DOI: 10.1002/zaac.201100475

Hafnium Trialkyls Stabilized by Bulky, Electron-Rich Aminopyridinates

Muhammad Hafeez,[a] Winfried P. Kretschmer,[a] and Rhett Kempe*[a]

Keywords: Hafnium; N ligands; Aminopyridinates; NMR spectroscopy; X-ray diffraction

Abstract. A series of hafnium aminopyridinates were synthesized and spectroscopically analyzed. In addition, selected examples of these hafnium complexes were characterized by X-ray single crystal structure analysis. The aminopyridinato ligands used here carry an additional dialkylamine substituent to enhance the electron donating ability of the ligands. Structural data and low temperature NMR spectroscopic investigations are indicative of the increased donating ability of the ligands. Ethylene polymerization studies revealed a rather low catalytic activity most likely due to catalyst instability. Details of the deactivation reaction were investigated by NMR spectroscopy.

Introduction

Group 4 metal alkyls stabilized by aminopyridinato (= Ap) ligands (Figure 1) have been frequently used as alternatives to metallocenes or cyclopentadienyl ligand stabilized alkyl complexes of these metals, also in terms of developing catalysts for olefin polymerization.[1–4] Ap ligands are non-symmetric versions of bidentate mono-anionic N-ligands suited to stabilize early (and late) transition metals and can be considered as related to amidinate[5] or diketiminate[6] ligands.

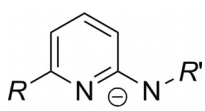


Figure 1. Aminopyridinato ligands (*R*, *R′* = alkyl, aryl or silyl substituents).

Most of the (coordination) chemistry involving Ap ligands has been dedicated to titanium[7] and zirconium.[7a,f,i,r,8] Hafnium complexes are nearly unexplored. Pioneering work in this regard was done by *Polamo* et al. employing his direct synthesis route – the reaction of the metal chloride in the melted ligand.[9] The Ap ligands used by him have a rather low steric bulk and highly nitrogen coordinated complexes were observed. The application of bulky aminopyridinates can address ligand redistribution problems.[10] We recently reported hafnium complexes stabilized by bulky aminopyridinates[8l] and report here the synthesis and structure of hafnium tribenzyl complexes stabilized by bulky Ap ligands possessing a strong electron donation ability due to the presence of an addition dialkylamine functionality (Figure 2).

* Prof. Dr. R. Kempe
Fax: +49-921-55-2157
E-Mail: kempe@uni-bayreuth.de
[a] Lehrstuhl für Anorganische Chemie II
Universität Bayreuth
Universitätsstr. 30
95440 Bayreuth, Germany

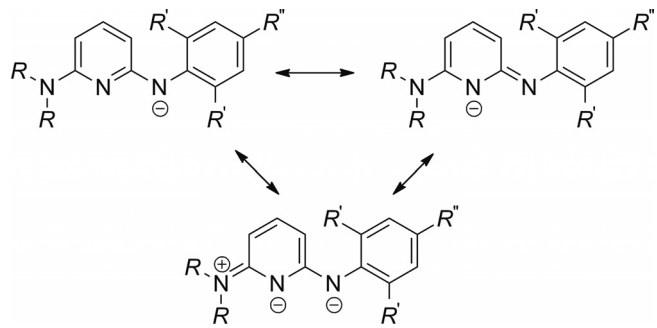


Figure 2. Schematic representation of the increased electron donor ability of Ap ligands by introducing a dialkylamine moiety (*R*, *R′*, *R″* = alkyl substituents).

Results and Discussion

Synthesis of the Complexes

The ligands used here are listed in Figure 3. They were synthesized following a published procedure.[7t]

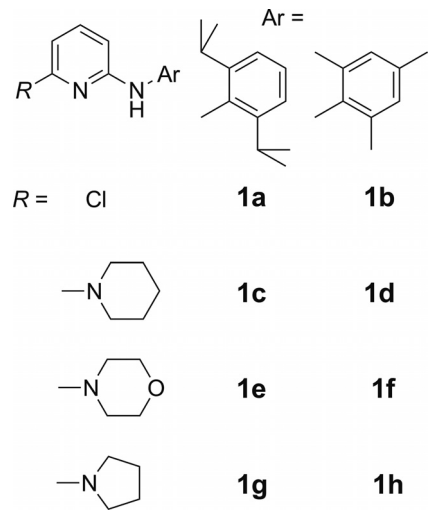
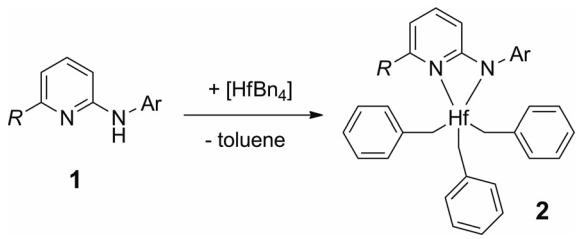


Figure 3. Applied aminopyridines.

