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ARTICLE

Pyridylamido Hafnium Complexes with the Silylene Bridge: Synthesis and Olefin Polymerization†

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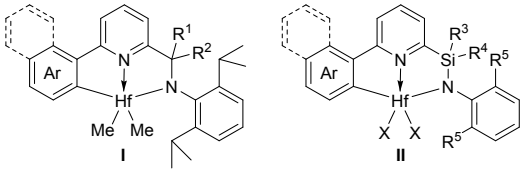
The synthesis and characterisation of six novel C_s-symmetric pyridylamido hafnium complexes with silylene bridge of the type [ArPy(R_2Si)NAr']HfAlk_2 is reported. Four complexes have been structurally characterised using single crystal X-ray diffraction. Appreciable diffirences between solid state structures of these complexes and the pyridylamido hafnium complexes with CRR' bridge were noted. Reactions with $[Ph_3C][B(C_6F_5)_4]$ and $[HMe_2NPh][B(C_6F_5)_4]$ yielded catalysts active for the homopolymerisations of propene and 1-hexene and ethene/1-octene copolymerization. In spite of C_s-symmetry of the precatalysts, isotactically enriched polypropylene and poly(1-hexene) were obtained. The fact that mechanism of the catalyst activation includes insertion of alkene into the Hf-C_{Ar} bond was demonstrated. It was found that the structure of Ar and R_2Si bridge influence, activity, molecular weight capability and 1-hexene affinity of the catalyst.

Introduction

Polyolefins are among the most important products of chemical industry with production of 178 million tons in 2015.[1] Free-radical processes are used to produce less than 20% of these polyolefins, with the bulk being produced in processes using coordinative olefin polymerization catalysts. Traditional Ziegler-Natta catalysts dominate polyolefin production in terms of volume, but the use of single-site catalysts continues to be of great interest due to the ability of such catalysts to control the molecular architecture (e.g. molecular weight distribution (MWD), compositional distribution, long chain branching, sequence distribution) of a polymer chain.[2]

One of the notable examples of success in the field of single-site olefin polymerization catalysis are the Symyx-Dow pyridylamido hafnium catalysts of type **I** (Fig. 1), which were discovered and developed using high throughput screening technologies.[3,4] These catalysts were reported to produce high MW isotactic polypropylene with T_m≈150 °C at process temperatures above 100 °C. It should be noted that the two *ortho*-isopropyl substituents of the aniline moiety are necessary to achieve the combination of high activity and MW capability at a high process temperature.[4] Additionally, pyridylamido hafnium catalysts have been shown to be excellent incorporators of higher α-olefins in ethylene/1-hexene and ethylene/1-octene copolymerizations in solution at high temperature.[5] These catalysts have also been used to produce olefin block copolymers through chain shuttling polymerization.[6]



Ia, $R^1 = R^2$ = H, Ar = Ph
Ib, R^1 = 2-*i*PrPh, R^2 = H, Ar = 1-Napht
Ic, $R^1 = R^2$ = Me, Ar = 1-Napht
Id, $R^1 = R^2$ = Me, Ar = Ph

Figure 1. Pyridylamido hafnium precatalysts with C-bridge (**I**) and Si-bridge (**II**)

A critical structural feature of pyridylamido hafnium precatalysts **I** is *ortho*-metalation of the aryl moiety at the pyridyl ring. Based on computational and experimental studies, it was found, that, upon activation of **I**, the resulting cation inserts one molecule of an olefin into the Hf-aryl bond.[7,8,9] Due to this modification of the ligand *in situ*, even initially C_s-symmetrical complexes of structure **I**, where R^1=R^2, upon activation with $B(C_6F_5)_3$ are able to produce isoenriched poly(1-hexene) and polypropylene.[10] The *in situ* ligand modification, however, can form a mixture of active catalysts, which generally leads to a broadening of MWD and compositional distribution in the (co)polymer produced.

The performance of pyridylamido hafnium catalysts in polymerization significantly depends on the substitution at the C-bridge (R^1 and R^2 in **I**) between the pyridine and the aniline fragments. For example, catalyst derived from complex **Ia** (Fig. 1) produced polypropylene with [*mmmm*]=56%, M_w=72 kDa and PDI=1.05 in solution polymerization at 20 °C,[10] whereas catalyst **Ib** (Fig. 1) gives polypropylene with [*mmmm*]=94%, M_w=198 kDa and PDI=3.0 in solution polymerization even at 90 °C.[5] The bulky substituent at the C-bridge seems to be necessary for high stereoselectivity. It also appears to improve

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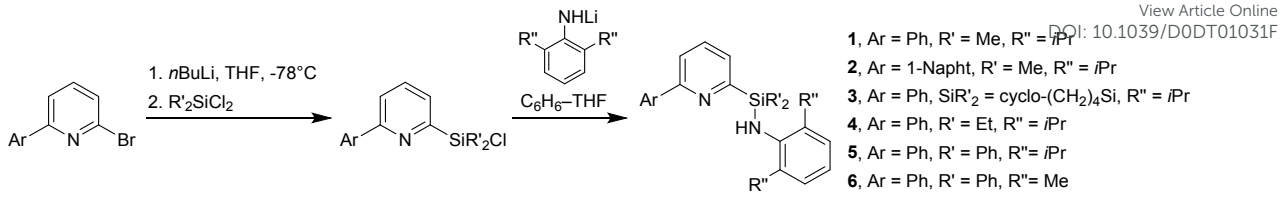


Scheme 1. Synthesis of pro-ligands **1**-**6** for pyridylamido hafnium precatalysts

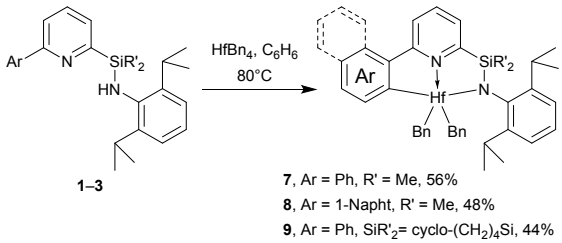
catalyst activity and MW capability in high temperature polymerization.[4c] Recently, it was reported that C_s-symmetric complex **Ic** (Fig. 1) upon activation with $B(C_6F_5)_3$ produces polypropylene with [*mmmm*]=91%, M_w=319 kDa and PDI=1.2 in solution polymerization at 20 °C.[11] It was found that the C-bridge substituents R^1 and R^2 affect the C(Py)-C(bridge)-N(aniline) angle thereby pushing the *ortho* substituents at the aniline moiety closer to the metal, and thus influencing the stereoselectivity and living behavior of the catalyst.[11] Since the development of pyridylamido hafnium catalysts, many analogous complexes have been synthesized and tested in olefin polymerization. The examples of variation of the structure include installation of different alkyl or aryl groups at the C-bridge and *ortho*-positions of the aniline moiety, or replacement of phenyl or naphtyl groups at the pyridine with heteroaryls.[4,10–13] We assumed that change of the C-bridge in **I** to the Si-bridge also might significantly modifies the geometry of the pyridylamido hafnium complexes and, consequently, change the polymerization performance of the respective catalysts. Herein, we report synthesis of novel pyridylamido hafnium complexes of type **II** (Fig. 1) and the results of their tests as olefin polymerization precatalysts. The effects of substituents R^3, R^4 and R^5 as well as aryl group at the pyridyl ring on activity, molecular weight capability and comonomer affinity of the generated catalysts were studied.

