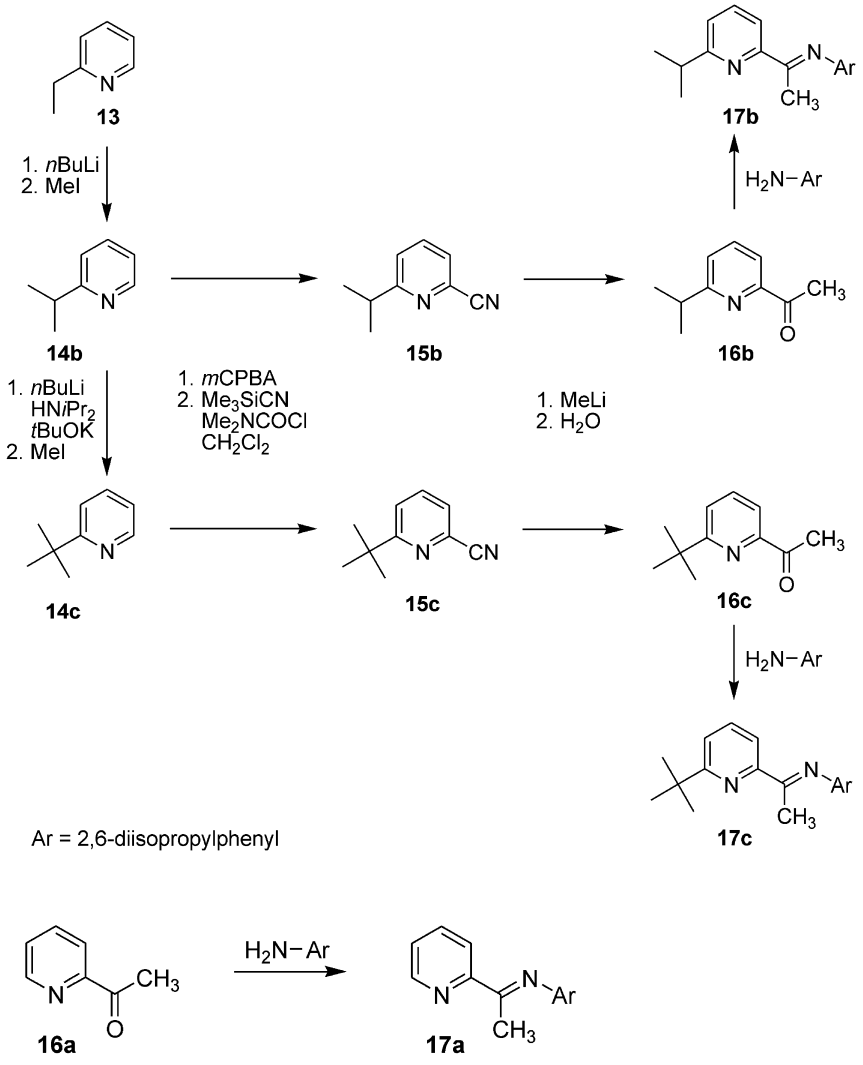
Two 2-acetylpyridines (**16b** and **16c**) were prepared by means of variants of the Reissert–Henze reaction (see Scheme 3) [10–12].

The 2-formylpyridines (**7a–c**) and 2-acetylpyridines (**16a–c**) were converted to the respective aldimines (**8a–c**) or ketimines (**17a–c**) by condensation with 2,6-diisopropylaniline (see Schemes 2 and 3) [13–16]. From these precursors (**8a–c**, **17a–c**) we have prepared three series of substituted (*N*-arylaminomethyl)pyridines that were then subsequently used for the synthesis of the respective κ^2N,N'-chelate ligand Group 4 metal complexes (see below).



Ar = 2,6-diisopropylphenyl.

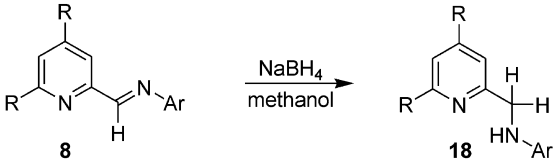
Scheme 2.



Scheme 3.

The imines **8a** and **8c**, respectively, were reduced with sodium borohydride to yield the 2-(N-2,6-diisopropylphenyl)aminomethylpyridines **18a** [14c] and **18c**, respectively (see Scheme 4).

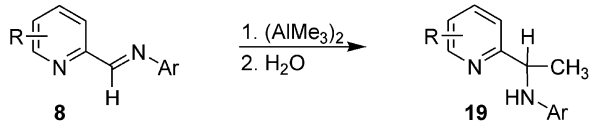
The aldimino pyridines (**8a** and **8b**) were treated with trimethylaluminum (ca. 2 equiv.) in toluene, to obtain the chiral (aminoethyl)pyridine products **19a** and **19b** each >90% yield after hydrolysis and chromatographic workup (see Scheme 5).



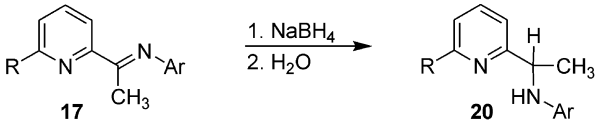
Ar = 2,6-diisopropylphenyl, R = H (**a**), R = *t*-Bu (**c**).

Scheme 4.

Two related examples (**20b** and **20c**, see Scheme 5) were prepared starting from the respective 6-substituted ketiminopyridine precursors (**17b** and **17c**). Their treatment with sodium borohydride eventually furnished the corresponding



R = H (**a**), benzo[*e*] (**b**).



R = *i*-Pr (**b**), *t*-Bu (**c**).

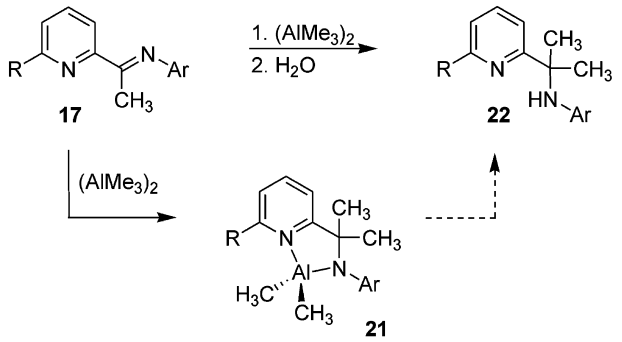
Ar = 2,6-diisopropylphenyl.

Scheme 5.

6-alkyl-2-(*N*-arylaminoethyl)pyridine products in good yield.

Eventually, the nucleophilic methylation route was also employed for the conversion of the ketimines **17**(**a**–**c**) to the respective 1-methylaminoethylpyridine products (**22a**–**c**). Thus, treatment of **17a** with a twofold excess of trimethylaluminum in toluene furnished **22a** [17] after hydrolysis and chromatographic purification. Analogously, the substituted ketimines **17b** and **17c**, respectively, were also converted to the corresponding 1-methylaminoethylpyridine products (**22b** and **22c**) by $AlMe_3$ treatment followed by hydrolysis.

In all three examples in separate experiments we were able to actually isolate the corresponding chelate aluminum compounds (**21a**–**c**) when the reactions and workup procedures were carried out under strictly anhydrous conditions. In these examples the amido(dimethyl)Al complexes were isolated as yellow solids in 75–85% yield. Two examples (**21b** and **21c**) were characterized by X-ray diffraction (see Scheme 6).



R = H (**a**), *i*-Pr (**b**), *t*-Bu (**c**); Ar = 2,6-diisopropylphenyl.

Scheme 6.

2.2. Structural characterization of the aminoalkylpyridine systems

Structures of examples of the iminopyridine systems were recently reported by us [11]. In the course of this present study we have now characterized a total of six examples of the various substituted aminomethyl- and aminoethylpyridines by X-ray diffraction (see Figs. 1–3 and Table 1).

Compound **18a** features an undistorted pyridine ring. The aminomethyl substituent is bonded at the α-position. The corresponding C2(pyridine)–C7(substituent) bond length is in the typical $C(sp^2)$–$C(sp^3)$ range [18]. The C7–N8 vector (1.456(2) Å) is markedly rotated out of the pyridine plane ($\theta = -74.3(2)°$). The C7–N8–C9 angle at the secondary amine nitrogen amounts to 118.4(1)°. This general conformational arrangement results in a relatively large spatial separation of the N–H function from the pyridine H-bridge acceptor (calculated N1–H(N8) distance: intra 2.849 Å; N1#–H(N8): inter 2.327 Å). The bulky 2,6-diisopropylphenyl ring is rotated almost normal to the C7–N8–C9 plane, as expected (see Fig. 1 and Table 1).

In contrast, the aminomethyl substituent in the related compound **18c**, which bears the more bulky 4,6-di-*tert*-butylpyridine moiety, is rotated close to in-plane with the pyridine plane ($\theta = 28.9(2)°$). Here we assume the presence of a marked hydrogen bonding interaction between the pyridine nitrogen and the amine N–H group (calculated N1–H(N8) distance: 2.251 Å).

The chiral *N*-arylaminoethylpyridine pair of compounds (**19a** and **20c**) shows structural and conformational features that are similar to those of **18a** (see Table 1 and Fig. 2), only that the substituent C7–N9 vector is slightly less rotated from the plane in **19a** (θ: 66.4(2)°) and **20c** (θ: −57.6(2)°) than it is observed for the parent compound **18a** (θ: −74.3(2)°).

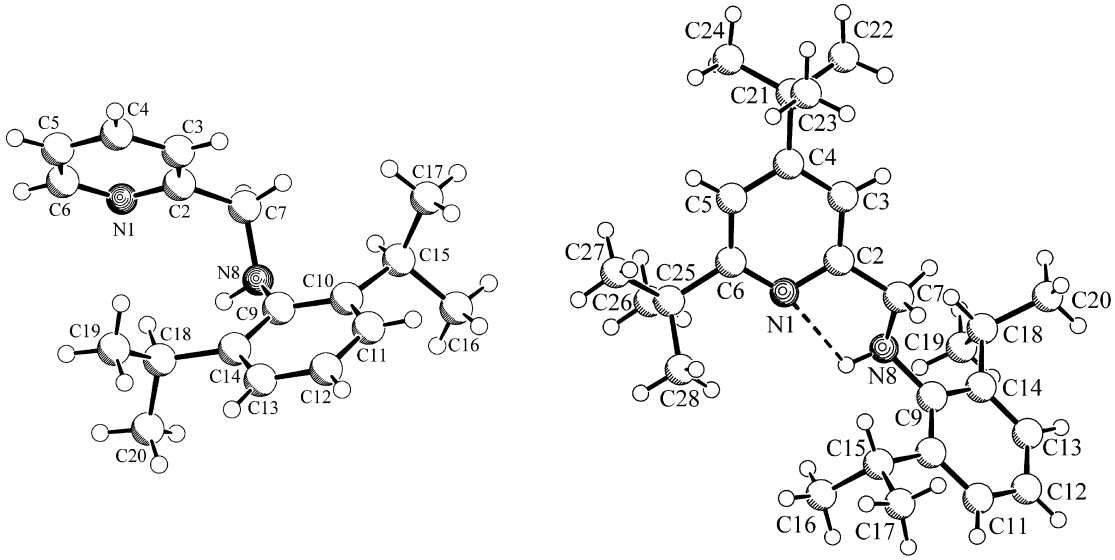


Fig. 1. Views of the molecular structures of the *N*-arylaminomethylpyridine derivatives **18a** (left) and **18c** (right).

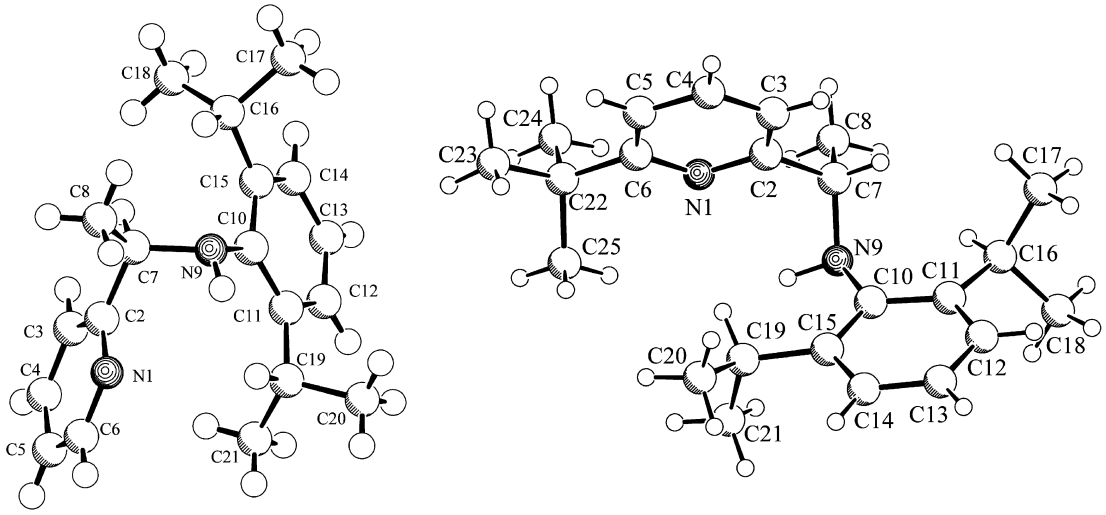


Fig. 2. Molecular structures of the compounds **19a** (left) and **20c** (right).

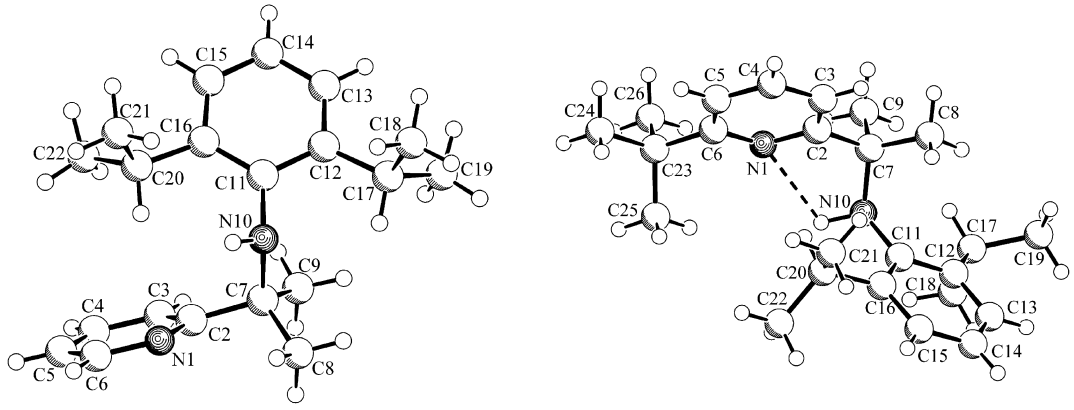


Fig. 3. Projections of the molecular structures of the compounds **22a** (left) and **22c** (right).