Zeitschrift für anorganische und allgemeine Chemie ZAAC Journal of Inorganic and General Chemistry

These ligands react smoothly (1:1 ratio) with tetrabenzylhafnium ($HfBn_4$) to give mono-Ap complexes ($ApHfBn_3$) (Scheme 1). NMR scale reactions are indicative of a quantitative conversion and isolated yields of around 80% could be obtained. Zr/Hf trialkyls stabilized by anionic N-ligands are documented for a few cases and known for amidinates,[11] guanidinates[12] diketiminate,[13] macrocyclic amides,[14] tropocoronands[15] and tris(pyrazolyl)borates.[16]



Scheme 1. Synthesis of **2**, for the assignment of **1a**–**1h** and **2a**–**2h** please refer to Figure 3 (Bn = benzyl).

NMR investigation of the compounds **2** revealed (as expected) one set of proton resonances for the Ap ligand and another set for all three benzyl ligands indicating a dynamic coordination. In the ^{1}H NMR spectra of **2c–h** the proton resonances for the 3 and 5 position of the pyridine ring appear between 4.9 and 5.6 ppm. These signals are quite up field for pyridine or aromatic protons and more typical for olefinic protons. The dialkylamine substituent increases the electron donating ability but weakens the ring current of the pyridine ring. In the case of the earlier reported $ApTiCl_3$ complexes[7t] we could confirm the increased bond order for the $C_{pyridine}$–$N_{dialkylamine}$ bond by observing a high rotation barrier in low temperature NMR experiments. A similar experiment for hafnium compound **2c** (Figure 4) between –70 to –10 °C showed a very strong temperature depending shift of the piperidyl proton resonances at δ = 2.8 and 1.1 ppm but did not result in a chemical inequivalence of the same protons. However, for the benzyl ligand resonances at 2.4 ppm, a split into two sets of multiplet signals below –50 °C with a ratio of 1:2 was observed. This is most likely due to a reversible η^3 coordination of one of the benzyl ligands to reduce the electron deficit of the metal atom.

Structural Studies

Crystals of **2a** suitable for X-ray analysis were grown from a concentrated n-hexane solution at room temperature. For the molecular structure of **2a** please see Figure 5. Crystallographic

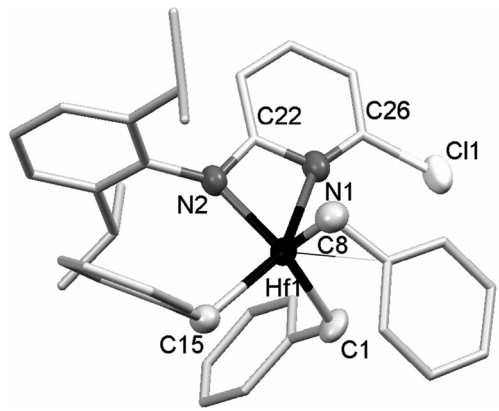


Figure 5. Molecular structure of complex **2a**: Selected bond lengths /Å and bond angles /°: Hf1–C1 2.259(7), Hf1–C8 2.213(8), Hf1–C9 2.645(9), Hf1–C15 2.230(8), Hf1–N1 2.389(7), Hf1–N2 2.146(6), C1–C2 1.477(11), C8–C9 1.466(11), C15–C16 1.494(10), C26–Cl1 1.736(8), N1–C22 1.370(9), N1–C26 1.329(10), N2–C22 1.348(9), N2–C27 1.447(9), C2–C1–Hf1 109.5(1), C9–C8–Hf1 89.5(5), C16–C15–Hf1 122.2 (5), N2–Hf1–N1 58.3(2).