Results and Discussions

Synthesis of complexes

Synthesis of pro-ligands for the desired Si-bridged pyridylamido hafnium complexes was achieved using a simple two-step method from readily available 6-phenyl- and 2-bromo-6-(1-naphtyl)pyridines (Scheme 1). The first step of the technique was reaction of the lithiated pyridines with various dichlorodialkylsilanes or dichlorodiphenylsilane. The reactions proceeded in almost quantitative yields, and the resultant chlorosilanes were used in the next step without any additional purification. The choice of substitution on the dichlorosilanes was dictated by our desire to explore the influence of sterics at the Si-bridge on the polymerization performance of the respective catalysts. In the second step of the ligand synthesis the (2-pyridyl)chlorosilanes were combined with lithium anilides in benzene. A drop of tetrahydrofuran (THF) was added to the stirring mixtures to aid the dissolution of the lithium reagents. The reactions produced the desired pyridylamines in almost quantitative yields and good purity, which allowed the skipping of purification before synthesis of complexes. Five pyridylamine pro-ligands were prepared from the lithium salt of 2,6-diisopropylaniline and one from lithium 2,6-dimethylanilide. The latter was used for synthesis of pyridylamine pro-ligand **6** to test whether isopropyl groups in *ortho* positions of the aniline moiety are still necessary to achieve high activity and molecular weight capability if the corresponding catalyst contains the bulky Ph_2Si bridge. The two-step sequence we used is shorter than the method used to synthesize C-bridged pro-ligands for hafnium complexes (such as **I**) from 6-aryl-2-bromopyridines.[4] Moreover, this synthetic route led to excellent yields of the desired pro-ligands without any purification, which is not generally the case in the synthesis of the related carbon-bridged pyridylamine pro-ligands.

Syntheses of complexes **7**–**9** were performed by reaction of pro-ligands **1**–**3** with tetrabenzylhafnium in benzene overnight at 80 °C (Scheme 2). All three products were crystallized from toluene/hexane mixture and were isolated in good yields (44–56%). The ^{13}C NMR spectra for each of these complexes contained a downfield resonance at 201.2–204.2 ppm which is consistent with *ortho*-metalation of the aryl group at pyridine.[8] Surprisingly, this synthetic method did not work in case of pro-ligands **4**–**6**, and only starting compounds were observed in the reaction mixture. Perhaps, the aminogroups in **4**–**6** are less reactive toward tetrabenzylhafnium due to the relatively large Et_2Si and Ph_2Si bridges in these ligands. Interestingly, the cyclo$(CH_2)_4Si$ bridge in **3** did not hinder reaction of the pro-ligand with $HfBn_4$, whereas the Et_2Si-bridge in **4** suppressed the reaction completely.



Scheme 2. Synthesis of pyridylamido hafnium precatalysts **7**–**9**.

For synthesis of Si-bridged pyridylamido hafnium precatalysts from pyridylamines **4**–**6**, an alternative approach was applied. First, pro-ligands **4**–**6** were reacted with dibenzylhafnium dichloride etherate ($Hf_2Bn_2Cl_2(Et_2O)_2$) in benzene overnight at 80 °C followed by methylation of the resultant dichloride complexes with MeMgBr in toluene at 70 °C (Scheme 3). The target complexes **10**-**12** were obtained in 19-52% isolated yields; the lower isolated yields are attributed to the higher solubility of the products in hydrocarbon solvents. Formation of

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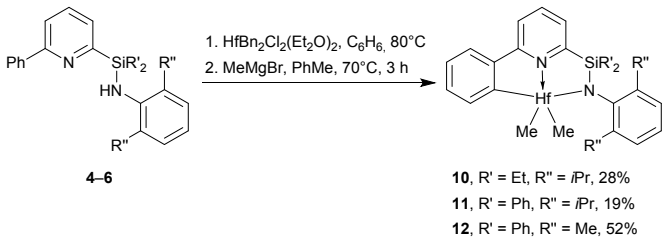

Scheme 3. Synthesis of pyridylamido hafnium precatalysts **10–12**.

the Hf-phenyl bond in **10–12** was confirmed by the presence of resonances at 202.0–202.4 ppm in the ^{13}C NMR spectra of **10–12**.[8]

Single-crystal X-ray structures

Solid-state structures were obtained for four complexes (**7**, **8**, **9** and **11**) via single crystal X-ray analysis. Thermal ellipsoid diagrams and selected metrical parameters are presented in Figures 2–5. Although these complexes exhibit C_s symmetry in solution as evidenced by ^1H NMR spectroscopy, in the solid state all of them adopt distorted square-pyramidal geometry with one benzyl or methyl group situated in the apical position. Bond distances associated with the chelate ligand skeleton showed little variation throughout the series. For example, the Hf-N(Py) bond distance only varied from 2.307 to 2.349 Å, and the Hf-N(aniline) distances appear in the similarly small range 2.094–2.119 Å. The Hf-C(phenyl/naphthyl) distances range within 2.266-2.312 Å, with the shortest and longest distances observed for **11** and **8**, respectively. Interestingly, hafnium atom does not lie in the (C,N,N)-plane of the chelate ligands while in the described complexes of type **I** it does.[5,11] The distance between Hf and (C,N,N)-plane varies from 0.474 Å for **11** to 0.726 Å for **8**. Bond distances in Si- bridge of complexes-**7–9** and **11** Si-C(Py) (1.884–1.892 Å) and Si-N(aniline) (1.7203–1.736 Å) are significantly longer compared to the C(bridge)-C(Py) (1.469–1.518 Å) and C(bridge)-C(aniline) (1.438–1.489 Å) in C_s-symmetric pyridylamido hafnium complexes with C-bridge.[11] The longer bonds in the silicon bridge make the C-Si-N angle remarkably smaller (99.18–100.15°) than the respective C-C-N angle in the C-bridged complexes (106.50–111.48°)[11] and the angle in a perfect tetrahedron 109.47°. The smaller angle in Si-bridge leads to the strain in molecules of complexes which results in the longer Hf-N(Py) and Hf-N(aniline) (*vide supra*) bond distances compared to those for C-bridged analogues (for complexes **I** Hf-N(Py): 2.280–2.308 Å and Hf-N(aniline): 2.067–2.089 Å).[11] Also it is interesting to compare complexes **8** and **Ic** (Fig. 1). In the solid state, **8** exhibits a torsion angle between *ortho*-metalated naphtalene and pyridine of 27.7° (Figure 3) which is significantly larger than the respective torsion angle in **Ic** (16.5°).[11]

For complexes **7–9** the Hf-C(Bn_a) bond distance (2.222–2.228 Å) between hafnium and carbon atom of the apical benzyl is slightly shorter than the Hf-C(Bn_b) distance between the metal

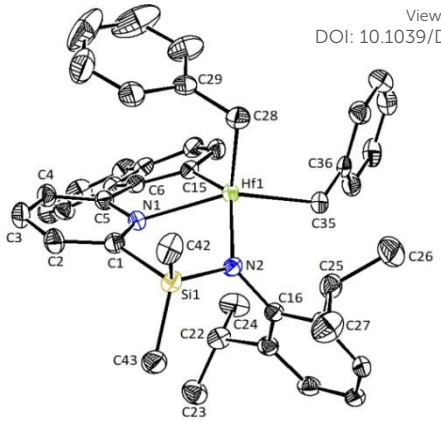

Figure 3. Molecular structure for **8**. Hydrogen atoms were removed for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°): Hf1–N1 = 2.307(2), Hf1-N2 = 2.096(2), Hf1-C15 = 2.312(3), Hf1-C28 = 2.224(3), Hf1-C35 = 2.257(2), Si1-N2 =1.736(2), Si1-C1 = 1.892(3), Si1-C42 = 1.865(3), Si1-C43 = 1.852(3); N1-Hf1-N2 = 77.44(7), C15-Hf1-N1 = 70.37(8), C28-Hf1-N1 = 106.48(9), C28-Hf1-C35 = 101.36(10), C1-Si1-N2 = 99.78(11), C42-Si1-C43 = 108.75(14).