Table 1
Selected structural parameters of aminoalkylpyridine derivatives[a]

Compound	C2–C7	C7–N8	N1–H(N8)	N1–C2–C7–N8	C2–C7–N8–C9	C7–N8–C9–C10/C14
18a	1.508(2)	1.456(2)	2.849[c] 2.327[b]	−74.3(1)	−73.8(2)	−79.7(2)
18c	1.514(2)	1.456(2)	2.251[c]	28.9(2)	−163.3(1)	−87.6(2)
Compound	C2–C7	C7–N9	N1–H(N9)	N1–C2–C7–N9	C2–C7–N9–C10	C7–N9–C10–C11/C15
19a	1.509(2)	1.462(2)	2.651[c] 2.675[b]	66.4(2)	78.0(2)	75.0(2)
20c	1.523(3)	1.472(3)	2.509[c]	−57.6(2)	−84.0(2)	−73.0(3)
Compound	C2–C7	C7–N10	N1–H(N10)	N1–C2–C7–N10	C2–C7–N10–C11	C7–N10–C11–C12/C16
22a	1.533(2)	1.503(2)	2.524[c]	−66.6(1)	−91.0(1)	−91.1(1)
22c	1.537(3)	1.498(2)	2.294[c]	−50.3(2)	−103.0(2)	−93.6(2)

[a] Bond lengths in Å, dihedral angles in °.
[b] N1#–H(N8)$_{inter}$.
[c] N1–H(N8)$_{intra}$.

Compound **22a** shows a core geometry that is very similar to that of **18a** (see Table 1 and Fig. 3), only the 2,6-diisopropylphenyl substituents here are oriented almost ideally normal to the adjacent plane. The rotation of the C7–N vector is very similar to the observed value in **20c**. In the more bulky system **22c** the C7–N10 vector is rotated closer to the

pyridine plane (θ: −50.3(2)°) which brings the attached N–H hydrogen into μ-H bonding distance to the pyridine nitrogen atom (calculated N1–H(N10) distance: 2.294 Å).

The chelate amido aluminum complex intermediates (**21b** and **21c**) used for the preparation of the geminal dimethyl compounds **22** were also characterized by X-ray diffraction (see Fig. 4 and Table 2). The *tert*-butyl-substituted complex **21c** features an almost perfectly planar five-membered chelate ring. The amide nitrogen to aluminum bond is short (1.825(1) Å), the pyridine nitrogen donor to Al acceptor linkage is markedly longer (2.047(1) Å) [19]. The Al center in **21c** features a pseudo-tetrahedral coordination geometry with a small endocyclic N1–Al–N10 angle (84.83(4)°) and a much larger exocyclic C27–Al–C28 angle (114.49(7)°). The bulky 2,6-diisopropylphenyl ring is found rotated perpendicular to the mean central complex plane (θ(C7–N10–C11–C12): 92.5(1)°). Complex **21b** features a very similar structure, but here the central chelate unit deviates slightly from planarity (θ(N1–C2–C7–N10): −12.8(2)°).

2.3. Formation of the zirconium and hafnium complexes

We have synthesized a series of zirconium and hafnium complexes from these substituted aminomethyl- and aminoethylpyridine chelate ligands by in situ deprotonation [20]. For that purpose the respective neutral ligand systems were treated with tetrabenzylzirconium [21] or tetrakis(dimethylamido)zirconium or -hafnium [22]. As can be seen from the compilation shown in Scheme 7, these reactions were sensitive to steric hindrance. From the very hindered substrates (gem. dimethyl plus 6-iso-propyl or 6-*tert*-butyl) we could not obtain the respective products under our typical reaction conditions. With less sterically encumbered systems these reactions usually went smoothly and furnished the respective metal complexes in fair yields (for details see the Section 3).

Here are two typical examples: the reaction of the 1-methyl-aminoethylpyridine (**22a**) with $Zr(NMe_2)_4$ gave complex **24e** in close to 80% yield. The ^{1}H NMR spectrum of complex **24e** (see Fig. 5 top) features a 6H intensity singlet of the "bridging" pyridyl–$C(CH_3)_2$–[N]– moiety (δ 1.39) and a pair of diastereotopic iso-propyl methyl resonances at δ 1.22, 1.16, each of 6H intensity, with a single corresponding –C*H*Me_2 septet at δ 3.51 (2H). Complex **24e** features only one broad ^{1}H NMR resonance of the [Zr]–$N(CH_3)_2$ methyl protons a δ 2.63 (18H), indicating rapid positional equilibration of the NMe_2 ligands at Zr on the NMR time scale. In some of the prepared complexes this rotational/pseudorotational equilibration process is sufficiently slowed down or even frozen on the NMR time scale at room temperature, so that the corresponding symmetry related appearance of the NMR spectra can actually be observed at ambient conditions.

A typical example is complex **24d**. It was isolated from the reaction of the aminoethylquinoline ligand (**19b**) with $Zr(NMe_2)_4$ in 78% yield as a yellow solid. In the ambient temperature ^{1}H NMR spectrum (see Fig. 5 bottom) it features a total of nine separate signals of the Ar–methine hydrogens at the quinoline nucleus and of the 2,6-diisopropylphenyl substituent. The inherent chirality of the systems has resulted in the diastereotopic splitting of the non-equivalent pairs of iso-propyl substituents to give a total of four $CH(CH_3)_2$ methyl doublets and two $CH(CH_3)_2$ methine

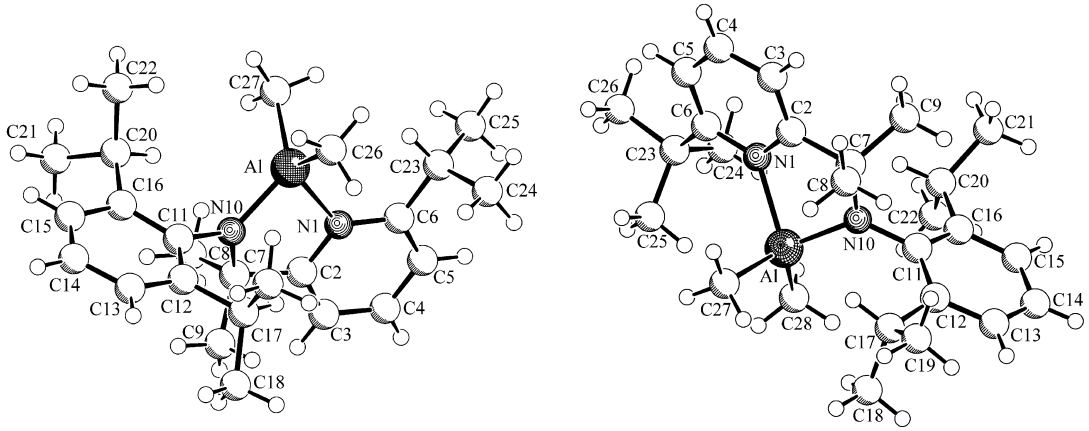
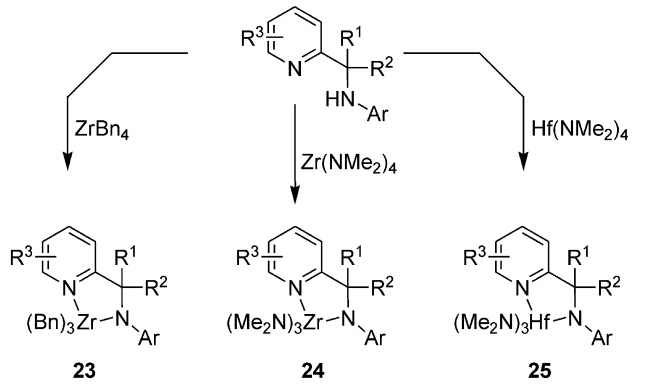


Fig. 4. Views of the molecular structures of the Al–chelate complexes **21b** (left) and **21c** (right).

Table 2
Selected structural parameters of the chelate aluminum complexes **21**(**b**, **c**)[a]

Compound	N1–Al	N10–Al	N1–Al–N10	Me–Al–Me	N1–C2–C7–N10	C2–C7–N10–C11
21b	1.996(1)	1.829(1)	85.25(5)	113.71(8)	−12.8(2)	−163.3(1)
21c	2.047(1)	1.825(1)	84.83(4)	114.49(7)	0.5(2)	160.7(1)

[a] Bond lengths in Å, angles and dihedral angles in °.



23 **24** **25**

R^3, R^2, R^1			
H, H, H	**23a**	-	**25a**
4,6-^{t}Bu, H, H	n.o.	**24b**	**25b**
H, H, Me	-	**24c**	**25c**
benzo[e], H, Me	-	**24d**	-
H, Me, Me	**23e**	**24e**	-
6-^{i}Pr, Me, H	-	**24f**	**25f**
6-^{t}Bu, Me, H	n.o.	n.o.	-
6-^{i}Pr, Me, Me	n.o.	n.o.	-
6-^{t}Bu, Me, Me	n.o.	n.o.	-

Scheme 7.

septets. Most remarkably, we observe three separate methyl singlets of the three $-NMe_2$ ligands at zirconium, each of 6H intensity.

2.4. Structural characterization of the zirconium and hafnium chelate complexes

A series of seven of the κ^2N, N'-chelate tris(dimethylamido) Group 4 metal complexes were characterized by X-ray diffraction (four Zr, three Hf complexes), and in addition the structure of the tribenzyl Zr–chelate complex **23e** was determined. All these complexes are of the same overall structural type. The overall structural characteristics of this general class of compounds shall be illustrated with the example of the parent hafnium complex **25a** (see Fig. 6 and Table 3).

Complex **25a** features a distorted trigonal–bipyramidal coordination geometry at the central hafnium atom. The pyridine nitrogen (N1) and one of the $-NMe_2$ ligand nitrogen atoms (N24) are found in trans-apical positions (angle N1–Hf–N24: 170.8(1)°). The remaining pair of $-NMe_2$ ligands and the chelate ligand amide nitrogen center form the basal arrangement. All three Hf–N(Me) bonds are short (2.048(4)–2.050(5) Å), the Hf–N(chelate) bonds are markedly longer (Hf–N8: 2.110(3) Å, Hf–N1: 2.380(3) Å). The N1–Hf–N8 angle, i.e. the cone angle of the chelate ligand, amounts to 70.6(1)°, which is markedly smaller than the adjacent angles (N21–Hf–N27: 113.2(2)°, N21–Hf–N8: 122.9(1)°, N24–Hf–N8: 101.2(1)°, N21–Hf–N24: 96.9(2)°, N27–Hf–N24: 98.1(1)°, N27–Hf–N8: 117.1(1)°, N27–Hf–N1: 89.5(1)°, N21–Hf–N1: 84.7(2)°). The plane

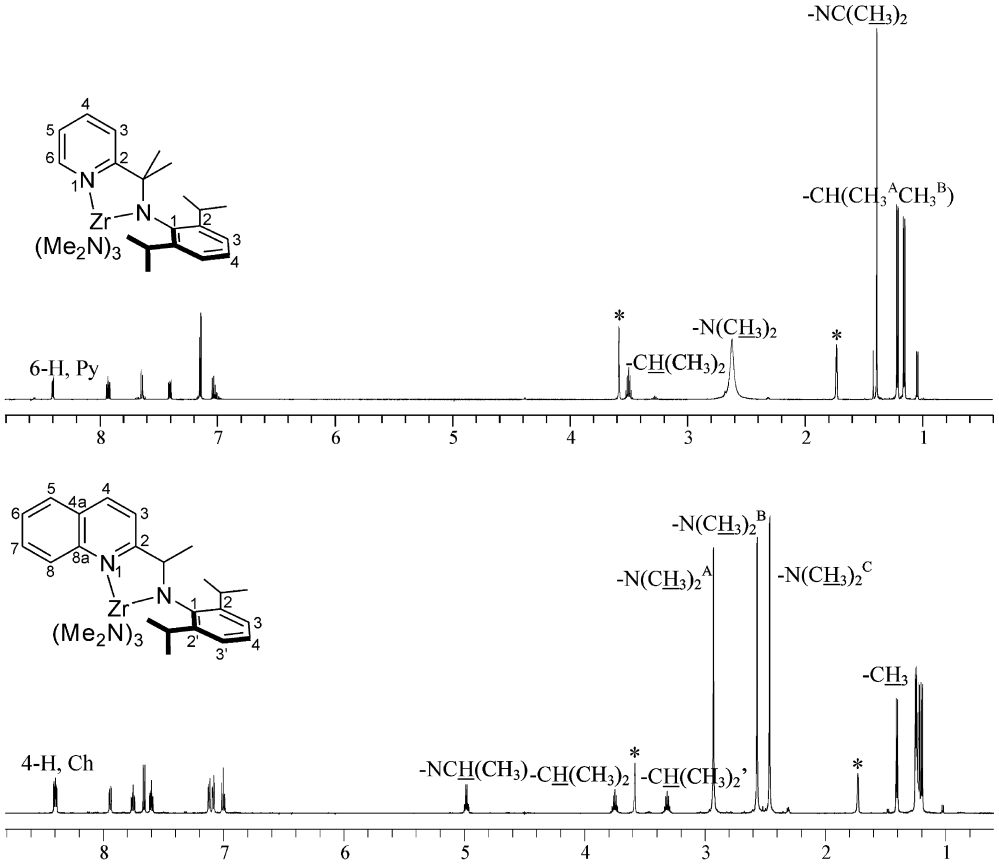


Fig. 5. ^{1}H NMR spectra of the complexes **24e** (top) and **24d** (bottom), 600 MHz, 298K, d_8-THF (*).

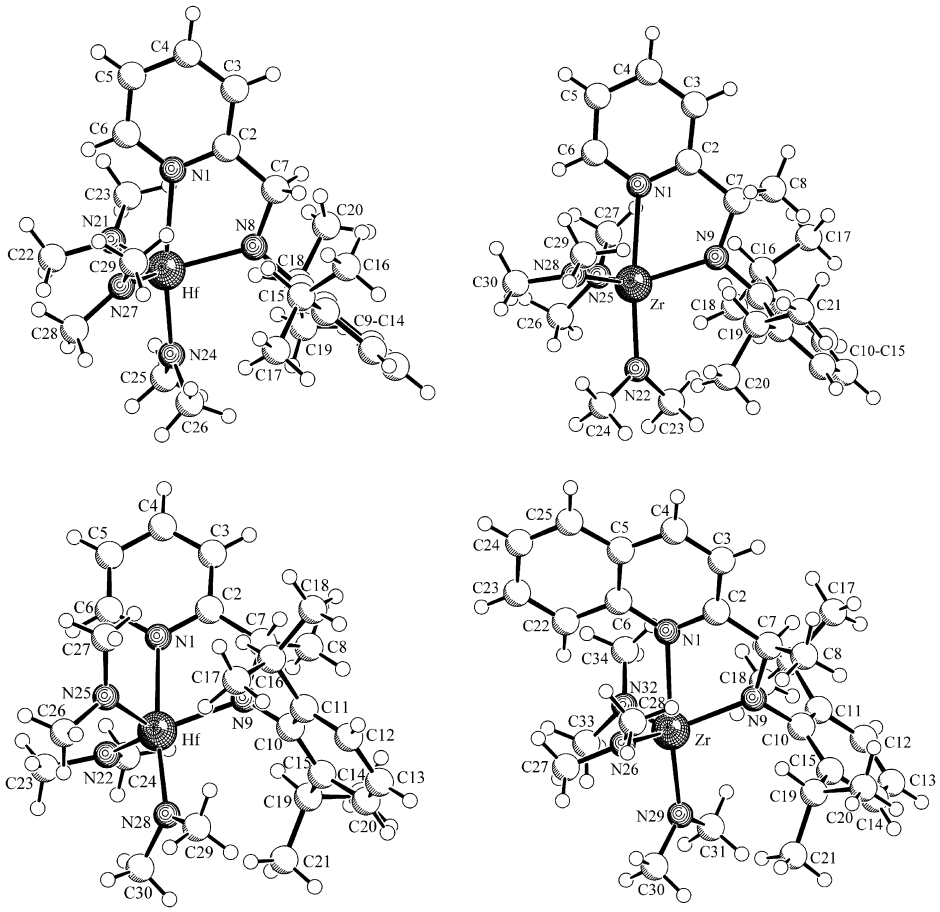


Fig. 6. Views of the molecular structures of the complexes **25a** (top left), **24c** (top right), **25c** (bottom left) and **24d** (bottom right).