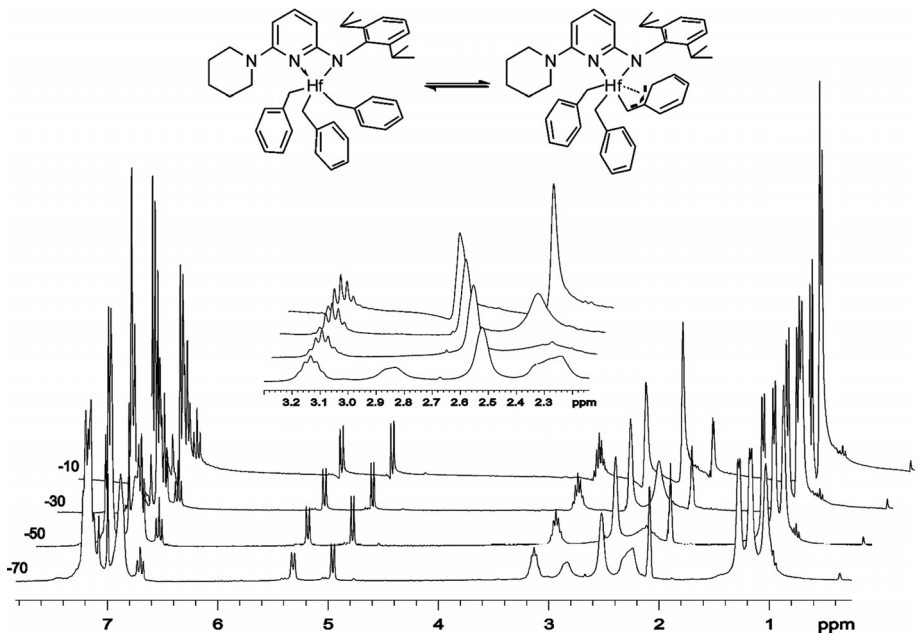


Figure 4. Variable ^{1}H low temperature NMR spectra of **2c** ([D_8]toluene, –70 to –10 °C, 0–8 ppm).

data are given in Table 1. Two of the three benzyl ligands are η^1 coordinated [C2–C1–Hf1 109.6 (4)°, C16–C15–Hf1 122.3 (5)°] whereas the third one is η^2-coordinated [C9–C8–Hf1 90.5 (5)°]. The Hf–CH_2 bond lengths of the η^2 coordinated benzyl ligand is slightly shorter than that of the two other Hf–CH_2 distances. The Hf–$N_{pyridine}$ bond length [2.385(6) Å] is significantly longer than the Hf–N_{amido} bond length [2.143(6) Å], indicating that the anionic function of the ligand is localized on the amido nitrogen atom (N2).

Table 1. Selected experimental details of the X-ray crystal structure analyses.

Compound	**2a**	**2e**
Formula	$C_{38}H_{41}ClHfN_2$	$C_{42}H_{49}HfN_3O$
Formula weight	739.67	790.33
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P21/n$
a /Å	10.836 (1)	9.878 (1)
b /Å	11.069 (1)	34.175 (2)
c /Å	14.320 (1)	11.904 (1)
α /°	74.569 (6)	
β /°	87.029 (7)	112.831 (3)
γ /°	78.008 (7)	
Cell volume	1619.5 (2)	3704(3)
Z	2	4
Crystal size /mm	0.41 × 0.37 × 0.31	0.34 × 0.23 × 0.11
Habit	prism	plate
Color	yellow	yellow
Density /g·cm^{-3}	1.52	1.42
T /K	133	133
Theta range	1.48–25.72	1.2–25.64
Unique reflections	6090	6982
Observed reflections	4973	3339
No of parameters	379	424
*wR*2 (all data)	0.117	0.038
R value	0.049	0.079

Compound **2e** was crystallized from n-hexane solution at –24 °C. The molecular structure of **2e** is given in Figure 6 and crystallographic details are listed in Table 1. In contrast to **2a**, all the three benzyl ligands are η^1-coordinated. Hf–CH_2–C_{ipso} angles between 117.2(6) and 109.7(6)° were observed. The averaged Hf–CH_2 bond is 2.222 Å, which is slightly shorter than the average value of such a bond (2.2696 Å)[17]. The N1–C26 bond length is 1.379(9) Å, which is in between a Csp^2–N double (approx. 1.29 Å) and a Csp^2–N single bond (approx. 1.48 Å) indicating a bond order higher than one.[18] The calculated sum of all angles around N1 is 351° indicating an almost planar nitrogen atom, which is more typical for a sp^2-hybridized nitrogen atom. The sp^2-hybridization of N1 together with the short N1–C26 distances is indicative that the lone pair of N1 participats in the ligands π-system increasing the electron donating ability of the amine functionalized Ap ligand.