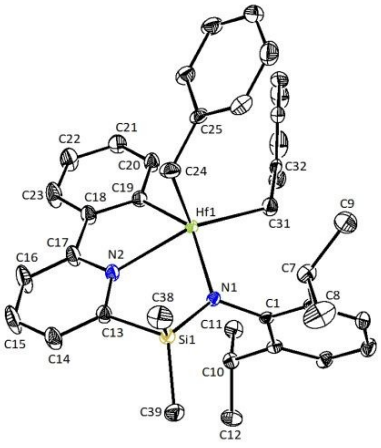

Figure 2. Molecular structure for **7**. Hydrogen atoms were removed for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°): Hf1-N2 = 2.3333(18), Hf1–N1 = 2.0946(17), Hf1-C19 = 2.294(2), Hf1-C24 = 2.222(2), Hf1-C31 = 2.253(2), Si1-N1 = 1.7285(18), Si1-C13 = 1.888(2), Si1-C38 = 1.873(2), Si1-C39 = 1.860(2); N1-Hf1-N2 = 77.17(6), C19-Hf1-N2 = 70.71(7), C24-Hf1-N2 = 94.26(8), C24-Hf-C31 = 110.33(9), C13-Si1-N1 = 99.18(9), C38-Si1-C39 = 107.45(12).

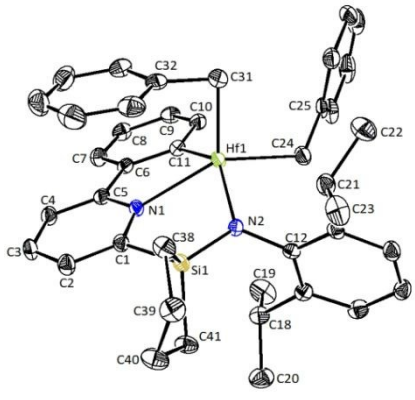

Figure 4. Molecular structure for **9**. Hydrogen atoms were removed for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°): Hf1–N1 = 2.323(2), Hf1-N2 = 2.119(2), Hf1-C11 = 2.277(3), Hf1-C31 = 2.228(3), Hf1-C24 = 2.254(3), Hf1-C32 = 2.710(3), Si1-N2 = 1.728(2), Si1-C1 = 1.884(3), Si1-C38 = 1.890(3), Si1-C41 = 1.892(3); N1-Hf1-N2 = 77.46(8), C11-Hf1-N1 = 70.93(9), C31-Hf1-N1 = 115.99(9), C31-Hf1-C24 = 98.13(11), Hf1-C31-C32 = 91.58(17), C1-Si1-N2 = 100.15(11), C38-Si1-C41 = 95.25(13).

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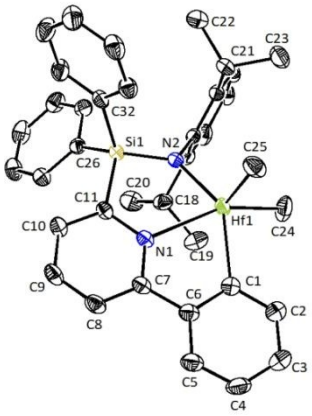

Figure 5. Molecular structure for **11**. Hydrogen atoms were removed for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°): Hf1–N1 = 2.3490(15), Hf1-N2 = 2.0995(15), Hf1-C1 = 2.266(2), Hf1-C24 = 2.226(2), Hf1-C25 = 2.216(2), Si1-N2 = 1.7203(16), Si1-C11 = 1.8876(18), Si1-C26 = 1.8684(19), Si1-C32 = 1.8818(19); C1-Hf1-N1 = 70.55(6), N2-Hf1-N1 = 76.82(5), N1-Hf1-C25 = 110.50(8), C25-Hf1-C24 = 102.02(10), C11-Si1-N2 = 99.66(8), C26-Si1-C32 = 105.41(8).

and the benzyl carbon in the base of the square pyramid (2.253–2.257 Å). In complex **8** bond angle Hf1-C28-C29 = 101.58° (Fig. 3) which is significantly smaller than the corresponding angle in the second benzyl group in the complex (123.97°) and in the benzyl groups in **7** (119.06°, 122.59°). The reduced bond angle and a relatively short Hf1-C29 bond distance 2.915 Å suggests the presence of η^2 bonding of benzyl group in the crystal of **8** which is a common thing for benzylic complexes of hafnium.[14–16] Moreover, an even smaller bond angle Hf1-C31-C32 = 91.58° and shorter bond distance Hf1-C32 = 2.710 Å in **9** is observed (Fig. 4), and η^2 bonding of one of the benzyl group is even more obvious. Furthermore, for the latter complex π-π interactions between the η^2-benzyl group and the pyridine ring of the ligand are present; the distance between the C_6H_5 group centroid and the plane of the pyridine ring is 3.268 Å, and an angle of 10.33° is formed between the benzyl and pyridine planes.[16]

Olefin polymerization

Upon activation with $B(C_6F_5)_3$, $[HMe_2NPh][B(C_6F_5)_4]$ ("anilinium borate", AB), or $[Ph_3C][B(C_6F_5)_4]$ ("trityl borate", TTB) complexes **7** and **8** formed active catalysts of 1-hexene polymerization at room temperature and at 60 °C (Table 1).

Catalyst **7**/TTB (Table 1, entry 6) appeared to behave similarly to its Me_2C-bridged analogue **Id**[10]/TTB (Table 1, entry 8), in terms of the activity and MWD as both produced bimodal polyhexene. Increase of the polymerization temperature to 60 °C narrowed down MWD of the polymer produced by **7**/TTB (Table 1, entry 11), and the shape of the GPC curve changed from clearly bimodal to the peak with a shoulder.

Replacement of TTB with $B(C_6F_5)_3$ also resulted in a narrowing of the MWD observed for the polyhexene produced with both **Id**- and **7**-based catalysts (Table 1, entries 5 and 3, respectively). The substantially lower activity of the latter in comparison with **Id**/$B(C_6F_5)_3$may be due the difference of alkyl ligands ($HfBn_2$ in **7** and $HfMe_2$ in **Id**) at the metal in the precatalysts.[17]

Activation of **7** with AB resulted in unimodal MWD of the polymer (Table 1, entries 1, 9). Interestingly, catalysts derived from **8** gave unimodal polymers with narrow MWD (M_w/M_n = 1.3–1.7) under all the activation and polymerization conditions studied.