Table 3
Selected structural parameters of the chelate zirconium and hafnium complexes **23**–**25**[a]

Compound	M	N1–M	N8/N9/N10–M	N1–M–N8/N9/N10	N_{ax}–M–N1	$\sum N_{eq}$–M–N_{eq}
25a	Hf	2.380(3)	2.110(3)	70.6(1)	170.8(1)	353.2
24c	Zr	2.407(2)	2.128(2)	69.0(1)	172.2(1)	351.0
25c	Hf	2.380(3)	2.115(3)	69.8(1)	172.2(1)	351.8
24d	Zr	2.462(2)	2.107(2)	70.3(1)	174.7(1)	351.2
24e	Zr	2.413(2)	2.135(1)	68.9(1)	173.1(1)	349.6
24f	Zr	2.479(2)	2.116(2)	71.0(1)	174.5(1)	354.8
25f	Hf	2.452(3)	2.091(3)	71.7(1)	174.2(1)	354.9
23e	Zr	2.382(2)	2.048(3)	72.2(1)	172.4(1)[b]	348.6

[a] Bond lengths in Å, angles in °.
[b] C31–M–N1.

of the 2,6-diisopropylphenyl substituent is oriented almost normal to the Hf-chelate plane (dihedral angle C7–N8–C9–C10: 75.7(5)°). Complex **24d** as well as the pair of Zr/Hf-complexes **24c** and **25c**, which all exhibit an *N*-aryl-aminoethylpyridine chelate ligand, show very similar structural features (see Fig. 6 and Table 3).

The X-ray crystal structure analysis of the tribenzyl zirconium chelate complex **23e** revealed a closely related structural framework. The complex geometry is distorted trigonal–bipyramidal. The pyridine nitrogen atom (N1–Zr: 2.382(2) Å) and one of the benzylic σ-carbon ligands (Zr–C31: 2.305(3) Å) occupy the apical positions (angle N1–Zr–C31: 172.4(1)°). Again, the Zr–N(amide) bond is short (Zr–N10: 2.048(3) Å). The remaining Zr–C(benzyl) bond lengths amount to 2.281(4) Å (Zr–C41) and 2.302(3) Å (Zr–C51), respectively. The corresponding C41–Zr–C51 angle was found at 118.8(2)°. Again, the bulky 2,6-diisopropylphenyl substituent at the amide nitrogen center is found rotated almost perpendicular to the mean chelate ligand plane (dihedral angle C7–N10–C11–C12: 90.9(3)°). The angle between the C–methyl vectors at C7 amounts to 107.8(3)° (C8–C7–C9). Fig. 7 shows a

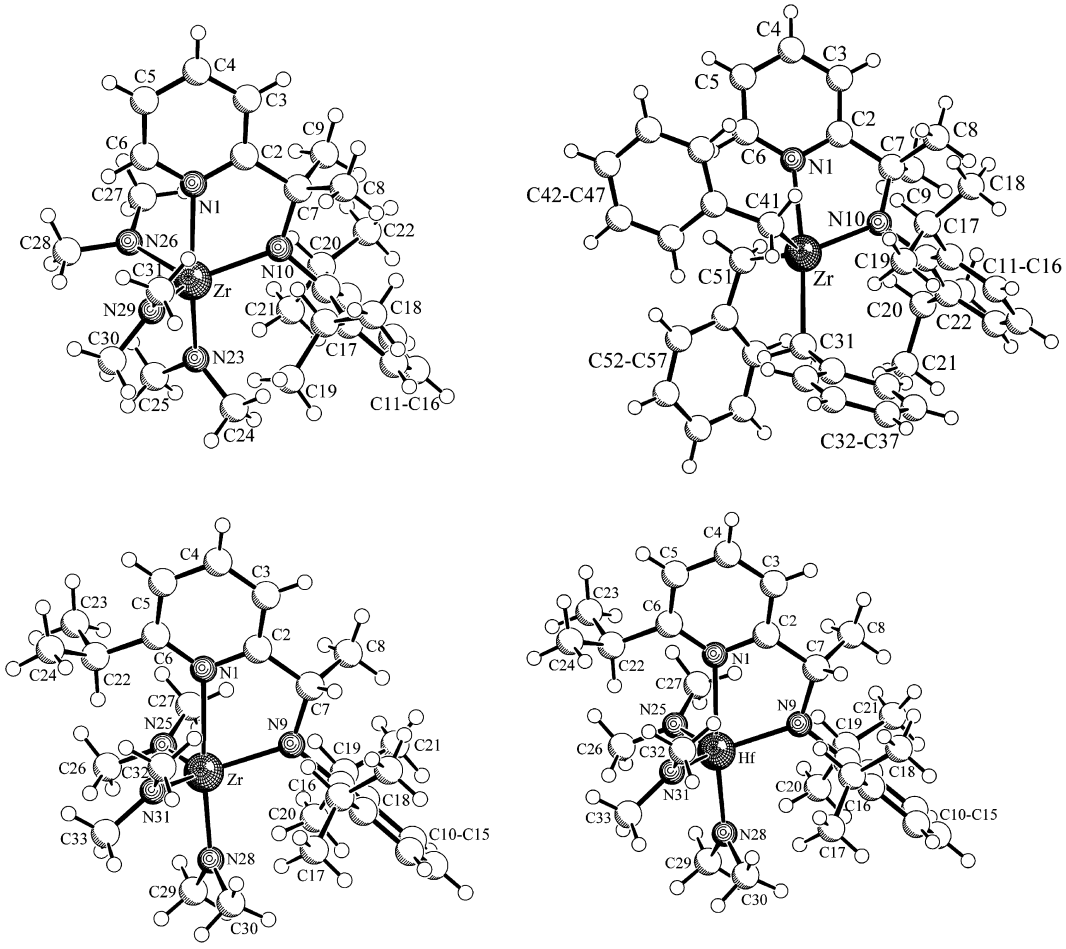


Fig. 7. Projections of the molecular structures of the complexes **24e** (top left), **23e** (top right), **24f** (bottom left) and **25f** (bottom right).

view of complex **23e** (top right) along with its corresponding tris(dimethylamido)Zr(chelate ligand) analogues **24e** (top left) and a pair of the 2-isopropyl-substituted complexes **24f** and **25f**.

2.5. Polymerization reactions

We have carried out a series of preliminary polymerisation experiments to examine the potential of using the chelate complexes **23**, **24** or **25** as components of active homogeneous Ziegler–Natta catalysts for olefin polymerization. The catalysts were generated in situ by treatment with a large excess of methylalumoxane in toluene (Al/Zr > 1000) [23]. Ethylene polymerization experiments were carried out at 25 °C with 2 bar ethene. The results of selected experiments are listed in Table 4. In all these cases linear polyethylene was formed with a rather low molecular weight as judged from the observed melting points and the ^{1}H NMR spectra.

From the obtained data some trends have become apparent. Both the (chelate ligand)Zr(benzyl)$_3$ systems tested (**23a** and **23e**) give very active ethene polymerization catalysts. The latter is even in the high activity region [2]. Apparently the introduction of some steric bulk in the bridging C atom inside the chelate is advantageous with regard to activity. The (chelate ligand)Zr(NMe$_2$)$_3$ systems (**24**) were found to give markedly less active ethene polymerization catalysts (see Table 4). Again, the series of examples investigated has revealed that the introduction of some steric bulk at the α-carbon position inside the chelate ring markedly and steadily increased the catalyst activity. However, the presence of a bulky alkyl substituent (e.g., ^{i}Pr, ^{t}Bu) in the pyridine 6-position diminished the

Table 4
Ethene polymerization with the (chelate ligand)ZrX$_3$ (**23**/**24**)/MAO catalysts[a]

Compound	X	mol[Zr] (×10^5)	*t* (min)	g PE	act[b]	T_m
23a	CH_2Ph	2.5	17	5.47	438	122
23e	CH_2Ph	0.63	15	6.00	1905	121
24b	NMe_2	2.5	15	–	–	–
24c	NMe_2	2.5	15	0.53	42	120
24d	NMe_2	2.5	15	0.96	77	122
24e	NMe_2	2.5	15	2.13	170	122
24f	NMe_2	2.5	17	0.87	70	117

[a] Selected examples.
[b] g PE/(mmol[Zr] h bar).

catalyst activity or shut if off completely. The corresponding hafnium complexes gave no active ethene polymerization reactions under the applied reaction conditions.

2.6. Some conclusions

We have carried out a series of syntheses of substituted 2-iminopyridine derivatives that were subsequently converted to the corresponding aminomethyl- or aminoethylpyridines by either reduction with sodium borohydride or by treatment with trimethylaluminum followed by hydrolysis. Many of these ligand systems could be converted to the corresponding (chelate ligand)M(IV)X_3 complexes of the Group 4 metals zirconium or hafnium employing in situ NH deprotonation using either tetrabenzylzirconium or tetrakis(dimethylamido)Zr or -Hf reagents. Limitations of this attractive organometallic synthetic route became apparent when a combination of very bulky substituents at both α-positions of the pyridine nucleus in the neutral organic substrates prevented the formation of the respective metal complexes by this method. The complexes were characterized by X-ray diffraction. Especially the (chelate ligand)Zr(benzyl)$_3$ systems gave very active homogeneous Ziegler–Natta catalysts upon activation with methylalumoxane.

3. Experimental section

All reactions involving air or moisture sensitive compounds were carried out under inert atmosphere using *Schlenk*-type glassware or in a glovebox. Solvents were dried and distilled prior to use. The following instruments were used for physical characterization of the compounds: Melting points, DSC 2010 TA-instruments; elemental analyses, Foss-Heraeus CHNO-Rapid; MS, Micromass Quattro LC-Z electrospray mass spectrometer; NMR, Bruker AC 200 P (^{1}H: 200 MHz, ^{13}C: 50 MHz), ARX 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) or Varian UNITY plus NMR spectrometer (^{1}H: 600 MHz, ^{13}C: 151 MHz). X-ray crystal structure determinations: Data sets were collected with Nonius KappaCCD diffractometers, in case of Mo-radiation a rotating anode generator was used. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, 1997, *276*, 307–326), absorption correction SORTAV (R.H. Blessing, *Acta Cryst.* 1995, *A51*, 33–37; R.H. Blessing, *J. Appl. Cryst.* 1997, *30*, 421–426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* 2003, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* 1990, *A46*, 467–473), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

Tetrakis(dimethylamido)zirconium [22a], tetrakis(dimethylamido)hafnium [22b], tetrabenzylzirconium [21], **8a** [13], **8b** [14c], **12** [8], **6c** and **7c** ([9], Supporting Information), and **17a–c** [11,13–15] were synthesized according to procedures reported in the literature.

General procedure: preparation of aminoalkylpyridines by imine reduction with $NaBH_4$ (18a, c; 20b, c). At 0 °C $NaBH_4$ was added slowly to a stirred solution of the respective imines in methanol. The reaction mixture was warmed to room temperature and then refluxed for 3–4 days. The progress of the reaction was monitored by TLC. The reaction mixture was allowed to cool to room temperature and then quenched with sodium carbonate solution. The organic phase was separated and the aqueous phase was extracted with dichloromethane again. The organic solutions were combined and dried with $MgSO_4$. Then the solvent was removed and finally the crude product was purified by column chromatography on silica gel.

Preparation of (18a) [13c]. The reaction of **8a** (7.16 g, 26.9 mmol) with $NaBH_4$ (15.3 g, 403 mmol) in methanol (400 ml) yielded after column chromatography (SiO_2; pentane/methanol/chloroform/triethylamine, 100:1:1:1) the product as a white solid (5.92 g, 82%). Crystallization from methanol gave crystals suitable for X-ray diffraction. M.p. 50 °C (DSC). Anal. Calc. for $C_{18}H_{24}N_2$: C, 80.55; H, 9.01; N, 10.44; Found: C, 80.24; H, 8.98; N, 10.51%. MS–ESI (*m*/*z*, ES+): 269.2 $[M+H]^+$, 291.2 $[M+Na]^+$.^{1}H NMR (499.8 MHz, $CDCl_3$, 298 K): $\delta = 8.62$ (m, 1H, 6-H^{Py}), 7.68 (td, $^3J = 7.7$ Hz, $^4J = 1.4$ Hz, 1H, 4-H^{Py}), 7.33 (d, $^3J = 7.7$ Hz, 1H, 3-H^{Py}), 7.23 (m, 1H, 5-H^{Py}), 7.11 (m, 2H, 3-H^{Ar}), 7.07 (m, 1H, 4-H^{Ar}), 4.22 (s, 2H, NCH_2), 3.35 (sept, $^3J = 6.9$ Hz, 2H, CH(CH$_3$)$_2$), 1.22 (d, $^3J = 6.9$ Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 298 K): $\delta = 158.5$ (C2^{Py}), 148.8 (C6^{Py}), 142.7 (C2^{Ar}), 142.6 (C1^{Ar}), 137.0 (C4^{Py}), 124.2 (C4^{Ar}), 123.7 (C3^{Ar}), 122.4 (C5^{Py}), 122.2 (C3^{Py}), 56.4 (NCH_2), 27.7 (CH(CH$_3$)$_2$), 24.2 (CH(CH_3)$_2$). X-ray crystal structure analysis for **18a**: formula $C_{18}H_{24}N_2$, $M = 268.39$, colorless crystal $0.40 \times 0.20 \times 0.15$ mm, $a = 8.373(1)$, $b = 9.703(1)$, $c = 10.899(1)$ Å, $\alpha = 75.09(1)$, $\beta = 83.01(1)$, $\gamma = 70.09(3)°$, $V = 803.95(15)$ Å^3, $\rho_{calc} = 1.109$ g cm^{-3}, $\mu = 0.493$ mm^{-1}, empirical absorption correction ($0.827 \leqslant T \leqslant 0.930$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 1.54178$ Å, $T = 223$ K, ω and ϕ scans, 8489 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 2726 independent ($R_{int} = 0.029$) and 2549 observed reflections [$I \geqslant 2\sigma(I)$], 188 refined parameters, $R = 0.047$, $wR^2 = 0.125$, max. residual electron density 0.18 (−0.14) e Å^{-3}, hydrogen atom at N8 from difference fourier maps and refined free, other calculated and refined as riding atoms.