Reactions of the Hafnium Complexes with Trialkyl Aluminum Compounds

Ethylene polymerization studies with selected examples of the tribenzyl complexes revealed no activity for the activation with MAO and very low activities of around 5–10 $kg_{PE}/mol_{cat}\cdot h\cdot bar_{ethylene}$ in the presence of dMAO (trimethylaluminum component was removed). Borate activation in the presence of a aluminum scavenger did not improve the activity significantly. We ascribe this observation to transfer of Ap ligand from hafnium to aluminum. The Ap ligand might become transferred from hafnium to aluminum and the Ap ligand free hafnium compound is inactive.[8i] To support this hypothesis we studied the stability of **2c** against trimethylaluminum (TMA, Figure 7). A very fast coordination of TMA (Scheme 2, spectrum after 5 min) with a subsequent ligand transfer reaction was observed (spectrum after 16 h). To confirm the ligand transfer we independently synthesized the corresponding Ap containing dimethylaluminum complex **3c** by the reaction of the aminopyridine **1c** with one equivalent of TMA in toluene according to a published procedure (Figure 7, above).[7i]

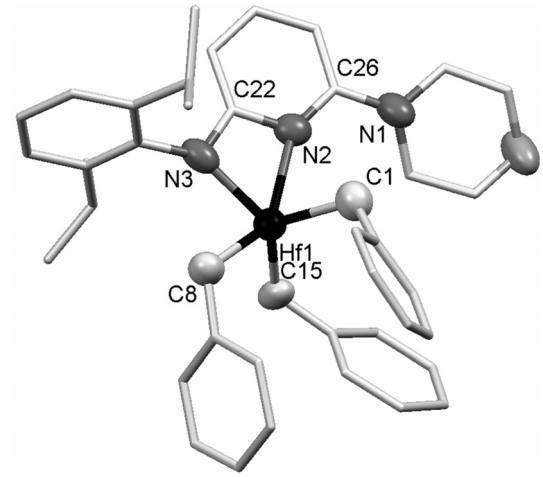


Figure 6. Molecular structure of complex **2e**: Selected bond lengths /Å and bond angles /°: Hf1–C1 2.218(7), Hf1–C8 2.238(7), Hf1–C15 2.210(8), Hf1–N2 2.364(6), Hf1–N3 2.092(5), N2–C22 1.378(8), N2–C26 1.362(8), N1–C26 1.379(9), N3–C22 1.345(8), C2–C1–Hf1 122.0(5), C9–C8–Hf1 113.8(5), C16–C15–Hf1 117.2(6), N3–C22–N2 109.7(6), N2–C26–N1 116.4(7), N3–Hf1–N2 59.43(19).

Conclusions

Several conclusions can be drawn from this study. First, mono-Ap hafnium complexes are selectively formed by reacting tetrabenzylhafnium with the corresponding bulky aminopyridines. Second, the additional dialkylamine substituent increases the electron donor ability of the Ap ligand. Third, a low ethylene polymerization activity was observed due to fast aluminum coordination at the Ap ligand and a subsequent but slower transfer of the Ap ligand towards aluminum during the polymerization reaction.

Experimental Section

All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in an nitrogen filled glove box (mBraun 120-G) with a high-capacity recirculator (< 0.1 ppm O_2). Deuterated solvents were obtained from Eurisotop. Benzene-*d*6 was dried with sodium/potassium alloy and bromobenzene-*d*5 over molecular sieves, degassed and dis-

Zeitschrift für anorganische und allgemeine Chemie ZAAC Journal of Inorganic and General Chemistry