Comparing the 1-hexene homopolymerization data, we can conclude that silicon bridged pyridylamide catalysts might be a good alternative to the carbon-bridged prototypes.

Complexes **7** and **8** yielded isotactically enriched polyhexene (Fig. S7 and S8, *Supporting Information*). It was previously described by Domski et. al.[10] that C_s-symmetric pyridylamido hafnium catalysts are able to give isotactic polyolefins due to desymmetrization of the catalytic species *in situ* via α-olefin insertion into the Hf-C_{Ar} bond. To test a hypothesis that the studied complexes undergo similar post-activation alkene insertion into the Hf-C_{Ar} bond, we performed 4-methyl-1-pentene polymerizations catalyzed by **7**/TTB and **8**/TTB. After quenching the polymerizations with methanol, the obtained mixtures containing the products of decomposition of the catalyst were analysed with GC-MS. The mixtures were

Table 1. 1-Hexene polymerization data for complexes **7-12** and **Ic**[a]

Entry	Complex	Activator	T_{pol}, °C	Yield, mg	Conversion, %	M_n,[b] kDa	M_w,[b] kDa	$Đ$[b]
1	**7**	AB	25	370	27	18	48	2.6
2	**8**	AB	25	107	8	14	18	1.3
3	**7**	$B(C_6F_5)$	33	267	20	14	32	2.3[e]
4	**8**	$B(C_6F_5)$	33	1305	96	17	27	1.6
5	**Id**	$B(C_6F_5)$	33	1212	89	20	43	2.1
6	**7**	TTB	33	1267	93	9	119	14[e]
7	**8**	TTB	33	1341	99	10	17	1.7
8	**Id**	TTB	33	1145	84	10	38	3.8[e]
9	**7**	AB	60(±2)	987	73	6	8	1.4
10	**8**	AB	60(±2)	522	38	11	15	1.3
11	**7**	TTB	60(±2)	662	49	6	11	1.8[e]
12	**8**	TTB	60(±2)	865	64	7	10	1.4

[a]Polymerization conditions: **7**, **8**,or **1d**, 10 µmol, [B]/[Hf] = 1.0, 8.0 mL toluene, 2.0 mL 1-hexene, 30 min. [b]Determined using gel permeation chromatography in THF at 35 °C vs polystyrene standards. [e]Bimodal molecular weight distribution.

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Table 2. Propylene polymerization data for complexes **7-12** and **Ib** at 70 °C[a]

Entry	Complex	Activity, g·mmol^{-1}·h^{-1}	M_w[c], kDa	M_n[c], kDa	$Đ$[c]	T_m[d], °C
1	**7**	7220	31	18	1.7	131
2	**8**	270	n.d.	n.d.	n.d.	n.d.
3	**9**	5060	37	22	1.7	135
4	**10**	2280	22	10	2.3	138
5	**11**	2820	21	12	2.4	134
6	**12**	3320	54	28	1.9	n.d.
7[e]	**Ib**	48200	1469	812	1.8	148

[a]Polymerization conditions: 0.04 µmol complexes; 0.044 µmol AB activator; propylene = 1 mL; total volume: 5.1 mL; 3.8 mL isohexane; 0.5 µmol of (nOct)$_3$Al; temperature: 70 °C; 800 rpm stirring speed. [b]Reactor quenched at 12 psig uptake (quench value, see Supporting Information for details) or at a maximum time of 45 minutes. [c]Determined using gel permeation chromatography in 1,2,4-$C_6H_3Cl_3$ at 135 °C vs polystyrene standards. [d]Determined via differential scanning calorimetry. [e]0.06 µmol of complex used.

found to contain significant amounts of 2-(2-(1,3-dimethylbutyl)phenyl)pyridine or 2-(2-(4-methylpentan-2-yl)naphthalen-1-yl)pyridine (Fig. S2 and S5, *Supporting Information*), which could only be formed via decomposition of the products of insertion of 4-methyl-1-pentene into Hf-C_{Ar} bonds of the catalysts. This observation, together with the fact that the catalysts based on **7** and **8** give isotacticaly enriched poly(α-olefins), proves that the insertion of alkene does occur during the activation of the silicon-bridged precatalysts.

Since **7** and **8** were active in 1-hexene and 4-methylpentene polymerization and, moreover, gave isotactically enriched polymers, propylene homopolymerization and ethylene/1-octene copolymerization experiments were carried out in parallel pressure reactors, as generally described elsewhere.[3,18–21] The industrially relevant catalyst **Ib**[5] was used for comparison.

Propylene homopolymerization. Propylene polymerizations were carried out using complexes **7-12** as catalyst components. Run details and characterization data are presented in Table 2. The propylene polymerizations were performed at 70 °C under identical conditions. For each run, the reactor was loaded with liquid propylene, trioctylaluminum scavenger, and isohexane solvent. Lastly, separate toluene solutions of AB and the hafnium complex were sequentially added to begin the polymerization. The polymerization was quenched by the addition of compressed air to the reactor.

Every complex except **8** gave active catalyst for propylene homopolymerization, although the activities for the Si-bridged catalysts were lower than that observed for the well-optimized catalyst **Ib**. In the most active Si-bridged catalyst **7**/AB (ca. 1/7 of activity of **Ib**/AB), the silylene bridge is the least sterically hindered. Interestingly, replacement of the phenylene moiety in **7** with 1,2-naphtalenediyl in **8** resulted in a dramatic drop in activity in propylene polymerization although the same change in the structure of Me_2C-bridged catalyst resulted in a 5-fold increase of activity.[10]

Catalysts derived from **7** and **9**-**11** gave crystalline polypropyl ene (T_m = 131–138 °C) which is an evidence in favor of the formation of isotactically enriched polymer, similar to what was observed for Me_2C-bridged pyridylamido hafnium catalysts **Ic** and **Id**.[11] **Ic** gave polypropylene with T_m = 133 °C when the polymerization was conducted at 20 °C ($B(C_6F_5)_3$ activation) and T_m = 127 °C when performed at 50 °C.[11] Comparison of these values with T_m = 131 °C of polypropylene produced by **7**/AB at even higher polymerization temperature (70 °C) indicates that catalysts derived from C_s-symmetric silicon-bridged pyridylamido hafnium complexes can be more stereoselective than carbon-bridged analogues such as **Ic** and **Id**.