Preparation of 18c. A mixture of 4,6-di-*tert*-butylpyridine-2-carbaldehyde (**7c**) (1.25 g, 5.69 mmol) and 2,6-diisopropylaniline (1.11 g, 6.25 mmol) in methanol (30 ml) was refluxed for several hours. The progress of the condensation reaction was followed by NMR spectroscopy. Then $NaBH_4$ (21.5 g, 0.57 mol) was added and the mixture was refluxed for another 2 days. After general workup and purification by column chromatography on silica gel (pentane/ethyl acetate/triethylamine, 80:1:1) the product was obtained as a white solid (1.30 g, 60%). Crystallization from methanol gave crystals suitable for X-ray diffraction. M.p. 56 °C (DSC). Anal. Calc. for $C_{26}H_{40}N_2$: C, 82.05; H,

10.59; N, 7.36; Found: C, 81.75; H, 10.62; N, 7.21%. MS–ESI (*m*/*z*, ES+): 381.3 $[M+H]^+$. ^{1}H NMR (599.8 MHz, $CDCl_3$, 298 K): $\delta = 7.22$ (s, 1H, 5-H^{Py}), 7.13 (m, 2H, 3-H^{Ar}), 7.07 (m, 1H, 4-H^{Ar}), 6.97 (s, 1H, 3-H^{Py}), 4.92 (br s, 1H, N*H*), 4.15 (s, 2H, NCH_2), 3.56 (sept, $^3J = 6.8$ Hz, 2H, C*H*$(CH_3)_2$), 1.42 (s, 9H, 6-C(CH_3)$_3$), 1.30 (s, 9H, 4-C(CH_3)$_3$), 1.28 (d, $^3J = 6.8$ Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (150.8 MHz, $CDCl_3$, 298 K): $\delta = 168.4$ ($C6^{Py}$), 160.5 ($C4^{Py}$), 156.2 ($C2^{Py}$), 144.3 ($C1^{Ar}$), 142.3 ($C2^{Ar}$), 123.4 ($C3^{Ar}$), 123.3 ($C4^{Ar}$), 116.1 ($C3^{Py}$), 114.2 ($C5^{Py}$), 56.5 (N*C*H$_2$), 37.5 (6-*C*$(CH_3)_3$), 34.8 (4-*C*$(CH_3)_3$), 30.7 (4-C(*C*H_3)$_3$), 30.3 (6-C(*C*H_3)$_3$), 27.7 (*C*H$(CH_3)_2$), 24.3 (CH(*C*H_3)$_2$). X-ray crystal structure analysis for **18c**: formula $C_{26}H_{40}N_2$, $M = 380.60$, colorless crystal 0.50 × 0.30 × 0.30 mm, $a = 11.3668(4)$, $b = 21.0615(7)$, $c = 10.5678(4)$ Å, $\beta = 109.028(2)°$, $V = 2391.71(15)$ Å^3, $\rho_{calc} = 1.057$ g cm^{-3}, $\mu = 0.453$ mm^{-1}, empirical absorption correction ($0.805 \leqslant T \leqslant 0.876$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 1.54178$ Å, $T = 223$ K, ω and ϕ scans, 17355 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 4212 independent ($R_{int} = 0.033$) and 3860 observed reflections [$I \geqslant 2\sigma(I)$], 267 refined parameters, $R = 0.048$, $wR^2 = 0.127$, max. residual electron density 0.18 (−0.19) e Å^{-3}, hydrogen atom at N8 from difference fourier maps and refined free, other calculated and refined as riding atoms.

Preparation of 20b. The reaction of **17b** (906 mg, 2.81 mmol) with $NaBH_4$ (10.6 g, 0.28 mol) in methanol (500 ml) yielded after column chromatography (SiO_2; pentane/ethylacetate, 40:1) the product as a colourless oil (560 mg, 62%). Anal. Calc. for $C_{22}H_{32}N_2$: C, 81.43; H, 9.94; N, 8.63; Found: C, 81.13; H, 9.92; N, 8.55%. MS–ESI (*m*/*z*, ES+): 325.3 $[M+H]^+$, 347.3 $[M+Na]^+$. ^{1}H NMR (599.8 MHz, $CDCl_3$, 298 K): $\delta = 7.45$ (t, $^3J = 7.5$ Hz, 1H, 4-H^{Py}), 7.06 (m, 2H, 3-H^{Ar}), 7.01 (d, $^3J = 7.5$ Hz, 1H, 5-H^{Py}), 7.01 (m, 1H, 4-H^{Ar}), 6.83 (d, $^3J = 7.5$ Hz, 1H, 3-H^{Py}), 4.60 (br s, 1H, NH), 4.24 (q, $^3J = 6.6$ Hz, 1H, NC*H*(CH_3)), 3.33 (sept, $^3J = 6.8$ Hz, 2H, C*H*$(CH_3CH_3)^{Ar}$), 3.08 (sept, $^3J = 6.9$ Hz, 1H, C*H*$(CH_3CH_3)^{Py}$), 1.39 (d, $^3J = 6.6$ Hz, 3H, NCH(CH_3)), 1.35 (d, $^3J = 6.9$ Hz, 3H, CH(CH_3^ACH$_3^B$)^{Py}), 1.34 (d, $^3J = 6.9$ Hz, 3H, CH(CH$_3^A$CH_3^B)^{Py}), 1.25 (d, $^3J = 6.8$ Hz, 6H, CH(CH_3^ACH$_3^B$)^{Ar}), 1.11 (d, $^3J = 6.8$ Hz, 6H, CH(CH$_3^A$CH_3^B)^{Ar}). ^{13}C{^{1}H} NMR (150.8 MHz, $CDCl_3$, 298 K): $\delta = 166.7$ ($C6^{Py}$), 162.2 ($C2^{Py}$), 142.1 ($C2^{Ar}$), 142.0 ($C1^{Ar}$), 136.5 ($C4^{Py}$), 123.3 ($C3^{Ar}$), 122.8 ($C4^{Ar}$), 119.1 ($C5^{Py}$), 118.8 ($C3^{Py}$), 60.2 (NC*H*(CH_3)), 36.2 (C*H*$(CH_3CH_3)^{Py}$), 27.6 (C*H*$(CH_3CH_3)^{Ar}$), 24.2 (CH(*C*H_3^ACH_3^B)^{Ar}), 24.0 (CH(*C*H_3^ACH$_3^B$)^{Ar}), 22.5 (CH(*C*H_3^ACH_3^B)^{Py}), 22.4 (CH(*C*H_3^ACH$_3^B$)^{Py}), 22.2 (NCH(*C*H_3)).

Preparation of 20c. The reaction of **17c** (2.02 g, 6.00 mmol) with $NaBH_4$ (22.7 g, 0.60 mol) in methanol (700 ml) yielded after column chromatography (SiO_2; pentane/ethylacetate, 40:1) **20c** as a white solid (1.75 g, 86%). Crystals suitable for the X-ray diffraction were obtained from a mixture of methanol and triethylamine by evaporation of the solvent at room temperature. M.p. 74 °C (DSC). Anal. Calc. for $C_{23}H_{34}N_2$: C, 81.60; H, 10.12; N, 8.28; Found: C, 81.47; H, 10.02; N, 8.28%. MS–ESI (*m*/*z*, ES+): 339.3 $[M+H]^+$, 361.3 $[M+Na]^+$. ^{1}H NMR (599.8 MHz, $CDCl_3$, 298 K): $\delta = 7.48$ (t, $^3J = 7.7$ Hz, 1H, 4-H^{Py}), 7.20 (d, $^3J = 7.7$ Hz, 1H, 5-H^{Py}), 7.07 (m, 2H, 3-H^{Ar}), 7.02 (m, 1H, 4-H^{Ar}), 6.83 (d, $^3J = 7.7$ Hz, 1H, 3-H^{Py}), 4.62 (br s, N*H*), 4.26 (q, $^3J = 6.5$ Hz, 1H, NC*H*(CH_3)), 3.34 (sept, $^3J = 6.8$ Hz, 2H, C*H*$(CH_3)_2$), 1.41 (s, 9H, C(CH_3)$_3$), 1.38 (d, $^3J = 6.5$ Hz, 3H, NCH(CH_3)), 1.25 (d, $^3J = 6.8$ Hz, 6H, CH(CH_3^ACH$_3^B$)), 1.11 (d, $^3J = 6.8$ Hz, 6H, CH(CH$_3^A$CH_3^B)). ^{13}C{^{1}H} NMR (150.8 MHz, $CDCl_3$, 298 K): $\delta = 168.8$ ($C6^{Py}$), 161.5 ($C2^{Py}$), 142.2 ($C2^{Ar}$), 141.9 ($C1^{Ar}$), 136.4 ($C4^{Py}$), 123.3 ($C3^{Ar}$), 122.9 ($C4^{Ar}$), 118.5 ($C3^{Py}$), 117.3 ($C5^{Py}$), 60.2 (N*C*H(CH_3)), 37.5 (*C*$(CH_3)_3$), 30.1 (C(*C*H_3)$_3$), 27.6 (*C*H$(CH_3)_2$), 24.2 (CH(CH$_3^A$CH_3^B)), 24.0 (CH(*C*H_3^ACH$_3^B$)), 22.1 (NCH(*C*H_3)). X-ray crystal structure analysis for **20c**: formula $C_{23}H_{34}N_2$, $M = 338.52$, colorless crystal 0.30 × 0.20 × 0.15 mm, $a = 10.0180(5)$, $c = 21.4529(9)$ Å, $V = 2153.02(18)$ Å^3, $\rho_{calc} = 1.044$ g cm^{-3}, $\mu = 0.453$ mm^{-1}, empirical absorption correction ($0.876 \leqslant T \leqslant 0.935$), $Z = 4$, tetragonal, space group $P4_1$ (No.76), $\lambda = 1.54178$ Å, $T = 223$ K, ω and ϕ scans, 9097 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 2806 independent ($R_{int} = 0.040$) and 2604 observed reflections [$I \geqslant 2\sigma(I)$], 238 refined parameters, $R = 0.045$, $wR^2 = 0.117$, Flack parameter −0.1(7), max. residual electron density 0.15 (−0.19) e Å^{-3}, hydrogen atom at N9 from difference fourier maps and refined free, other calculated and refined as riding atoms.

General procedure: preparation of aminoalkylpyridines by reaction with $(AlMe_3)_2$(19a,b; 22a–c). Trimethylaluminium was added to a solution of the respective imines in toluene at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. A sodium hydroxide solution was added carefully to quench the reaction. The organic phase was separated and the aqueous phase was extracted with chloroform again. The organic phases were combined and dried with $MgSO_4$. Then the solvent was removed and the crude product was purified by column chromatography on silica gel.

Preparation of 19a. The reaction of **8a** (3.11 g, 11.7 mmol) with trimethylaluminium (2.25 ml, 1.69 g, 23.4 mmol) in toluene (80 ml) yielded after column chromatography (SiO_2; pentane/ethylacetate/triethylamine, 60:1:1) the product as a white solid (3.00 g, 91%). Crystals suitable for the X-ray diffraction were obtained from a mixture of ethylacetate and triethylamine by evaporation of the solvent at room temperature. M.p. 51 °C (DSC). Anal. Calc. for $C_{19}H_{26}N_2$: C, 80.80; H, 9.28; N, 9.92; Found: C, 80.89; H, 9.29; N, 9.83%. MS–ESI (*m*/*z*, ES+): 283.2 $[M+H]^+$, 305.2 $[M+Na]^+$, 587.4 $[2M+Na]^+$. ^{1}H NMR (599.8 MHz, $CDCl_3$, 298 K): $\delta = 8.64$ (ddd, $^3J = 4.8$ Hz, $^4J = 1.8$ Hz, $^5J = 0.9$ Hz, 1H, 6-H^{Py}), 7.46 (td, $^3J = 7.6$ Hz, $^2J = 1.8$ Hz, 1H, 4-H^{Py}), 7.09 (ddd, $^3J = 7.6$ Hz, $^3J = 4.8$ Hz, $^4J = 1.1$ Hz, 1H, 5-H^{Py}), 7.08 (m, 2H, 3-H^{Ar}), 7.02 (m, 1H, 4-H^{Ar}), 6.98 (ddd,

$^3J = 7.6$ Hz, $^4J = 1.1$ Hz, $^5J = 0.9$ Hz, 1H, 3-H^{Py}), 4.23 (q, $^3J = 6.7$ Hz, 1H, NC*H*(CH_3)), 4.14 (br s, NH), 3.30 (sept, $^3J = 6.9$ Hz, 2H, C*H*(CH_3)$_2$), 1.55 (d, $^3J = 6.7$ Hz, 3H, NCH(C*H*$_3$)), 1.27 (d, $^3J = 6.9$ Hz, 6H, CH(C*H*$_3^A$CH$_3^B$)), 1.10 (d, $^3J = 6.9$ Hz, 6H, CH(CH$_3^A$C*H*$_3^B$)). $^{13}C\{^1H\}$ NMR (150.8 MHz, $CDCl_3$, 298 K): $\delta = 163.0$ (C2^{Py}), 149.3 (C6^{Py}), 141.8 (C2^{Ar}), 141.4 (C1^{Ar}), 135.9 (C4^{Py}), 123.2 (C3^{Ar}), 123.0 (C4^{Ar}), 121.8 (C5^{Py}), 121.5 (C3^{Py}), 60.7 (N*C*H(CH_3)), 27.3 (*C*H(CH_3)$_2$), 24.0 (CH(*C*H$_3^A$CH$_3^B$)), 23.9 (CH(CH$_3^A$*C*H$_3^B$)), 21.5 (NCH(*C*H$_3$)). X-ray crystal structure analysis for **19a**: formula $C_{19}H_{26}N_2$, $M = 282.42$, colorless crystal $0.40 \times 0.30 \times 0.15$ mm, $a = 10.8222(1)$, $b = 11.1476(1)$, $c = 14.1578(1)$ Å, $\beta = 92.171(1)°$, $V = 1706.79(3)$ Å^3, $\rho_{calc} = 1.099$ g cm^{-3}, $\mu = 0.485$ mm^{-1}, empirical absorption correction ($0.811 \leqslant T \leqslant 0.931$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 1.54178$ Å, $T = 223$ K, ω and ϕ scans, 15080 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 3068 independent ($R_{int} = 0.050$) and 2727 observed reflections [$I \geqslant 2\sigma(I)$], 199 refined parameters, $R = 0.051$, $wR^2 = 0.139$, max. residual electron density 0.35 (-0.19) e Å^{-3}, hydrogen atom at N9 from difference fourier maps and refined free, other calculated and refined as riding atoms.