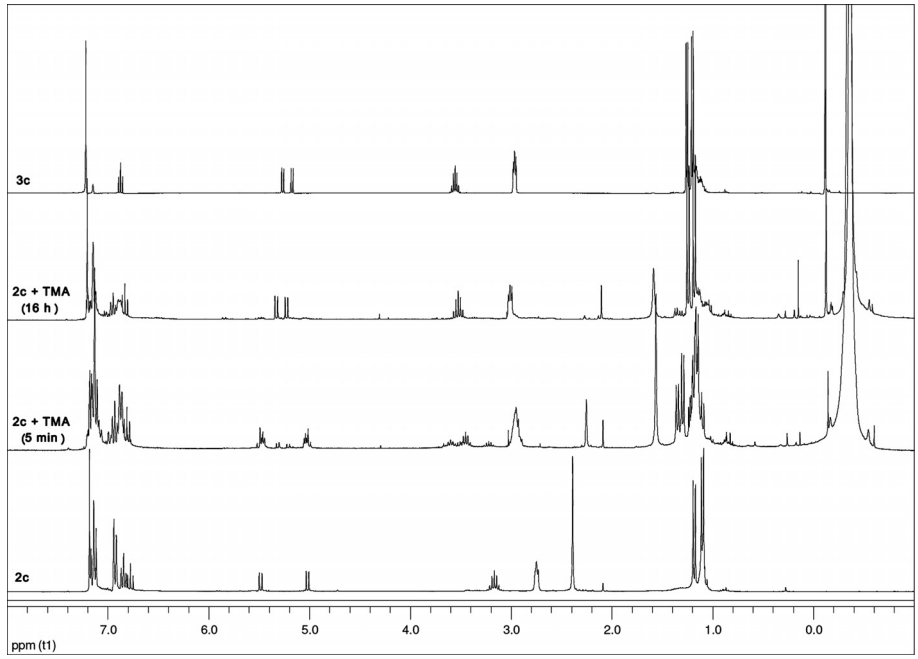
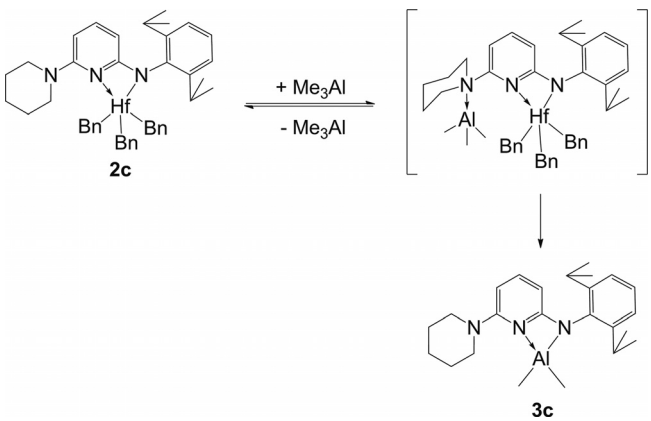


Figure 7. ^{1}H NMR spectra (C_6D_6, 26 °C, 0–8 ppm) of $ApAlMe_2$ (**3c**) top, $ApHfBn_3$ (**2c**) bottom, **2c** + 30 equiv. TMA after 5 min and after 16 h (middle).

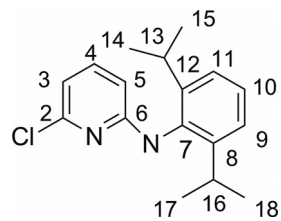


Scheme 2. Ligand transfer reaction.

tilled prior to use. Commercial $HfCl_4$ (Across Organics) was used as received. Tetrabenzylhafnium was prepared according to the literature procedures.[19] NMR spectra were recorded on a Varian Inova (400 MHz) or Varian Inova (300 MHz) spectrometer. The chemical shifts are reported in ppm referenced to internal TMS for ^{1}H and ^{13}C. Elemental analyses (CHN) were determined using Vario ELIII instrument. X-ray crystal structure analyses were performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97,[20] SHELXL97,[21] and WinGX.[22] Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-849066 (compound **2a**) and CCDC-849067 (compound **2e**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk; web: www.ccdc.cam.ac.uk/conts/retrieving.html.

Synthesis of Complexes:

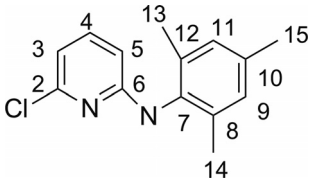
Synthesis of 2a: Aminopyridine **1a** (0.288 g, 1.0 mmol in 15.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 20.0 mL toluene). The color changed from yellow to red. The resultant solution was stirred for 12h at room temperature. The toluene was removed under vacuum and the yellow product was extracted with n-hexane. The volume of the n-hexane extract was reduced and the product was crystallized at –24 °C. Yield 0.50 g (67 %). $C_{38}H_{41}ClHfN_2$ (739.27): calcd. C 61.68, H 5.59, N 3.79 found; C 61.45, H 5.50, N 3.38 %.