The only catalyst that gave amorphous polypropylene was **12**/AB. This result can be considered as an additional proof that isopropyl groups in the aniline moiety of pyridylamide ligands

Table 3. Ethylene/1-octene copolymerization data for complexes **7-12** and **Ib** at 80 °C[a]

Entry	Complex	Activity, g·mmol^{-1}·h^{-1}·bar[C_2H_4]$^{-1}$	M_w[c], kDa	M_n[c], kDa	$Đ$[c]	T_m[d], °C	Octene content, wt %
1	**7**	3580	384	110	3.5	116	7
2	**8**	160	n.d.	n.d.	n.d.	n.d.	n.d.
3	**9**	990	87	64	1.4	120	8
4	**10**	2350	110	84	1.3	110	10
5	**11**	2770	112	80	1.4	108	12
6	**12**	390	71	54	1.3	119	8
7[e]	**Ib**	15600	402	263	1.5	76	22

[a]Polymerization conditions: 0.04 µmol complexes; 0.04 µmol AB activator; 3.8 mL isohexane; ethylene pressure 75 psi, 0.1 mL 1-octene; 0.3 µmol of (nOct)$_3$Al; temperature: 80 °C; 800 rpm stirring speed. [b]Reactor quenched at 10 psig ethylene (quench value, see Supporting Information for details) uptake or at a maximum time limit of 30 minutes. [c]Determined using gel permeation chromatography in 1,2,4-$C_6H_3Cl_3$ at 135 °C vs polystyrene standards. [d]Determined via differential scanning calorimetry. [e]0.02 µmol of complex used.

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are essential for stereo-induction in the pyridylamido hafnium catalysts.[11]

Relatively low molecular weights of the resulting polymers (M_w ~ 22–54 kDa) can be in part associated with the presence of trioctylaluminum (added as a scavenger) also acting as a chain-transfer agent, which impact can be more pronounced at lower rate of chain propagation.[6,22]

Ethylene/1-octene copolymerization. Ethylene/1-octene copolymerizations were carried out using complexes **7-12** as catalyst components. Run details and characterization data are presented in Table 3. Each of the copolymerizations were performed at 80 °C under identical conditions. For each run, the reactor was pressurized with ethylene to 75 psi, loaded with 1-octene, trioctylaluminum scavenger, and isohexane solvent. Lastly, separate toluene solutions of AB and the hafnium complex were sequentially added to begin the polymerization. The polymerization was quenched by the addition of compressed air to the reactor.

Similar to what was observed for the propylene polymerization, **8**/AB was the least and **7**/AB was the most active silicon-bridged catalyst, the latter being 4.4 times less active than the reference **Ib**. Catalyst **7**/AB also displayed the highest molecular weight capability among the Si-bridged catalysts approaching that of **Ib**, but produced the polymer with comparatively broad molecular weight distribution (Table 3, entry 1). The rest of the catalysts gave copolymers with narrow molecular weight distributions. Replacement of the Me_2Si bridge in **7** with cyclo-$(CH_2)_4Si$ in **9** (Entry 3, Table 3) or isopropyl groups in aniline moiety in **11** with methyls in **12** (Table 3, entry 6) thus lowering steric hindrance around hafnium lead to the lower activity of the respective catalysts and lower molecular weights of the obtained copolymers. Combination of high activity and high comonomer insertion is demonstrated by catalysts **10**/AB and **11**/AB with the bulkiest ligands.[23]

Conclusions

Six new R_2Si-bridged pyridylamido hafnium post-metallocene complexes were synthesized, four of which were characterized by X-ray structure analysis. The ligands were prepared in a simple two-step procedure from easily available 2-bromo-6-phenylpyridine and 2-bromo-6-(napht-1-yl)pyridine. The complexes were synthesized either by reaction of the ligands with tetrabenzylhafnium or via a two-step procedure including reaction of the ligands with $HfBn_2Cl_2(Et_2O)_2$ followed by methylation of the dichloride complexes formed. In 1-hexene polymerization, Me_2Si-bridged catalysts **7** and **8** appeared to behave similarly to the Me_2C-bridged analogue **Id** and produced isotactically enriched polymer.

Propylene homopolymerization and ethylene/1-octene copolymerization experiments revealed that catalytic performance of the prepared complexes depended on the structure of the ligand. Catalysts **7** and **9–11** containing 2,6-diisopropylaniline fragment upon activation give crystalline polypropylene. In ethylene/1-octene copolymerization catalyst **7** was approached the molecular weight capability of **Ib**, one of the best C-bridged pyridylamido hafnium catalysts for olefin copolymerization. Catalysts **10** and **11** also gave copolymers with the highest content of incorporated 1-octene units in the series of newly prepared catalysts.

Using polymerization of 4-methylpentene as a model, it was demonstrated that alkene insertion into the Hf-C_{Ar} bond occurs during catalyst activation, resulting in *in situ* formation of the C_1-symmetric active species (from the initially C_s-symmetric precatalyst), which is consistent with the observed isoselective 1-hexene polymerization and formation of crystalline rather than amorphous polypropylene.

Experimental part

All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware or in a nitrogen-filled Vacuum Atmospheres glove box (<1 ppm O_2). Toluene, CH_2Cl_2, hexane, pentane, chloroform-d1 and dichloromethane-d2 were dried using 4Å molecular sieves activated for 24 h at 200-230 °C under dynamic vacuum. Diethyl ether and tetrahydrofuran were refluxed over Na/benzophenone and distilled prior to use. All dry solvents were stored under an argon atmosphere. MeMgBr, (3.0 M solution in Et_2O), *n*BuLi (2.5 M solution in hexanes), dichlorodimethylsilane, dichlorodiethylsilane, 1,1-dichlorosilolane, dichlorodiphenylsilane, 2,6-dimethylaniline, 2,6-diisopropylaniline and $HfBn_4$ were purchased from commercial supplier and used as received. $HfBn_2Cl_2(Et_2O)_2$ was prepared by reaction of one equivalent of $HfBn_4$ with $HfCl_4$ in diethyl ether for 5 h followed by filtration and crystallization of the product from the mother liquor at -30 °C.[24] 2-Bromo-6-phenylpyridine and 2-bromo-6-(1-naphtyl)pyridine were synthesized following the literature methods.[25,26] Referral complexes **Ib** and **Id** were prepared following the literature methods.[5,11] NMR spectra were recorded on Bruker Avance 400 MHz spectrometer at ambient temperature (external standard TMS for ^1H, ^{13}C). Elemental analysis (C,H,N) was performed on Elementar Vario MICRO cube analyser. Mass spectra were collected with an Agilent Technologies 6530A Q-TOF using manual injection regime. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å, ω-scan technique).

General procedure A for preparation of (2-chlorodialkylsilyl)-6-arylpyridines and (2-chlorodiphenylsilyl)-6-phenylpyridine. To a solution of a 2-bromo-6-arylpyridine (7.91 mmol) in tetrahydrofuran (35 mL) a 2.5 M hexane solution of *n*BuLi (3.16 mL, 7.91 mmol) was added dropwise at -78 °C to form a clear orange solution. After 20 min, a dialkyldichlorosilane or diphenyldichlorosilane (31.6 mmol) was added in one portion. The mixture was warmed up to ambient temperature and the volatiles were removed under reduced pressure to afford a white solid or a turbid oil. The solid was extracted into Et_2O (15 mL) and filtered. Removal of the volatiles afforded the product as a white solid or a colorless oil of suitable purity, which was used in the next step without additional purification.

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(2-Chlorodimethylsilyl)-6-phenylpyridine. General procedure A was applied using 2-bromo-6-phenylpyridine (1.85 g, 7.91 mmol) and dichlorodimethylsilane (3.85 mL, 31.6 mmol). Yield: 1.86 g (95%) were isolated as a white solid. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.09 (m, 2H), 7.76–7.78 (m, 1H), 7.70 (m, 1H), 7.44–7.52 (m, 4H), 0.78 (s, 6H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 163.6, 157.2, 139.6, 135.8, 129.5, 129.1, 127.7, 127.2, 121.0, 1.6.