Preparation of 19b. The reaction of **8b** (3.02 g, 9.54 mmol) with trimethylaluminium (1.84 ml, 1.38 g, 19.1 mmol) in toluene (100 ml) yielded after column chromatography (SiO_2; pentane/ethylacetate/triethylamine, 60:1:1) the product as a colourless oil (2.99 g, 94%). Anal. Calc. for $C_{23}H_{28}N_2$: C, 83.09; H, 8.49; N, 8.43; Found: C, 82.96; H, 8.47; N, 8.28%. MS–ESI (*m*/*z*, ES+): 333.2 [M+H]$^+$. ^{1}H NMR (599.8 MHz, $CDCl_3$, 298 K): $\delta = 8.10$ (d, $^3J = 8.3$ Hz, 1H, 8-H^{Ch}), 8.03 (d, $^3J = 8.4$ Hz, 1H, 4-H^{Ch}), 7.77 (dd, $^3J = 8.1$ Hz, $^4J = 1.2$ Hz, 1H, 5-H^{Ch}), 7.70 (ddd, $^3J = 8.3$ Hz, $^3J = 6.9$ Hz, $^4J = 1.2$ Hz, 1H, 7-H^{Ch}), 7.49 (ddd, $^3J = 8.1$ Hz, $^3J = 6.9$ Hz, $^4J = 1.1$ Hz, 1H, 6-H^{Ch}), 7.21 (d, $^3J = 8.4$ Hz, 1H, 3-H^{Ch}), 7.04 (m, 2H, 3-H^{Ar}), 6.99 (m, 1H, 4-H^{Ar}), 4.69 (br s, 1H, N*H*), 4.50 (q, $^3J = 6.7$ Hz, 1H, NC*H*(CH_3)), 3.41 (sept, $^3J = 6.8$ Hz, 2H, C*H*(CH_3)$_2$), 1.48 (d, $^3J = 6.7$ Hz, 3H, NCH(C*H*$_3$)), 1.24 (d, $^3J = 6.8$ Hz, 6H, CH(C*H*$_3^A$CH$_3^B$)), 1.08 (d, $^3J = 6.8$ Hz, 6H, CH(CH$_3^A$C*H*$_3^B$)). $^{13}C\{^1H\}$ NMR (150.8 MHz, $CDCl_3$, 298 K): $\delta = 163.6$ (C2^{Ch}), 147.6 (C8a^{Ch}), 142.1 (C2^{Ar}), 141.7 (C1^{Ar}), 136.2 (C4^{Ch}), 129.3 (C7^{Ch}), 129.1 (C8^{Ch}), 127.4 (C5^{Ch}), 127.3 (C4a^{Ch}), 126.0 (C6^{Ch}), 123.4 (C3^{Ar}), 123.0 (C4^{Ar}), 120.2 (C3^{Ch}), 60.5 (N*C*H(CH_3)), 27.7 (*C*H(CH_3)$_2$), 24.11 (CH(CH$_3^A$*C*H$_3^B$)), 24.06 (CH(*C*H$_3^A$CH$_3^B$)), 22.1 (NCH(*C*H$_3$)).

Preparation of 22a [17]. The reaction of **17a** (2.00 g, 7.13 mmol) with trimethylaluminium (1.37 ml, 1.03 g, 14.3 mmol) in toluene (50 ml) yielded after column chromatography (SiO_2; pentane/methanol/chloroform/triethylamine, 100:1:1:1) the product as a white solid (1.65 g, 78%). Crystals suitable for the X-ray diffraction were obtained from a mixture of pentane, methanol, chloroform and triethylamine by evaporation of the solvent at room temperature. Anal. Calc. for $C_{20}H_{28}N_2$: C, 81.03; H, 9.52; N, 9.45; Found: C, 80.65; H, 9.56; N, 9.45%. MS–ESI (*m*/*z*, ES+): 297.2 [M + H]$^+$, 319.2 [M+Na]$^+$. ^{1}H NMR (599.8 MHz, $CDCl_3$, 298 K): $\delta = 8.61$ (ddd, $^3J = 4.8$ Hz, $^4J = 1.8$ Hz, $^4J = 0.9$ Hz, 1H, 6-H^{Py}), 7.64 (ddd, $^3J = 8.0$ Hz, $^3J = 7.5$ Hz, $^4J = 1.8$ Hz, 1H, 4-H^{Py}), 7.55 (d, $^3J = 8.0$ Hz, 1H, 3-H^{Py}), 7.15 (ddd, $^3J = 7.5$ Hz, $^3J = 4.8$ Hz, $^4J = 1.1$ Hz, 1H, 5-H^{Py}), 7.05 (m, 3H, 3,4-H^{Ar}), 4.14 (br s, 1H, N*H*), 3.14 (sept, $^3J = 6.9$ Hz, 2H, C*H*(CH_3)$_2$), 1.46 (s, 6H, NC(C*H*$_3$)$_2$), 1.06 (d, $^3J = 6.9$ Hz, 12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (150.8 MHz, $CDCl_3$, 298 K): $\delta = 168.4$ (C2^{Py}), 148.4 (C6^{Py}), 146.3 (C2^{Ar}), 140.5 (C1^{Ar}), 136.2 (C4^{Py}), 124.3 (C4^{Ar}), 122.9 (C3^{Ar}), 121.2 (C5^{Py}), 119.3 (C3^{Py}), 59.0 (N*C*(CH_3)$_2$), 29.2 (NC(*C*H$_3$)$_2$), 28.2 (*C*H(CH_3)$_2$), 23.9 (CH(*C*H$_3$)$_2$). X-ray crystal structure analysis for **22a**: formula $C_{20}H_{28}N_2$, $M = 296.44$, colorless crystal $0.40 \times 0.35 \times 0.25$ mm, $a = 16.886(1)$, $b = 11.739(1)$, $c = 18.347(1)$ Å, $V = 3636.8(4)$ Å^3, $\rho_{calc} = 1.083$ g cm^{-3}, $\mu = 0.476$ mm^{-1}, empirical absorption correction ($0.833 \leqslant T \leqslant 0.890$), $Z = 8$, orthorhombic, space group *P*bca (No. 61), $\lambda = 1.54178$ Å, $T = 223$ K, ω and ϕ scans, 17996 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 3226 independent ($R_{int} = 0.034$) and 2949 observed reflections [$I \geqslant 2\sigma(I)$], 209 refined parameters, $R = 0.054$, $wR^2 = 0.115$, max. residual electron density 0.15 (-0.15) e Å^{-3}, hydrogen atom at N10 from difference fourier maps and refined free, other calculated and refined as riding atoms.

Preparation of 22b. The reaction of **17b** (1.85 g, 5.74 mmol) with trimethylaluminium (1.10 ml, 0.83 g, 11.5 mmol) in toluene (50 ml) yielded after column chromatography (SiO_2; pentane/methanol/chloroform/triethylamine, 150:1:1:1) the product as a colourless oil (1.30 g, 67%). Anal. Calc. for $C_{23}H_{34}N_2$: C, 81.60; H, 10.12; N, 8.28; Found: C, 81.53; H, 10.30; N, 8.17%. MS–ESI (*m*/*z*, ES+): 339.3 [M+H]$^+$. ^{1}H NMR (599.8 MHz, $CDCl_3$, 298 K): $\delta = 7.55$ (t, $^3J = 7.7$ Hz, 1H, 4-H^{Py}), 7.20 (d, $^3J = 7.7$ Hz, 1H, 3-H^{Py}), 7.07 (m, 3H, 3,4-H^{Ar}), 7.03 (d, $^3J = 7.7$ Hz, 1H, 5-H^{Py}), 4.80 (br s, 1H, N*H*), 3.37 (sept, $^3J = 6.9$ Hz, 2H, C*H*(CH_3)$_2^{Ar}$), 3.10 (sept, $^3J = 6.9$ Hz, 1H, C*H*(CH_3)$_2^{Py}$), 1.42 (s, 6H, NC(C*H*$_3$)$_2$), 1.34 (d, $^3J = 6.9$ Hz, 6H, CH(C*H*$_3$)$_2^{Py}$), 1.07 (d, $^3J = 6.9$ Hz, 12H, CH(C*H*$_3$)$_2^{Ar}$). $^{13}C\{^1H\}$ NMR (150.8 MHz, $CDCl_3$, 298 K): $\delta = 166.9$ (C2^{Py}), 165.8 (C6^{Py}), 147.0 (C2^{Ar}), 140.7 (C1^{Ar}), 136.7 (C4^{Py}), 124.4 (C4^{Ar}), 122.9 (C3^{Ar}), 118.2 (C5^{Py}), 116.0 (C3^{Py}), 59.1 (N*C*(CH_3)$_2$), 36.3 (*C*H(CH_3)$_2^{Py}$), 29.0 (NC(*C*H$_3$)$_2$), 28.0 (*C*H(CH_3)$_2^{Ar}$), 24.2 (CH(*C*H$_3$)$_2^{Ar}$), 22.6 (CH(*C*H$_3$)$_2^{Py}$).

Preparation of 22c. The reaction of **17c** (1.78 g, 5.32 mmol) with trimethylaluminium (1.02 ml, 0.77 g, 10.6 mmol) in toluene (30 ml) yielded after column chromatography (SiO_2; pentane/methanol/chloroform/ triethylamine, 150:1:1:1) the product as a white solid (1.43 g, 77%). Crystals suitable for X-ray diffraction were obtained from a mixture of pentane, methanol, chloroform and triethylamine by evaporation of the solvent at room temperature. M.p. 77 °C (DSC). Anal. Calc. for $C_{24}H_{36}N_2$: C, 81.76; H, 10.29; N, 7.95; Found: C, 81.62; H, 10.32; N,

7.70%. MS–ESI (m/z, ES+): 353.3 $[M+H]^+$, 375.3 $[M+Na]^+$. ^1H NMR (599.8 MHz, $CDCl_3$, 298 K): $\delta = 7.55$ (t, $^3J = 7.8$ Hz, 1H, 4-H^{Py}), 7.18 (dd, $^3J = 7.8$ Hz, $^4J = 0.7$ Hz, 1H, 5-H^{Py}), 7.17 (dd, $^3J = 7.8$ Hz, $^4J = 0.7$ Hz, 1H, 3-H^{Py}), 7.05 (m, 3H, 3,4-H^{Ar}), 4.56 (br s, 1H, N*H*), 3.33 (sept, $^3J = 6.9$ Hz, 2H, C*H*$(CH_3)_2$), 1.40 (s, 6H, NC(C*H*$_3)_2$), 1.39 (s, 9H, C(C*H*$_3)_3$), 1.04 (d, $^3J = 6.9$ Hz, 12H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (150.8 MHz, $CDCl_3$, 298 K): $\delta = 167.9$ (C6^{Py}), 166.3 (C2^{Py}), 147.1 (C2^{Ar}), 140.4 (C1^{Ar}), 136.5 (C4^{Py}), 124.4 (C4^{Ar}), 122.9 (C3^{Ar}), 116.4 (C5^{Py}), 115.6 (C3^{Py}), 59.4 (N*C*$(CH_3)_2$), 37.6 (*C*$(CH_3)_3$), 30.2 (C(*C*H$_3)_3$), 28.7 (NC(*C*H$_3)_2$), 28.0 (*C*H$(CH_3)_2$), 24.2 (CH(*C*H$_3)_2$). X-ray crystal structure analysis for **22c**: formula $C_{24}H_{36}N_2$, $M = 352.55$, colorless crystal $0.30 \times 0.15 \times 0.10$ mm, $a = 10.745(1)$, $b = 14.093(1)$, $c = 14.765(1)$ Å, $V = 2235.9(3)$ Å^3, $\rho_{calc} = 1.047$ g cm^{-3}, $\mu = 0.452$ mm^{-1}, empirical absorption correction ($0.876 \leqslant T \leqslant 0.956$), $Z = 4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda = 1.54178$ Å, $T = 223$ K, ω and ϕ scans, 10155 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 3904 independent ($R_{int} = 0.041$) and 3517 observed reflections [$I \geqslant 2\sigma(I)$], 248 refined parameters, $R = 0.046$, $wR^2 = 0.114$, Flack 0.7(6), max. residual electron density 0.12 (−0.14) e Å^{-3}, hydrogen atom at N10 from difference fourier maps and refined free, other calculated and refined as riding atoms.

General procedure: preparation of amidoalkylpyridine aluminium complexes (21a–c). Two equivalents of $AlMe_3$ were added carefully to a stirred solution of the respective imine (1 equiv.) in toluene at 0 °C. Then the reaction mixture was allowed to warm to room temperature over night. The volatiles were removed in vacuo and the residue was washed with pentane. The product was obtained as a yellow powder.

Preparation of 21a. The iminopyridine **17a** (2.00 g, 7.13 mmol) in toluene (50 ml) was reacted with trimethylaluminium (1.37 ml, 1.03 g, 14.3 mmol) to yield **21a** (1.95 g, 78%). M.p. 153 °C (DSC). Anal. Calc. for $C_{22}H_{33}N_2Al$: C, 74.96; H, 9.44; N, 7.95; Found: C, 74.78; H, 9.39; N, 7.93%. ^1H NMR (599.8 MHz, [D$_6$]-benzene, 298 K): $\delta = 7.68$ (ddd, $^3J = 5.4$ Hz, $^4J = 1.7$ Hz, $^5J = 1.0$ Hz, 1H, 6-H^{Py}), 7.28 (m, 2H, 3-H^{Ar}), 7.24 (m, 1H, 4-H^{Ar}), 6.85 (ddd, $^3J = 8.2$ Hz, $^3J = 7.5$ Hz, $^4J = 1.7$ Hz, 1H, 4-H^{Py}), 6.71 (ddd, $^3J = 8.2$ Hz, $^4J = 1.0$ Hz, $^5J = 1.0$ Hz, 1H, 3-H^{Py}), 6.32 (ddd, $^3J = 7.5$ Hz, $^3J = 5.4$ Hz, $^4J = 1.0$ Hz, 1H, 5-H^{Py}), 3.88 (sept, $^3J = 6.8$ Hz, 2H, C*H*$(CH_3)_2$), 1.32 (d, $^3J = 6.8$ Hz, 6H, CH(C*H*$_3^A$CH$_3^B$)), 1.27 (d, $^3J = 6.8$ Hz, 6H, CH(CH$_3^A$C*H*$_3^B$)), 1.24 (s, 6H, NC(C*H*$_3)_2$), −0.25 (Al(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (150.8 MHz, [D$_6$]-benzene, 298 K): $\delta = 172.0$ (C2^{Py}), 151.4 (C2^{Ar}), 143.3 (C6^{Py}), 142.3 (C1^{Ar}), 139.5 (C4^{Py}), 124.8 (C4^{Ar}), 123.9 (C3^{Ar}), 122.4 (C5^{Py}), 121.5 (C3^{Py}), 64.2 (N*C*$(CH_3)_2$), 30.4 (NC(*C*H$_3)_2$), 28.05 (*C*H$(CH_3)_2$), 28.01 (CH(CH$_3^A$*C*H$_3^B$), Ar), 23.8 (CH(*C*H$_3^A$CH$_3^B$)), −6.8 (Al(*C*H$_3)_2$).

Preparation of 21b. The iminopyridine **17b**(1.01 g, 3.13 mmol) in toluene (30 ml) was reacted with trimethylaluminium (0.60 ml, 0.45 g, 6.26 mmol) to yield **21b** (950 mg, 77%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **21b** in pentane at −30 °C. M.p. 170 °C (DSC). Anal. Calc. for $C_{25}H_{39}N_2Al$: C, 76.10; H, 9.96; N, 7.10; Found: C, 76.18; H, 10.22; N: 7.04%. ^1H NMR (599.8 MHz, [D$_6$]-benzene, 298 K): $\delta = 7.28$ (m, 2H, 3-H^{Ar}), 7.23 (m, 1H, 4-H^{Ar}), 6.99 (t, $^3J = 7.9$ Hz, 1H, 4-H^{Py}), 6.73 (dd, $^3J = 7.9$ Hz, $^4J = 1.0$ Hz, 1H, 3-H^{Py}), 6.51 (dd, $^3J = 7.9$ Hz, $^4J = 1.0$ Hz, 1H, 5-H^{Py}), 3.88 (sept, $^3J = 6.8$ Hz, 2H, C*H*$(CH_3)_2^{Ar}$), 3.55 (sept, $^3J = 6.9$ Hz, 1H, C*H*$(CH_3)_2^{Py}$), 1.34 (s, 6H, NC(C*H*$_3)_2$), 1.32 (d, $^3J = 6.8$ Hz, 6H, CH(C*H*$_3^A$CH$_3^B)_2^{Ar}$), 1.31 (d, $^3J = 6.8$ Hz, 6H, CH(CH$_3^A$C*H*$_3^B)_2^{Ar}$), 1.02 (d, $^3J = 6.9$ Hz, 6H, CH(C*H*$_3)_2^{Py}$), −0.21 (s, 6H, Al(C*H*$_3)_2$). $^{13}C\{^1H\}$-NMR (150.8 MHz, [D$_6$]-benzene, 298 K): $\delta = 171.8$ (C2^{Py}), 165.5 (C6^{Py}), 151.2 (C2^{Ar}), 142.9 (C1^{Ar}), 140.3 (C4^{Py}), 124.7 (C4^{Ar}), 123.9 (C3^{Ar}), 119.1 (C5^{Py}), 118.9 (C3^{Py}), 63.9 (N*C*$(CH_3)_2$), 35.3 (*C*H$(CH_3)_2^{Py}$), 31.0 (NC(*C*H$_3)_2$), 28.1 (*C*H$(CH_3)_2^{Ar}$), 27.8 (CH(CH$_3^A$*C*H$_3^B)_2^{Ar}$), 24.1 (CH(*C*H$_3^A$CH$_3^B)_2^{Ar}$), 23.0 (CH(*C*H$_3)_2^{Py}$), −6.0 (Al(*C*H$_3)_2$). X-ray crystal structure analysis for **21b**: formula $C_{25}H_{39}AlN_2$, $M = 394.56$, colorless crystal $0.35 \times 0.30 \times 0.25$ mm, $a = 10.0002(2)$, $b = 14.3444(3)$, $c = 17.6315(1)$ Å, $\beta = 99.352(1)°$, $V = 2495.57(8)$ Å^3, $\rho_{calc} = 1.050$ g cm^{-3}, $\mu = 0.093$ mm^{-1}, empirical absorption correction ($0.968 \leqslant T \leqslant 0.977$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 19477 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å^{-1}, 5942 independent ($R_{int} = 0.055$) and 3986 observed reflections [$I \geqslant 2\sigma(I)$], 263 refined parameters, $R = 0.051$, $wR^2 = 0.140$, max. residual electron density 0.22 (−0.25) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of 21c. The iminopyridine **17c** (2.04 g, 6.06 mmol) in toluene (40 ml) was reacted with trimethylaluminium (1.16 ml, 0.87 g, 12.1 mmol) to yield **21c** (2.13 g, 86%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **21c** in pentane at −30 °C. M.p. 159 °C (DSC). Anal. Calc. for $C_{26}H_{41}N_2Al$: C, 76.43; H, 10.11; N, 6.86; Found: C, 75.98; H, 9.97; N, 6.97%. ^1H-NMR (599.8 MHz, [D$_6$]-benzene, 298 K): $\delta = 7.26$ (m, 2H, 3-H^{Ar}), 7.23 (m, 1H, 4-H^{Ar}), 6.94 (t, $^3J = 7.9$ Hz, 1H, 4-H^{Py}), 6.81 (dd, $^3J = 7.9$ Hz, $^4J = 1.0$ Hz, 1H, 3-H^{Py}), 6.73 (dd, $^3J = 7.9$ Hz, $^4J = 1.0$ Hz, 1H, 5-H^{Py}), 3.83 (sept, $^3J = 6.8$ Hz, 2H, C*H*$(CH_3)_2$), 1.42 (s, 6H, NC(C*H*$_3)_2$), 1.33 (d, $^3J = 6.8$ Hz, 6H, CH(C*H*$_3^A$CH$_3^B$)), 1.31 (d, $^3J = 6.8$ Hz, 6H, CH(CH$_3^A$C*H*$_3^B$)), 1.31 (s, 9H, C(C*H*$_3)_3$), −0.23 (s, 6H, Al(C*H*$_3)_2$). $^{13}C\{^1H\}$-NMR (150.8 MHz, [D$_6$]-benzene, 298 K): $\delta = 174.2$ (C2^{Py}), 166.4 (C6^{Py}), 150.7 (C2^{Ar}), 143.9 (C1^{Ar}), 139.6 (C4^{Py}), 124.6 (C4^{Ar}), 123.8 (C3^{Ar}), 120.1 (C5^{Py}), 119.2 (C3^{Py}), 63.2 (N*C*$(CH_3)_2$), 37.8 (*C*$(CH_3)_3$), 31.2 (NC(*C*H$_3)_2$), 30.6 (C(*C*H$_3)_3$), 28.2 (*C*H$(CH_3)_2$), 26.8 (CH(CH$_3^A$*C*H$_3^B)_2$), 24.1 (CH(*C*H$_3^A$CH$_3^B)_2$), −3.0 (Al(*C*H$_3)_2$). X-ray crystal structure analysis for **21c**: formula $C_{26}H_{41}AlN_2$, $M = 408.59$, colorless crystal $0.40 \times 0.35 \times 0.15$ mm, $a = 10.528(1)$, $b = 16.085(1)$, $c = 15.029(1)$ Å, $\beta = 95.69(1)°$, $V = 2532.5(3)$ Å^3, $\rho_{calc} =$

1.072 g cm^{-3}, $\mu = 0.094$ mm^{-1}, empirical absorption correction ($0.964 \leqslant T \leqslant 0.986$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 21 016 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 6137 independent ($R_{int} = 0.050$) and 4955 observed reflections [$I \geqslant 2\sigma(I)$], 273 refined parameters, $R = 0.041$, $wR^2 = 0.111$, max. residual electron density 0.29 (−0.25) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

General procedure: preparation of amidoalkylpyridine Group 4 metal complexes (23a,e; 24b–f; 25a–c,f). The respective metal complex precursor in toluene was added to a stirred solution of the respective amine in toluene. The reaction mixture was heated at 60 °C for 3 h, concentrated in vacuo to 1/3 of the volume and the precipitated product was collected by filtration.

Preparation of 23a. The reaction of **18a** (105 mg, 0.39 mmol) with tetrabenzylzirconium (178 mg, 0.39 mmol) in toluene (5 ml) yielded the product as a yellow solid (185 mg, 74%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **23a** in toluene. ^{1}H NMR (599.8 MHz, C_6D_6, 298 K): $\delta = 7.42$ (d, $^3J = 5.6$ Hz, 1H, 6-H^{Py}), 7.20 (m, 3H, 3,4-H^{Ar}), 7.07 (ps t, 6H, 3-H^{Bn}), 6.86 (t, $^3J = 7.5$ Hz, 3H, 4-H^{Bn}), 6.75 (ddd, $^3J = 8.2$ Hz, $^3J = 7.6$ Hz, $^4J = 1.5$ Hz, 1H, 4-H^{Py}), 6.62 (ps d, 6H, 2-H^{Bn}), 6.33 (d, $^3J = 8.2$ Hz, 1H, 3-H^{Py}), 6.29 (ddd, $^3J = 7.6$ Hz, $^3J = 5.6$ Hz, $^4J = 0.8$ Hz, 1H, 5-H^{Py}), 4.61 (s, 2H, NCH_2), 3.39 (sept, $^3J = 6.8$ Hz, CH(CH$_3$)$_2$), 2.23 (s, 6H, CH_2Ph), 1.33 (d, $^3J = 6.8$ Hz, 6H, CH(CH_3^ACH$_3^B$)), 1.13 (d, $^3J = 6.8$ Hz, 6H, CH(CH$_3^A$CH_3^B)). ^{13}C{^{1}H} NMR (150.8 MHz, C_6D_6, 298 K): $\delta = 163.1$ (C2^{Py}), 149.4 (C1^{Ar}), 148.4 (C6^{Py}), 145.31 (C2^{Ar}), 145.29 (C1^{Bn}), 137.7 (C4^{Py}), 129.5 (C3^{Bn}), 127.2 (C2^{Bn}), 126.2 (C4^{Ar}), 124.6 (C3^{Ar}), 122.1 (C4^{Bn}), 121.0 (C5^{Py}), 120.2 (C3^{Py}), 72.7 (CH_2Ph), 67.6 (NCH_2), 28.1 (CH(CH$_3$)$_2$), 27.2 (CH(CH$_3^A$CH_3^B)), 24.3 (CH(CH_3^ACH$_3^B$)).

Preparation of 23e [6b–h]. The reaction of **22a** (151 mg, 0.51 mmol) with tetrabenzylzirconium (232 mg, 0.51 mmol) in toluene (4 ml) yielded the product as a yellow solid (302 mg, 90%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **23e** in toluene. M.p. 104 °C (DSC). ^{1}H NMR (599.8 MHz, C_6D_6, 298 K): $\delta = 7.34$ (ddd, $^3J = 5.5$ Hz, $^4J = 1.5$ Hz, $^5J = 1.0$ Hz, 1H, 6-H^{Py}), 7.20 (m, 3H, 3,4-H^{Ar}), 7.08 (ps t, 6H, 3-H^{Bn}), 6.85 (m, 4H, 4-H^{Bn}, 4-H^{Py}), 6.74 (ps d, 6H, 2-H^{Bn}), 6.55 (dt, $^3J = 8.1$ Hz, $^4J = {}^5J = 1.0$ Hz, 1H, 3-H^{Py}), 6.28 (ddd, $^3J = 7.3$ Hz, $^3J = 5.5$ Hz, $^4J = 1.0$ Hz, 1H, 5-H^{Py}), 3.43 (sept, $^3J = 6.7$ Hz, 2H, CH(CH$_3$)$_2$), 2.54 (s, 6H, CH_2Ph), 1.35 (d, $^3J = 6.7$ Hz, 6H, CH(CH_3^A CH$_3^B$)), 1.15 (d, $^3J = 6.7$ Hz, 6H, CH(CH$_3^A$CH_3^B)), 1.05 (s, 6H, NC(CH_3)$_2$). ^{13}C{^{1}H} NMR (150.8 MHz, C_6D_6, 298 K): $\delta = 172.4$ (C2^{Py}), 149.5 (C2^{Ar}), 148.2 (C6^{Py}), 147.3 (C1^{Bn}), 139.7 (C1^{Ar}), 138.3 (C4^{Py}), 129.0 (C3^{Bn}), 127.3 (C4^{Ar}), 126.6 (C2^{Bn}), 125.5 (C3^{Ar}), 121.5 (C4^{Bn}), 121.1 (C5^{Py}), 120.2 (C3^{Py}), 75.3 (CH_2Ph), 72.2 (NC(CH$_3$)$_2$), 30.9 (NC(CH_3)$_2$), 28.4 (CH(CH$_3$)$_2$), 27.3 (CH(CH_3^ACH$_3^B$)), 25.5 (CH(CH$_3^A$CH_3^B)). X-ray crystal structure analysis for **23e**: formula $C_{41}H_{48}N_2Zr$, $M = 660.03$, yellow crystal $0.35 \times 0.15 \times 0.10$ mm, $a = 10.699(1)$, $b = 15.141(2)$, $c = 22.169(1)$ Å, $\beta = 103.68(1)°$, $V = 3489.4(4)$ Å^3, $\rho_{calc} = 1.256$ g cm^{-3}, $\mu = 0.345$ mm^{-1}, empirical absorption correction ($0.889 \leqslant T \leqslant 0.966$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 36 179 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 8521 independent ($R_{int} = 0.076$) and 6012 observed reflections [$I \geqslant 2\sigma(I)$], 403 refined parameters, $R = 0.056$, $wR^2 = 0.126$, max. residual electron density 1.36 (−1.16) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of 24b. The reaction of **18c** (131 mg, 0.34 mmol) with Zr(NMe$_2$)$_4$ (99 mg, 0.37 mmol) toluene (7 ml) yielded the product as a white solid (150 mg, 74%). Anal. Calc. for $C_{32}H_{57}N_5Zr$: C, 63.73; H, 9.53; N, 11.61; Found: C, 62.46; H, 9.52; N, 11.23%. ^{1}H NMR (599.8 MHz, [D$_8$]-THF, 298 K): $\delta = 7.50$ (d, $^4J = 1.9$ Hz, 1H, 5-H^{Py}), 7.17 (d, $^4J = 1.9$ Hz, 1H, 3-H^{Py}), 7.05 (m, 2H, 3-H^{Ar}), 6.92 (m, 1H, 4-H^{Ar}), 4.65 (s, 2H, NCH_2), 3.61 (sept, $^3J = 6.8$ Hz, 2H, CH(CH$_3$)$_2$), 2.66 (br s, 18H, N(CH_3)$_2$), 1.43 (s, 9H, 6-C(CH_3)$_3$), 1.32 (s, 9H, 4-C(CH_3)$_3$), 1.27 (d, $^3J = 6.8$ Hz, 6H, CH(CH_3^ACH$_3^B$)), 1.17 (d, $^3J = 6.8$ Hz, 6H, CH(CH$_3^A$CH_3^B)). ^{13}C{^{1}H} NMR (150.8 MHz, [D$_8$]-THF, 298 K): $\delta = 172.5$ (C6^{Py}), 163.6 (C2^{Py}), 162.5 (C4^{Py}), 151.4 (C1^{Ar}), 145.3 (C2^{Ar}), 124.0 (C4^{Ar}), 123.4 (C3^{Ar}), 117.8 (C5^{Py}), 117.2 (C3^{Py}), 66.1 (NCH_2), 43.2 (N(CH_3)$_2$), 39.0 (6-C(CH$_3$)$_3$), 35.5 (4-C(CH$_3$)$_3$), 30.4 (4-C(CH_3)$_3$), 30.3 (6-C(CH_3)$_3$), 28.7 (CH(CH$_3$)$_2$), 26.9 (CH(CH$_3^A$CH_3^B)), 24.1 (CH(CH_3^A CH$_3^B$)).