(2-Chlorodimethylsilyl)-6-(1-naphtyl)pyridine. General procedure A was applied using 2-bromo-6-(1-naphtyl)pyridine (2.25 g, 7.91 mmol) and dichlorodimethylsilane (3.85 mL, 31.6 mmol). Yield: 2.31 g (98%) were isolated as a yellowish oil. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.25 (d, J = 8.1 Hz, 1H), 8.01 (m, 2H), 7.86 (m, 2H), 7.67-7.69 (m, 1H), 7.63 (m, 2H), 7.56 (m, 2H), 0.84 (s, 6H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 163.4, 159.6, 139.3, 135.6, 134.4, 131.6, 129.3, 128.7, 128.0, 127.6, 126.7, 126.3, 126.2, 125.72, 125.70, 1.7.

2-(1-Chlorosilolan-1-yl)-6-phenylpyridine. General procedure A was applied using 2-bromo-6-phenylpyridine (1.85 g, 7.91 mmol) and 1,1-dichlorosilolane (4.9 g, 31.6 mmol). Yield: 1.73 g (80%) were isolated as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (m, 2H), 7.74 (m, 3H), 7.48 (m, 2H), 7.42 (m, 1H), 1.91 (m, 4H), 1.31 (m, 2H), 1.08 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.2, 156.8, 139.1, 135.2, 129.1, 128.7, 128.1, 126.8, 120.3, 26.6, 15.1.

(2-Chlorodiethylsilyl)-6-phenylpyridine. General procedure A was applied using 2-bromo-6-phenylpyridine (1.85 g, 7.91 mmol) and dichlorodiethylsilane (4.73 mL, 31.6 mmol). Yield: 2.14 g (98%) were isolated as a colorless oil. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.09 (m, 2H), 7.77 (m, 1H), 7.72 (m, 2H), 7.43–7.53 (m, 3H), 1.18-1.25 (m, 4H), 1.08–1.14 (m, 6H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 162.6, 157.2, 139.7, 135.7, 129.4, 129.1, 128.7, 127.2, 120.8, 8.1, 6.9.

(2-Chlorodiphenylsilyl)-6-phenylpyridine. General procedure A was applied using 2-bromo-6-phenylpyridine (1.85 g, 7.91 mmol) and dichlorodiphenylsilane (6.65 mL, 31.6 mmol). The excess of dichlorodiphenylsilane was distilled off at 190°C/0.01 mbar using Kugelrohr short-path distillation apparatus. Yield: 2.56 g (87%) were isolated as a grey solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (m, 2H), 7.91 (m, 4H), 7.86 (dd, J = 6.6 Hz, 2.0 Hz, 1H), 7.75–7.81 (m, 2H), 7.42-7.52 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.6, 156.9, 139.0, 135.5, 135.2, 132.7, 130.6, 129.1, 129.0, 128.7, 128.0, 126.8, 120.5.

General procedure B for preparation of pro-ligands 1–6. Benzene (20 mL) was added to a mixture of a (2-chlorodialkylsilyl)-6-arylpyridines or (2-chlorodiphenylsilyl)-6-phenylpyridine (5.0 mmol) with a substituted lithium anilide (5.0 mmol) previously prepared by reaction of 2,6-diisopropylaniline or 2,6-dimethylbenzene with one equivalent of *n*-butyllithium in hexane. To the stirred slurry thus obtained tetrahydrofuran was added (1 mL). The mixture was stirred for 1 h, the volatiles were then removed and the oily residue was redissolved in benzene (20 mL). The extract was filtered through Celite® and then evaporated to give the product as yellowish oil. The compound was used in the next step without additional purification.

N-(2,6-Diisopropylphenyl)-1,1-dimethyl-1-(6-phenylpyridin-2-yl)silanamine (1). General procedure B was applied using (2-chlorodimethylsilyl)-6-phenylpyridine (1.24 g, 5.0 mmol) and lithium 2,6-diisopropylanilide (0.92 g, 5.0 mmol). Yield: 1.69 g (87%) were isolated. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.12 (m, 2H), 7.72–7.76 (m, 2H), 7.43–7.57 (m, 4H), 7.07–7.09 (m, 2H), 6.99–7.05 (m, 1H), 3.67 (br.s, 1H), 3.49 (m, 2H), 1.14 (d, J = 6.9 Hz, 12H), 0.47 (s, 6H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 167.2, 157.1, 143.5, 140.3, 140.2, 135.3, 129.2, 129.0, 127.5, 127.3, 123.3, 123.1, 123.0, 120.2, 28.6, 23.7, -0.88. HRMS (APPI) m/z calcd for $C_{25}H_{33}N_2Si$ $[M+H]^+$: 389.2408; found: 389.2413.

N-(2,6-Diisopropylphenyl)-1,1-dimethyl-1-(6-(1-naphtyl)pyridin-2-yl)silanamine (2). General procedure B was applied using (2-chlorodimethylsilyl)-6-(1-naphtyl)pyridine (1.49 g, 5.0 mmol) and lithium 2,6-diisopropylanilide (0.92 g, 5.0 mmol). Yield: 1.95 g (89%) were isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38 (m, 1H), 8.10 (m, 2H), 7.84–7.90 (m, 2H), 7.77 (m, 2H), 7.63–7.69 (m, 3H), 7.26–7.30 (m, 2H), 7.19–7.23 (m, 1H), 4.06 (s, 1H), 3.65 (sep, J = 6.9 Hz, 2H), 1.28 (d, J = 6.9 Hz, 12H), 0.70 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.7, 158.9, 142.7, 139.9, 139.2, 134.3, 133.9, 131.3, 128.6, 128.2, 127.3, 126.7, 126.1, 125.8, 125.7, 125.2, 124.3, 122.8, 122.4, 28.1, 3.4, -0.9. HRMS (APPI) m/z calcd for $C_{29}H_{35}N_2Si$ $[M+H]^+$: 439.2564; found: 439.2566.

N-(2,6-Diisopropylphenyl)-1-(6-phenylpyridin-2-yl)silolan-1-amine (3). General procedure B was applied using (2-(1-chlorosilolan-1-yl)-6-phenylpyridine (1.37 g, 5.0 mmol) and lithium 2,6-diisopropylanilide (0.92 g, 5.0 mmol). Yield: 1.70 g (82%) were isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.17 (m, 2H), 7.71–7.78 (m, 2H), 7.48–7.58 (m, 5H), 7.18 (m, 1H), 7.13 (m, 1H), 3.95 (s, 1H), 3.59 (sep, J = 6.9 Hz, 2H), 1.86 (m, 4H), 1.27 (d, J = 6.9 Hz, 12H), 0.95–1.16 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 156.7, 142.7, 139.64, 139.63, 134.8, 128.8, 128.6, 127.7, 126.9, 123.0, 122.7, 119.8, 28.4, 26.7, 23.5, 12.2. HRMS (APPI) m/z calcd for $C_{27}H_{35}N_2Si$ $[M+H]^+$: 415.2564; found: 415.2560.

N-(2,6-Diisopropylphenyl)-1,1-diethyl-1-(6-phenylpyridin-2-yl)silanamine (4). General procedure B was applied using (2-chlorodiethylsilyl)-6-phenylpyridine (1.38 g, 5.0 mmol) and lithium 2,6-diisopropylanilide (0.92 g, 5.0 mmol). Yield: 1.85 g (89%) were isolated. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.13 (m, 2H), 7.72–7.75 (m, 2H), 7.43–7.55 (m, 4H), 7.07-7.09 (m, 2H), 6.98 (m, 1H), 4.01 (br.s, 1H), 3.48 (m, 2H), 1.16 (d, J = 6.9 Hz, 12H), 0.94-1.05 (m, 10H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 165.7, 165.6, 157.22, 157.21, 142.6, 142.4, 140.9, 140.3, 135.2, 129.2, 129.0, 128.1, 127.3, 123.3, 122.5, 122.4, 120.2, 120.1, 28.7, 23.7, 7.3, 6.39. HRMS (APPI) m/z calcd for $C_{27}H_{37}N_2Si$ $[M+H]^+$: 417.2721; found: 417.2727.

N-(2,6-Diisopropylphenyl)-1,1-diphenyl-1-(6-phenylpyridin-2-yl)silanamine (5). General procedure B was applied using (2-chlorodiphenylsilyl)-6-phenylpyridine (1.86 g, 5.0 mmol) and lithium 2,6-diisopropylanilide (0.92 g, 5.0 mmol). Yield: 2.0 g (78%) were isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (m, 2H), 7.73 (m, 1H), 7.66–7.69 (m, 4H), 7.64 (m, 1H), 7.34–7.54 (m, 10H), 7.00–7.04 (m, 2H), 6.93–6.96 (m, 1H), 5.14 (s, 1H), 3.48 (sep, J = 6.8 Hz, 2H), 0.91 (d, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.3, 156.9, 140.8, 139.9, 139.7, 135.7, 135.0, 134.4, 129.8, 129.3, 128.8, 128.6, 127.7, 127.1, 123.1, 121.6, 120.2, 28.7, 23.3. HRMS (APPI) m/z calcd for $C_{35}H_{37}N_2Si$ $[M+H]^+$: 513.2721; found: 513.2718.

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N-(2,6-Dimethylphenyl)-1,1-diphenyl-1-(6-phenylpyridin-2-yl)silanamine (6). General procedure B was applied using (2-chlorodiphenylsilyl)-6-phenylpyridine (1.86 g, 5.0 mmol) and lithium 2,6-diisopropylanilide (0.64 g, 5.0 mmol). Yield: 1.94 g (85%) were isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15 (m, 2H), 7.80 (m, 4H), 7.73 (m, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.37–7.56 (m, 10H), 6.95 (d, J = 7.4 Hz, 2H), 6.76 (m, 1H), 5.27 (s, 1H), 2.25 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.3, 156.8, 143.6, 139.6, 135.5, 135.19, 135.15, 129.8, 129.2, 128.9, 128.6, 128.54, 128.48, 127.8, 127.0, 120.2, 120.1, 20.8. HRMS (APPI) m/z calcd for $C_{31}H_{29}N_2Si$ $[M+H]^+$: 457.2095; found: 457.2094.

General procedure C for preparation of complexes 7–9. To a solution of pro-ligand **1**–**3** (2.3 mmol) in benzene (50 mL) solid tetrabenzylhafnium (1.25 g, 2.3 mmol) was added and the mixture was stirred overnight at 80 °C in the dark. After that, the mixture was filtered through Celite® and the volatiles were removed. Crystallization of the solid residue from toluene-hexane mixture afforded the product as an orange crystalline solid.

Complex 7. General procedure C was applied using **1** (0.894 g, 2.3 mmol). Yield: 963 mg (56%) were isolated. Calcd for $C_{39}H_{44}HfN_2Si$: C, 62.68; H, 5.93; N, 3.75; found: C, 62.75; H, 6.01; N, 3.68. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77–7.84 (m, 2H), 7.71 (d, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.45 (m, 2H), 7.14-7.27 (m, 4H), 7.05–7.09 (m, 1H), 6.87 (t, J = 7.6 Hz, 4H), 6.66 (t, J = 7.4 Hz, 2H), 6.39 (d, J = 7.3 Hz, 4H), 3.44 (m, 2H), 2.11 (d, J = 11.6 Hz, 2H) 1.79 (d, J = 11.7 Hz, 2H), 1.17 (d, J = 6.9 Hz, 6H), 1.09 (d, J = 6.9 Hz, 6H), 0.31 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 201.2, 170.3, 164.0, 146.0, 144.7, 144.0, 143.8, 139.4, 129.7, 129.0, 128.2, 127.8, 127.1, 126.6, 124.1, 123.4, 123.0, 122.0, 118.4, 86.6, 28.5, 25.3, 25.0, 0.9.

Complex 8. General procedure C was applied using **2** (1.01 g, 2.3 mmol). Yield: 880 mg (48%) were isolated. Calcd for $C_{43}H_{46}HfN_2Si$: C, 64.77; H, 5.81; N, 3.51; found: C, 64.92; H, 6.06; N, 3.40. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (d, J = 8.43, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.82–7.93 (m, 3H), 7.66 (d, J = 7.8 Hz, 1H), 7.42–7.52 (m, 3H), 7.18–7.20 (m, 2H), 7.09–7.13 (m, 1H), 6.86 (m, 4H), 6.63 (m, 2H), 6.42 (m, 4H), 3.56 (m, 2H), 2.18 (d, J = 11.9 Hz, 2H) 1.96 (d, J = 11.9 Hz, 2H), 1.18 (d, J = 6.9 Hz, 6H), 1.15 (d, J = 6.9 Hz, 6H), 0.38 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 204.2, 170.8, 164.9, 144.5, 144.0, 143.9, 143.4, 138.8, 135.4, 134.6, 129.8, 129.0, 128.1, 127.1, 126.2, 126.1, 125.1, 124.1, 124.1, 123.5, 123.3, 122.0, 87.7, 28.4, 25.3, 25.1, 0.9.

Complex 9. General procedure C was applied using **3** (0.954 g, 2.3 mmol). Yield: 783 mg (44%) were isolated. Calcd for $C_{41}H_{46}HfN_2Si$: C, 63.67; H, 6.00; N, 3.62; found: C, 63.85; H, 6.18; N, 3.48. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73–7.82 (m, 4H), 7.15–7.36 (m, 6H), 6.92 (t, J = 7.6 Hz, 4H), 6.68 (t, J = 7.4 Hz, 2H), 6.56 (d, J = 7.2 Hz, 4H), 3.54 (m, 2H), 2.40 (d, J = 11.8 Hz, 2H) 2.10 (d, J = 11.8 Hz, 2H), 1.68 (m, 4H), 1.25 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.8 Hz, 6H), 0.70-0.89 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 201.8, 170.5, 164.1, 146.1, 144.0, 143.3, 139.7, 139.0, 129.8, 129.0, 128.2, 128.1, 127.9, 127.4, 126.7, 125.3, 124.2, 123.7, 122.8, 122.1, 118.4, 89.1, 28.3, 26.6, 25.4, 24.9, 13.4.