Preparation of 24c. The reaction of **19a** (318 mg, 1.13 mmol) with Zr(NMe$_2$)$_4$ (318 mg, 1.19 mmol) in toluene (10 ml) yielded the product as a yellow solid (460 mg, 81%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **24c** in toluene. M.p. 161 °C (DSC). Anal. Calc. for $C_{25}H_{43}N_5Zr$: C, 59.47; H, 8.58; N, 13.87; Found: C, 59.32; H, 8.74; N, 13.42%. ^{1}H NMR (599.8 MHz, [D$_8$]-THF, 298 K): $\delta = 8.34$ (ddd, $^3J = 5.4$ Hz, $^4J = 1.7$ Hz, $^5J = 0.9$ Hz, 1H, 6-H^{Py}), 7.92 (ddd, $^3J = 8.0$ Hz, $^3J = 7.5$ Hz, $^4J = 1.7$ Hz, 1H, 4-H^{Py}), 7.59 (d, $^3J = 8.0$ Hz, 1H, 3-H^{Py}), 7.41 (m, 1H, 5-H^{Py}), 7.09 (dd, $^3J = 7.7$ Hz, $^4J = 1.7$ Hz, 1H, 3′-H^{Ar}), 7.06 (dd, $^3J = 7.7$ Hz, $^4J = 1.7$ Hz, 1H, 3-H^{Ar}), 6.98 (t, $^3J = 7.7$ Hz, 1H, 4-H^{Ar}), 4.81 (q, $^3J = 6.8$ Hz, 1H, NCH(CH$_3$)), 3.69 (sept, $^3J = 6.9$ Hz, 1H, CH(CH$_3$)$_2'$), 3.27 (sept, $^3J = 6.9$ Hz, 1H, CH(CH$_3$)$_2$), 2.67 (br, 18H, N(CH_3)$_2$), 1.28 (d, $^3J = 6.8$ Hz, 3H, NCH(CH_3)), 1.22 (d, $^3J = 6.9$ Hz, 3H, CH(CH_3^ACH$_3^B$)), 1.21 (d, $^3J = 6.9$ Hz, 3H, CH(CH$_3^A$CH_3^B)), 1.19 (d, $^3J = 6.9$ Hz, 3H, CH(CH_3^A CH$_3^B$)′), 1.17 (d, $^3J = 6.9$ Hz, 3H, CH(CH$_3^A$CH_3^B)′). ^{13}C{^{1}H} NMR (150.8 MHz, [D$_8$]-THF, 298 K): $\delta = 169.0$ (C2^{Py}), 148.5 (C6^{Py}), 147.9 (C2′^{Ar}), 147.6 (C1^{Ar}), 146.2 (C2^{Ar}), 138.8 (C4^{Py}), 124.7 (C4^{Ar}), 124.2 (C3^{Ar}), 124.0 (C3′^{Ar}), 122.9 (C5^{Py}), 122.5 (C3^{Py}), 69.7 (NCH(CH$_3$)), 43.6 (br, N(CH_3)$_2$), 28.7 (CH(CH$_3$)$_{2'}$), 28.4 (CH(CH$_3$)$_2$), 26.8 (CH(CH_3^ACH$_3^B$)), 25.3 (CH(CH$_3^A$CH_3^B)′), 24.6

($CH(CH_3^ACH_3^B)$), 24.1 ($CH(CH_3^ACH_3^B)'$), 23.4 ($NCH(CH_3)$). X-ray crystal structure analysis for **24c**: formula $C_{25}H_{43}N_5Zr$, $M = 504.86$, light yellow crystal $0.40 \times 0.30 \times 0.25$ mm, $a = 8.9173(2)$, $b = 9.4329(2)$, $c = 17.2670(3)$ Å, $\alpha = 101.540(1)$, $\beta = 95.897(1)$, $\gamma = 103.228(1)°$, $V = 1368.41(5)$ Å^3, $\rho_{calc} = 1.225$ g cm^{-3}, $\mu = 0.421$ mm^{-1}, empirical absorption correction ($0.850 \leqslant T \leqslant 0.902$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 14347 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å^{-1}, 6577 independent ($R_{int} = 0.036$) and 5983 observed reflections [$I \geqslant 2\sigma(I)$], 291 refined parameters, $R = 0.032$, $wR^2 = 0.082$, max. residual electron density 0.58 (-0.53) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of 24d. The reaction of **19b** (337 mg, 1.13 mmol) with $Zr(NMe_2)_4$ (318 mg, 1.19 mmol) in toluene (10 ml) yielded the product as a yellow solid (490 mg, 78%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **24d** in toluene. M.p. 189 °C (DSC). Anal. Calc. for $C_{29}H_{45}N_5Zr$: C, 62.77; H, 8.17; N, 12.62; Found: C, 62.29; H, 8.11; N, 12.15%. ^{1}H NMR (599.8 MHz, [D$_8$]-THF, 298 K): $\delta = 8.40$ (d, $^3J = 8.5$ Hz, 1H, 4-H^{Ch}), 8.39 (d, $^3J = 8.5$ Hz, 1H, 8-H^{Ch}), 7.94 (dd, $^3J = 8.0$ Hz, $^4J = 1.4$ Hz, 1H, 5-H^{Ch}), 7.75 (ddd, $^3J = 8.5$ Hz, $^3J = 6.9$ Hz, $^4J = 1.4$ Hz, 1H, 7-H^{Ch}), 7.66 (d, $^3J = 8.5$ Hz, 1H, 3-H^{Ch}), 7.60 (ddd, $^3J = 8.0$ Hz, $^3J = 6.9$ Hz, $^3J = 1.0$ Hz, 1H, 6-H^{Ch}), 7.12 (dd, $^3J = 7.7$ Hz, $^4J = 1.7$ Hz, 1H, 3-H^{Ar}), 7.09 (dd, $^3J = 7.7$ Hz, $^4J = 1.7$ Hz, 1H, 3′-H^{Ar}), 7.00 (t, $^3J = 7.7$ Hz, 1H, 4-H^{Ar}), 4.98 (q, $^3J = 6.9$ Hz, 1H, $NCH(CH_3)$), 3.75 (sept, $^3J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.31 (sept, $^3J = 6.9$ Hz, 1H, $CH(CH_3)_2'$), 2.93 (br s, 6H, $N(CH_3)_2^A$), 2.57 (br s, 6H, $N(CH_3)_2^B$), 2.46 (br s, 6H, $N(CH_3)_2^C$), 1.41 (d, $^3J = 6.9$ Hz, 3H, $NCH(CH_3)$), 1.25 (d, $^3J = 6.8$ Hz, $CH(CH_3^ACH_3^B)$), 1.245 (d, $^3J = 6.9$ Hz, $CH(CH_3^ACH_3^B)'$), 1.23 (d, $^3J = 6.9$ Hz, $CH(CH_3^ACH_3^B)'$), 1.20 (d, $^3J = 6.8$ Hz, $CH(CH_3^ACH_3^B)$). ^{13}C{^{1}H} NMR (150.8 MHz, [D$_8$]-THF, 298 K): $\delta = 170.6$ (C2^{Ch}), 147.7 (C2^{Ar}), 147.6 (C1^{Ar}), 146.6 (C8a^{Ch}), 146.3 (C2′^{Ar}), 139.3 (C4^{Ch}), 130.8 (C7^{Ch}), 128.5 (C5^{Ch}), 128.4 (C4a^{Ch}), 127.8 (C8^{Ch}), 127.3 (C6^{Ch}), 124.8 (C4^{Ar}), 124.2 (C3′^{Ar}), 124.1 (C3^{Ar}), 120.4 (C3^{Ch}), 70.8 ($NCH(CH_3)$), 44.1 ($N(CH_3)_2^C$), 43.6 ($N(CH_3)_2^B$), 42.6 ($N(CH_3)_2^A$), 28.6 ($CH(CH_3)_2$), 28.5 $CH(CH_3)_2'$), 27.0 ($CH(CH_3^ACH_3^B)'$), 25.5 ($CH(CH_3^ACH_3^B)$), 24.6 ($CH(CH_3^ACH_3^B)'$), 24.5 ($CH(CH_3^ACH_3^B)$), 23.3 ($NCH(CH_3)$). X-ray crystal structure analysis for **24d**: formula $C_{29}H_{45}N_5Zr$, $M = 544.92$, yellow crystal $0.35 \times 0.30 \times 0.20$ mm, $a = 11.7708(1)$, $b = 17.4066(2)$, $c = 18.4855(1)$ Å, $\beta = 128.624(1)°$, $V = 2959.01(5)$ Å^3, $\rho_{calc} = 1.246$ g cm^{-3}, $\mu = 0.396$ mm^{-1}, empirical absorption correction ($0.874 \leqslant T \leqslant 0.925$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 20000 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å^{-1}, 7216 independent ($R_{int} = 0.034$) and 6114 observed reflections [$I \geqslant 2\sigma(I)$], 338 refined parameters, $R = 0.043$, $wR^2 = 0.107$, C8 refined with split positions to a ratio of 0.73(1) to 0.27, max. residual electron density 0.63 (-0.62) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of 24e. The reaction of **22a** (212 mg, 0.72 mmol) with $Zr(NMe_2)_4$ (203 mg, 0.76 mmol) in toluene (5 ml) yielded the product as a yellow solid (298 mg, 79%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **24e** in toluene. M.p. 186 °C (DSC). Anal. Calc. for $C_{26}H_{45}N_5Zr$: C, 60.18; H, 8.74; N, 13.50; Found: C, 60.01; H, 8.81; N, 13.10%. ^{1}H NMR (599.8 MHz, [D$_8$]-THF, 298 K): $\delta = 8.41$ (ddd, $^3J = 5.4$ Hz, $^4J = 1.8$ Hz, $^5J = 1.0$ Hz, 1H, 6-H^{Py}), 7.92 (ddd, $^3J = 8.1$ Hz, $^3J = 7.4$ Hz, $^4J = 1.8$ Hz, 1H, 4-H^{Py}), 7.64 (dt, $^3J = 8.1$ Hz, $^4J = {}^5J = 1.0$ Hz, 1H, 3-H^{Py}), 7.40 (ddd, $^3J = 7.4$ Hz, $^3J = 5.4$ Hz, $^4J = 1.0$ Hz, 1H, 5-H^{Py}), 7.15 (m, 2H, 3-H^{Ar}), 7.04 (m, 1H, 4-H^{Ar}), 3.51 (sept, $^3J = 6.8$ Hz, 2H, $CH(CH_3)_2$), 2.63 (br, 18H, $N(CH_3)_2$), 1.39 (s, 6H, $NC(CH_3)_2$), 1.22 (d, $^3J = 6.8$ Hz, 6H, $CH(CH_3^ACH_3^B)$), 1.16 (d, $^3J = 6.8$ Hz, 6H, $CH(CH_3^ACH_3^B)$). ^{13}C{^{1}H} NMR (150.8 MHz, [D$_8$]-THF, 298 K): $\delta = 173.3$ (C2^{Py}), 149.8 (C2^{Ar}), 148.4 (C6^{Py}), 144.2 (C1^{Ar}), 139.0 (C4^{Py}), 125.4 (C4^{Ar}), 124.6 (C3^{Ar}), 122.6 (C5^{Py}), 121.7 (C3^{Py}), 70.9 ($NC(CH_3)_2$), 43.9 ($N(CH_3)_2$), 31.6 ($NC(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 25.4 ($CH(CH_3^ACH_3^B)$), 24.9 ($CH(CH_3^ACH_3^B)$). X-ray crystal structure analysis for **24e**: formula $C_{26}H_{45}N,Zr$, $M = 518.89$, colorless crystal $0.60 \times 0.50 \times 0.40$ mm, $a = 9.179(1)$, $b = 9.324(2)$, $c = 17.498(1)$ Å, $\alpha = 100.75(1)$, $\beta = 97.31(1)$, $\gamma = 102.77(2)°$, $V = 1412.5(2)$ Å^3, $\rho_{calc} = 1.220$ g cm^{-3}, $\mu = 0.410$ mm^{-1}, empirical absorption correction ($0.791 \leqslant T \leqslant 0.853$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223$ K, ω and ϕ scans, 14891 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å^{-1}, 6829 independent ($R_{int} = 0.035$) and 6129 observed reflections [$I \geqslant 2\sigma(I)$], 301 refined parameters, $R = 0.032$, $wR^2 = 0.082$, max. residual electron density 0.43 (-0.55) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of 24f. The reaction of **20b** (313 mg, 0.96 mmol) with $Zr(NMe_2)_4$ (268 mg, 1.00 mmol) in toluene (10 ml) yielded the product as a bright yellow solid (465 mg, 89%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **24f** in toluene. M.p. 177 °C (DSC). Anal. Calc. for $C_{28}H_{49}N_5Zr$: C, 61.49; H, 9.03; N, 12.80; Found: C, 61.19; H, 9.08; N, 12.53%. ^{1}H NMR (599.8 MHz, [D$_8$]-THF, 298 K): $\delta = 7.85$ (t, $^3J = 7.8$ Hz, 1H, 4-H^{Py}), 7.40 (d, $^3J = 7.8$ Hz, 1H, 5-H^{Py}), 7.34 (d, $^3J = 7.8$ Hz, 1H, 3-H^{Py}), 7.07 (dd, $^3J = 7.6$ Hz, $^4J = 1.7$ Hz, 1H, 3′-H^{Ar}), 7.05 (dd, $^3J = 7.6$ Hz, $^4J = 1.7$ Hz, 1H, 3-H^{Ar}), 6.95 (t, $^3J = 7.6$ Hz, 1H, 4-H^{Ar}), 4.74 (q, $^3J = 6.7$ Hz, 1H, $NCH(CH_3)$), 3.76 (sept, $^3J = 6.8$ Hz, 1H, $CH(CH_3)_2'^{Ar}$), 3.46 (sept, $^3J = 6.9$ Hz, 1H, $CH(CH_3)_2^{Py}$), 3.30 (sept, $^3J = 6.8$ Hz, 1H, $CH(CH_3)_2^{Ar}$), 3.04 (br, 6H, $N(CH_3)_2^A$), 2.63 (br, 6H, $N(CH_3)_2^B$), 2.43 (br, 6H, $N(CH_3)_2^C$), 1.31 (d, $^3J = 6.9$ Hz, 3H, $CH(CH_3^ACH_3^B)^{Py}$), 1.28 (d, $^3J = 6.7$ Hz, 3H, $NCH(CH_3)$), 1.26 (d, $^3J = 6.8$ Hz, 3H, $CH(CH_3^ACH_3^B)'^{Ar}$), 1.24 (d, $^3J = 6.8$ Hz, 3H, $CH(CH_3^ACH_3^B)^{Ar}$), 1.23 (d,