General procedure D for preparation of complexes 10–12. *Pyridylamido hafnium dichlorides.* To a solution of pro-ligand **4**–**6** (3.1 mmol) in benzene (60 mL) solid $HfBn_2Cl_2(Et_2O)_2$ (1.80 g, 3.1 mmol) was added and the mixture was stirred at 80 °C in the dark for 12 h. After that, the mixture was filtered through Celite® and the volatiles were removed. The residue was triturated with hexane, filtered off and dried in vacuum. This gave a pyridylamido hafnium dichloride complex of appropriate purity which was then methylated without any additional purification. *Pyridylamido hafnium dimethyl complexes.* A 3.0 M solution of MeMgBr in diethyl ether (2.5 mL, 7.5 mmol) was added to a solution of pyridylamido hafnium dichloride complex (1.5 mmol) in toluene (50 mL). The mixture was then stirred for 3 h at 70 °C. After that, the volatiles were removed under reduced pressure, and the residue was extracted with boiling hexane (3×30 mL). The volatiles were removed under reduced pressure, and the residue was washed with cold pentane and dried in vaccum to give a crude product as a white powdery solid. Recrystallization of the crude product from toluene-hexane mixture afforded the pure dimethylated complex.

Complex 10. General procedure D was applied using **4** (1.29 g, 3.1 mmol). Yield: 1.40 g (68%) of pyridylamido hafnium dichloride as a brown powder. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (m, 1H), 7.93–7.98 (m, 2H), 7.83 (m, 1H), 7.58 (dd, J = 6.4, 2.0 Hz, 2H), 7.34–7.39 (m, 2H), 7.08–7.16 (m, 3H), 3.41 (m, 2H), 1.29 (d, J = 6.7 Hz, 6H), 1.19 (d, J = 6.9 Hz, 6H), 1.00–1.09 (m, 2H), 0.89-0.93 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.5, 168.5, 164.1, 145.4, 143.9, 143.5, 143.4, 140.0, 130.7, 129.8, 128.4, 124.5, 123.8, 123.1, 119.0, 28.2, 26.1, 24.1, 7.5, 6.2. Yield of **10** on methylation step: 383 mg (41%) as a white solid. Calcd for $C_{29}H_{40}HfN_2Si$: C, 55.89; H, 6.47; N, 4.49; found: C, 56.02; H, 6.64; N, 4.21. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15 (m, 1H), 7.87–7.92 (m, 2H), 7.83 (d, J = 7.8 Hz, 1H), 7.52 (dd, J_1 = 5.6 Hz, J_2 = 2.8 Hz, 1H), 7.42 (m, 1H), 7.33 (m, 1H), 7.10–7.13 (m, 2H), 7.03–7.07 (m, 1H), 3.55 (m, 2H), 1.19 (d, J = 6.8 Hz, 6H), 1.17 (d, J = 6.8 Hz, 6H), 0.87–0.93 (m, 10H), 0.28 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 202.2, 169.8, 165.1, 146.4, 144.5, 142.0, 139.8, 139.0, 130.1, 128.4, 128.1, 123.7, 123.5, 122.9, 118.3, 64.3, 27.9, 25.8, 24.4, 7.6, 7.4.

Complex 11. General procedure D was applied using **5** (1.59 g, 3.1 mmol). Yield: 1.34 g (57%) of pyridylamido hafnium dichloride as a brown powder. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.21 (m, 1H), 8.09–8.11 (m, 2H), 7.96 (m, 1H), 7.63 (dd, J = 6.5, 2.2 Hz, 1H), 7.43 (m, 8H), 7.29 (m, 4H), 7.08–7.12 (m, 1H), 7.03 (s, 1H), 7.01 (d, J = 1.4 Hz, 1H) 3.18 (m, 2H), 1.16 (d, J = 6.9 Hz, 6H), 0.25 (d, J = 6.7 Hz, 6H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 199.7, 166.5, 164.6, 146.0, 145.0, 143.6, 141.3, 136.3, 135.6, 133.6, 131.3, 130.8, 130.7, 130.4, 128.6, 128.3, 124.4, 123.8, 120.1, 29.0, 26.5, 23.0. Yield of complex **11** on methylation step: 367 mg (34%) as a white solid. Calcd for $C_{37}H_{40}HfN_2Si$: C, 61.78; H, 5.61; N, 3.89; found: C, 61.99; H, 5.87; N, 3.72. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (m, 1H), 7.88–8.02 (m, 3H), 7.58 (m, 1H), 7.34–7.42 (m, 8H), 7.25–7.30 (m, 4H), 8.98–7.07 (m, 3H), 3.33 (m, 2H), 1.08 (d, J = 6.9 Hz, 6H), 0.41 (s, 6H), 0.32 (d, J = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 202.0, 167.1, 165.0, 146.4, 145.4, 140.0, 139.7, 139.4, 136.4, 135.7, 135.4, 135.1, 134.9, 130.3, 130.1, 129.7, 128.5, 127.8, 125.4, 124.1, 123.8, 123.6, 123.0, 118.8, 65.6, 64.6, 64.3, 34.7, 28.3, 27.8, 25.7, 25.5, 23.9, 23.4, 22.2, 14.2.

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Complex 12. General procedure D was applied using **6** (1.42 g, 3.1 mmol). Yield: 1.83 g (84%) of pyridylamido hafnium dichloride as a white powder. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30 (m, 1H), 8.03–8.08 (m, 2H), 7.90 (m, 1H), 7.63 (dd, J = 6.4 Hz, 1.9 Hz, 1H), 7.43 (m, 8H), 7.30 (m, 4H), 6.89–6.97 (m, 3H), 1.91 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.5, 167.1, 165.1, 145.2, 145.1, 142.6, 140.7, 135.4, 134.6, 133.5, 131.1, 130.3, 130.1, 130.0, 128.6, 127.9, 124.2, 123.2, 119.6, 20.5. Yield of complex **12** on methylation step: 617 mg (62%) as a white powder. Calcd for $C_{33}H_{32}HfN_2Si$: C, 59.76; H, 4.86; N, 4.22; found: C, 59.85; H, 5.02; N, 4.11. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (m, 1H), 8.01 (m, 1H), 7.87–7.95 (m, 2H), 7.56 (m, 1H), 7.50 (m, 1H), 7.35–7.42 (m, 7H), 7.27 (m, 4H), 6.85–6.92 (m, 3H), 1.83 (s, 6H), 0.43 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 202.4, 168.5, 166.2, 145.7, 142.8, 139.6, 139.4, 136.1, 135.3, 135.2, 130.5, 130.1, 129.8, 128.6, 128.4, 127.8, 123.2, 123.0, 119.0, 66.0, 20.5.

Propylene homopolymerization and ethylene/1-octene copolymerization – general procedure.

Polymerizations were carried out in 48-cell parallel, pressure reactors (PPR) developed by Symyx Technologies.[3,18] The detailed procedure may be found in *Supporting Information*.

Conflicts of interest

There are no conflicts to declare.

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Pyridylamido Hafnium Complexes with the Silylene Bridge: Synthesis and Olefin Polymerization

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Pyridylamido hafnium complexes with silylene bridge were synthesized, characterized with X-ray structure determination analysis and shown to polymerize 1-hexene, propene and copolymerize ethylene and 1-octene.