$^3J = 6.8$ Hz, 3H, CH($CH_3^ACH_3^B$)^{Ar}), 1.22 (d, $^3J = 6.9$ Hz, 3H, CH($CH_3^ACH_3^B$)^{Py}), 1.18 (d, $^3J = 6.8$ Hz, 3H, CH($CH_3^ACH_3^B$)$^{\prime Ar}$). $^{13}C\{^1H\}$ NMR (150.8 MHz, [D$_8$]-THF, 298 K): $\delta = 170.2$ (C6^{Py}), 168.7 (C2^{Py}), 148.8 (C1^{Ar}), 147.1 (C2$'^{Ar}$), 145.8 (C2^{Ar}), 139.1 (C4^{Py}), 124.4 (C4^{Ar}), 124.1 (C3^{Ar}), 123.9 (C3$'^{Ar}$), 120.1 (C3^{Py}), 119.7 (C5^{Py}), 70.0 (NCH(CH$_3$)), 44.4 (N(CH_3)$_2^C$), 43.7 (N(CH_3)$_2^B$), 42.4 (N(CH_3)$_2^A$), 35.8 ($CH(CH_3)_2^{Py}$), 28.6 ($CH(CH_3)_2^{\prime Ar}$), 28.3 ($CH(CH_3)_2^{Ar}$), 27.2 (CH(CH_3^ACH$_3^B$)^{Ar}), 25.8 (CH($CH_3^ACH_3^B$)^{Py}), 25.7 (CH(CH_3^ACH$_3^B$)$^{\prime Ar}$), 25.3 (NCH(CH_3)), 24.8 (CH($CH_3^ACH_3^B$)^{Ar}), 24.7 (CH($CH_3^ACH_3^B$)$^{\prime Ar}$), 23.1 (CH($CH_3^ACH_3^B$)^{Py}). X-ray crystal structure analysis for **24f**: formula $C_{28}H_{49}N_5Zr$, $M = 546.94$, colorless crystal $0.10 \times 0.10 \times 0.03$ mm, $a = 9.1486(2)$, $b = 9.2655(2)$, $c = 18.5008(8)$ Å, $\alpha = 84.608(1)$, $\beta = 80.723(1)$, $\gamma = 75.628(1)°$, $V = 1496.91(8)$ Å^3, $\rho_{calc} = 1.213$ g cm^{-3}, $\mu = 0.390$ mm^{-1}, empirical absorption correction ($0.962 \leqslant T \leqslant 0.988$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 14004 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 5369 independent ($R_{int} = 0.044$) and 4604 observed reflections [$I \geqslant 2\sigma(I)$], 320 refined parameters, $R = 0.041$, $wR^2 = 0.085$, max. residual electron density 0.41 (−0.41) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of 25a. The reaction of **18a** (182 mg, 0.69 mmol) with Hf(NMe$_2$)$_4$ (255 mg, 0.72 mmol) in toluene (25 ml) yielded the product as a bright yellow solid (310 mg, 78%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **25a** in toluene. Anal. Calc. for $C_{24}H_{41}N_5Hf$: C, 49.86; H, 7.15; N, 12.11; Found: C, 49.19; H, 7.13; N, 11.57%. ^1H NMR (599.8 MHz, [D$_8$]-THF, 298 K): $\delta = 8.39$ (ddd, $^3J = 5.5$ Hz, $^4J = 1.6$ Hz, $^5J = 0.9$ Hz, 1H, 6-H^{Py}), 7.91 (ddd, $^3J = 7.9$ Hz, $^3J = 7.4$ Hz, $^4J = 1.6$ Hz, 1H, 4-H^{Py}), 7.52 (dd, $^3J = 7.9$ Hz, $^4J = 0.9$ Hz, 1H, 3-H^{Py}), 7.42 (ddd, $^3J = 7.4$ Hz, $^3J = 5.5$ Hz, $^4J = 0.9$ Hz, 1H, 5-H^{Py}), 7.06 (m, 2H, 3-H^{Ar}), 6.95 (m, 1H, 4-H^{Ar}), 4.93 (s, 2H, NCH_2), 3.50 (sept, $^3J = 6.9$ Hz, 2H, CH(CH$_3$)$_2$), 2.85 (12H), 2.51 (6H) (each br, N(CH_3)$_2$), 1.26 (d, $^3J = 6.9$ Hz, 6H, CH($CH_3^ACH_3^B$)), 1.17 (d, $^3J = 6.9$ Hz, 6H, CH($CH_3^ACH_3^B$)). $^{13}C\{^1H\}$ NMR (150.8 MHz, [D$_8$]-THF, 298 K): $\delta = 164.8$ (C2^{Py}), 150.3 (C1^{Ar}), 148.6 (C6^{Py}), 146.0 (C2^{Ar}), 138.6 (C4^{Py}), 124.3 (C4^{Ar}), 123.5 (C3^{Ar}), 123.0 (C5^{Py}), 122.0 (C3^{Py}), 66.4 (NCH_2), 43.9, 43.1 (each br, N(CH_3)$_2$), 28.6 ($CH(CH_3)_2$), 27.1 (CH($CH_3^ACH_3^B$)), 24.2 (CH($CH_3^ACH_3^B$)). X-ray crystal structure analysis for **25a**: formula $C_{24}H_{41}HfN_5$, $M = 578.11$, colorless crystal $0.40 \times 0.30 \times 0.15$ mm, $a = 8.8170(2)$, $b = 9.5686(2)$, $c = 17.1548(5)$ Å, $\alpha = 97.262(1)$, $\beta = 104.504(1)$, $\gamma = 105.248(1)°$, $V = 1322.88(6)$ Å^3, $\rho_{calc} = 1.451$ g cm^{-3}, $\mu = 3.961$ mm^{-1}, empirical absorption correction ($0.300 \leqslant T \leqslant 0.588$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 13619 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å^{-1}, 6416 independent ($R_{int} = 0.045$) and 5534 observed reflections [$I \geqslant 2\sigma(I)$], 282 refined parameters, $R = 0.034$, $wR^2 = 0.080$, max. residual electron density 2.97 (−1.85) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of 25b. The reaction of **18c** (151 mg, 0.40 mmol) with Hf(NMe$_2$)$_4$ (156 mg, 0.44 mmol) in toluene (7 ml) yielded the product as a white solid (185 mg, 68%). Anal. Calc. for $C_{32}H_{57}N_5Hf$: C, 55.68; H, 8.32; N, 10.15; Found: C, 54.49; H, 8.09; N, 8.91%. ^1H NMR (599.8 MHz, [D$_8$]-THF, 298 K): $\delta = 7.53$ (d, $^4J = 1.9$ Hz, 1H, 5-H^{Py}), 7.19 (d, $^4J = 1.9$ Hz, 1H, 3-H^{Py}), 7.07 (ps d, 2H, 3-H^{Ar}), 6.92 (ps t, 1H, 4-H^{Ar}), 4.76 (s, 2H, NCH_2), 3.62 (sept, $^3J = 6.8$ Hz, 2H, CH(CH$_3$)$_2$), 2.67 (br, 18H, N(CH_3)$_2$), 1.46 (s, 9H, 6-C(CH_3)$_3$), 1.32 (s, 9H, 4-C(CH_3)$_3$), 1.28 (d, $^3J = 6.8$ Hz, 6H, CH(CH_3^ACH$_3^B$)), 1.17 (d, $^3J = 6.8$ Hz, 6H, CH(CH_3^ACH_3^B)). $^{13}C\{^1H\}$ NMR (150.8 MHz, [D$_8$]-THF, 298 K): $\delta = 172.9$ (C6^{Py}), 163.8 (C2^{Py}), 162.5 (C4^{Py}), 151.3 (C1^{Ar}), 145.6 (C2^{Ar}), 124.2 (C4^{Ar}), 123.4 (C3^{Ar}), 118.3 (C5^{Py}), 117.2 (C3^{Py}), 65.9 (NCH_2), 43.0 (N(CH_3)$_2$), 39.3 (6-C(CH$_3$)$_3$), 35.5 (4-C(CH$_3$)$_3$), 30.41 (4-C(CH_3)$_3$), 30.37 (6-C(CH_3)$_3$), 28.6 ($CH(CH_3)_2$), 27.0 (CH(CH_3^ACH$_3^B$)), 24.1 (CH($CH_3^ACH_3^B$)).

Preparation of 25c. The reaction of **19a** (227 mg, 0.80 mmol) with Hf(NMe$_2$)$_4$ (312 mg, 1.19 mmol) in toluene (10 ml) yielded the product as a white solid (420 mg, 89%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **25c** in toluene. M.p. 173 °C (DSC). Anal. Calc. for $C_{25}H_{43}N_5Hf$: C, 50.71; H, 7.32; N, 11.83; Found: C, 50.35; H, 7.35; N, 11.28%. ^1H NMR (599.8 MHz, [D$_8$]-THF, 298 K): $\delta = 8.37$ (ddd, $^3J = 5.4$ Hz, $^4J = 1.7$ Hz, $^5J = 0.9$ Hz, 1H, 6-H^{Py}), 7.95 (ddd, $^3J = 8.0$ Hz, $^3J = 7.5$ Hz, $^4J = 1.7$ Hz, 1H, 4-H^{Py}), 7.61 (ddd, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, $^5J = 0.9$ Hz, 1H, 3-H^{Py}), 7.44 (ddd, $^3J = 7.5$ Hz, $^3J = 5.4$ Hz, $^4J = 1.6$ Hz, 1H, 5-H^{Py}), 7.09 (dd, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz, 1H, 3-H^{Ar}), 7.06 (dd, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz, 1H, 3′-H^{Ar}), 6.97 (t, $^3J = 7.6$ Hz, 1H, 4-H^{Ar}), 4.94 (q, $^3J = 6.8$ Hz, 1H, NCH(CH$_3$)), 3.68 (sept, $^3J = 6.9$ Hz, 1H, CH(CH$_3$)$_2$), 3.27 (sept, $^3J = 6.9$ Hz, 1H, CH(CH$_3$)$_2'$), 2.70 (br, 18H, N(CH_3)$_2$), 1.27 (d, $^3J = 6.8$ Hz, 3H, NCH(CH_3)), 1.22 (d, $^3J = 6.9$ Hz, 3H, CH(CH_3^ACH$_3^B$)′), 1.215 (d, $^3J = 6.9$ Hz, 3H, CH(CH_3^ACH_3^B)′), 1.20 (d, $^3J = 6.9$ Hz, 3H, CH(CH_3^ACH$_3^B$)), 1.16 (d, $^3J = 6.9$ Hz, 3H, CH(CH_3^ACH_3^B)). $^{13}C\{^1H\}$ NMR (150.8 MHz, [D$_8$]-THF, 298 K): $\delta = 169.2$ (C2^{Py}), 148.5 (C6^{Py}), 148.0 (C2^{Ar}), 147.8 (C1^{Ar}), 146.3 (C2$'^{Ar}$), 138.9 (C4^{Py}), 124.6 (C4^{Ar}), 124.1 (C3$'^{Ar}$), 124.0 (C3^{Ar}), 123.2 (C5^{Py}), 122.6 (C3^{Py}), 69.9 (NCH(CH$_3$)), 43.5 (br, N(CH_3)$_2$), 28.6 ($CH(CH_3)_2$), 28.3 CH(CH_3)$_2'$), 27.0 (CH(CH_3^ACH$_3^B$)′), 25.3 (CH(CH_3^ACH$_3^B$)), 24.5 (CH(CH_3^ACH$_3^B$)′), 24.3 (CH($CH_3^ACH_3^B$)), 23.6 (NCH(CH_3)). X-ray crystal structure analysis for **25c**: formula $C_{25}H_{43}HfN_5$, $M = 592.13$, colorless crystal $0.30 \times 0.15 \times 0.10$ mm, $a = 8.9470(2)$, $b = 9.4417(2)$, $c = 17.2841(6)$ Å, $\alpha = 101.512(1)$, $\beta = 95.954(1)$, $\gamma = 103.489(2)°$, $V = 1373.82(6)$ Å^3, $\rho_{calc} = 1.431$ g cm^{-3}, $\mu = 3.816$ mm^{-1}, empirical absorption correction ($0.394 \leqslant T \leqslant 0.702$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 12583 reflections collected

($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.67 Å^{-1}, 6617 independent (R_{int} = 0.036) and 5968 observed reflections [$I \geqslant 2\sigma(I)$], 191 refined parameters, R = 0.027, wR^2 = 0.065, max. residual electron density 1.59 (−1.75) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of 25f. The reaction of **20b** (186 mg, 0.57 mmol) with $Hf(NMe_2)_4$ (224 mg, 0.63 mmol) in toluene (10 ml) yielded the product as a white solid (260 mg, 72%). Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **24f** in toluene. M.p. 190 °C (DSC). Anal. Calc. for $C_{28}H_{49}N_5Hf$: C, 53.02; H, 7.79; N, 11.04; Found: C, 52.60; H, 7.81; N, 10.80%. ^{1}H-NMR (599.8 MHz, [D$_8$]-THF, 298 K): δ = 7.88 (t, ^3J = 7.8 Hz, 1H, 4-H^{Py}), 7.43 (d, ^3J = 7.8 Hz, 1H, 5-H^{Py}), 7.36 (d, ^3J = 7.8 Hz, 1H, 3-H^{Py}), 7.09 (dd, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 1H, 3-H^{Ar}), 7.06 (dd, ^3J = 7.6 Hz, ^3J = 1.7 Hz, 1H, 3′-H^{Ar}), 6.95 (t, ^3J = 7.6 Hz, 1H, 4-H^{Ar}), 4.88 (q, ^3J = 6.7 Hz, 1H, NCH(CH$_3$)), 3.76 (sept, ^3J = 6.8 Hz, 1H, CH(CH$_3$)$_2^{Ar}$), 3.59 (sept, ^3J = 6.8 Hz, 1H, CH(CH$_3$)$_2^{Py}$), 3.30 (sept, ^3J = 6.8 Hz, 1H, CH(CH$_3$)$_2^{′Ar}$), 3.03 (s, 6H, N(CH_3)$_2^{A}$), 2.65 (s, 6H, N(CH_3)$_2^{B}$), 2.47 (s, 6H, N(CH_3)$_2^{C}$), 1.32 (d, ^3J = 6.8 Hz, 3H, CH(CH_3^{A}CH$_3^{B}$)^{Py}), 1.273 (d, ^3J = 6.7 Hz, 3H, NCH(CH_3)), 1.269 (d, ^3J = 6.8 Hz, 3H, CH(CH_3^{A}CH$_3^{B}$)^{Ar}), 1.24 (d, ^3J = 6.8 Hz, 9H, CH(CH$_3^{A}$CH_3^{B})^{Py}, CH(CH_3^{A}CH$_3^{B}$)$^{′Ar}$, CH(CH$_3^{A}$CH_3^{B})$^{′Ar}$), 1.18 (d, ^3J = 6.8 Hz, 3H, CH(CH$_3^{A}$CH_3^{B})^{Ar}). ^{13}C{^{1}H}-NMR (150.8 MHz, [D$_8$]-THF, 298 K): δ = 170.4 (C6^{Py}), 168.7 (C2^{Py}), 148.8 (C1^{Ar}), 147.3 (C2^{Ar}), 146.0 (C2′^{Ar}), 139.2 (C4^{Py}), 124.4 (C4^{Ar}), 124.0 (C3′^{Ar}), 123.9 (C3^{Ar}), 120.2 (C3^{Py}), 120.1 (C5^{Py}), 69.6 (NCH(CH$_3$)), 44.3 (N(CH_3)$_2^{C}$), 43.5 (N(CH_3)$_2^{B}$), 42.3 (N(CH_3)$_2^{A}$), 35.6 (CH(CH$_3$)$_2^{Py}$), 28.5 (CH(CH$_3$)$_2^{Ar}$), 28.2 (CH(CH$_3$)$_2^{′Ar}$), 27.4 (CH(CH_3^{A}CH$_3^{B}$)$^{′Ar}$), 25.9 (CH(CH$_3^{A}$CH_3^{B})^{Py}), 25.7 (CH(CH_3^{A}CH_3^{B})^{Ar}), 25.4 (NCH(CH_3)), 24.9 (CH(CH_3^{A}CH$_3^{B}$)^{Ar}), 24.8 (CH(CH$_3^{A}$CH_3^{B})$^{′Ar}$), 23.3 (CH(CH_3^{A}CH$_3^{B}$)^{Py}). X-ray crystal structure analysis for **25f**: formula $C_{28}H_{49}HfN_5$, M = 634.21, colorless crystal 0.20 × 0.12 × 0.06 mm, a = 9.1712(2), b = 9.2615(2), c = 18.5057(5) Å, α = 84.495(1), β = 80.958(1), γ = 75.169(1)°, V = 1498.05(6) Å^3, ρ_{calc} = 1.406 g cm^{-3}, μ = 3.505 mm^{-1}, empirical absorption correction (0.541 ⩽ T ⩽ 0.817), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and ϕ scans, 14 133 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.66 Å^{-1}, 7080 independent (R_{int} = 0.058) and 6140 observed reflections [$I \geqslant 2\sigma(I)$], 321 refined parameters, R = 0.037, wR^2 = 0.086, max. residual electron density 1.47 (−1.60) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

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Appendix A. Supplementary material

CCDC 658274, 658275, 658276, 658277, 658278, 658279, 658280, 658281, 658282, 658283, 658284, 658285, 658286, 658287, 658288 and 658289 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.12.004.

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