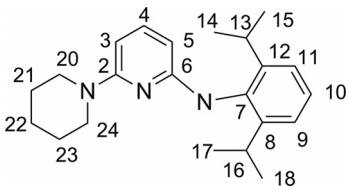
^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.96 (d, 6 H, $H^{14,15,17,18}$), 1.16 (d, 6 H, $H^{14,15,17,18}$), 2.40 (s, 6 H, $H^{CH2benzyl}$), 3.05 (sept, 2 H, $H^{13,16}$), 5.20 (d, 1 H, H^3), 5.91 (d, 1 H, H^5), 6.35 (t, 1 H, H^4), 6.86 (d, 6 H, $H^{CHbenzyl}$), 6.87–7.20 (m, 12 H, $H^{9,10,11,CHbenzyl}$) ppm. **^{13}C NMR** (100 MHz, C_6D_6, 298 K): δ = 23.98 ($C^{14,15,17,18}$), 24.13 ($C^{14,15,17,18}$), 25.20 ($C^{13,16}$), 80.02 ($C^{CH2benzyl}$), 96.25 (C^3), 97.90 (C^5), 122.90 (C^{benzyl}), 128.20 ($C^{9,11}$), 129.20 (C^{benzyl}), 129.62 (C^{10}), 133.50 ($C^{8,12}$), 137.80 (C^4), 142.87 (C^{benzyl}), 143.09 (C^7), 144.14 (C^{benzyl}), 144.67 (C^2), 159.38 (C^6) ppm.

Synthesis of 2b: Aminopyridine **1b** (0.246 g, 1.0 mmol in 20.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 25.0 mL toluene). The color changed from yellow to red. The resultant solution was stirred for 12h at room temperature. The toluene was removed under vacuum and the yellow product was extracted and crys-

tallized with n-hexane at –24 °C. Yield 0.485 g (69 %). $C_{35}H_{35}ClHfN_2$ (697.22): calcd. C 60.24, H 5.06, N 4.02; found C 59.78, H 5.50, N 4.22 %. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = 2.18 (s, 6 H, $H^{13,14}$), 2.24 (s, 3 H, H^{15}), 2.38 (s. 6 H, $H^{CH2benzyl}$), 5.18 (d, 1 H, H^3), 6.42 (d, 1 H, H^5), 6.65 (t, 1 H, H^4), 6.84 (d, 6 H, $H^{CH2benzyl}$), 6.90–7.20 (m, 11 H, $H^{9,11,CHbenzyl}$) ppm. **^{13}C NMR** (100 MHz, C_6D_6, 298 K): δ = 18.60 ($C^{13,14}$), 20.68 (C^{15}), 95.51 (C^3), 97.12 (C^5), 122.80 ($C^{9,11}$), 127.60 (C^{benzyl}), 128.76 (C^{10}), 129.20 (C^{benzyl}), 129.40 (C^{benzyl}), 134.69 ($C^{8,12}$), 143.78 (C^4), 143.94 (C^{benzyl}), 156.30 (C^7), 158.78 (C^2), 164.70 (C^6) ppm.

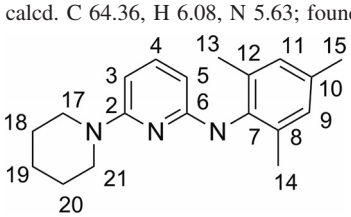


Synthesis of 2c: Aminopyridine **1c** (0.337 g, 1.0 mmol in 15.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 25.0 mL toluene). The color changed from yellow to red. The resultant solution was stirred for twelve hours at room temperature. The toluene was removed and the yellow product was extracted and crystallized with n-hexane at –24 °C. Yield 0.630 g (80 %). $C_{43}H_{51}HfN_3$ (787.90): calcd. C 65.49, H 6.52, N 5.33; found C 64.99, H 6.15, N 5.59 %.



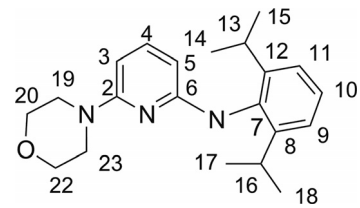
^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.11 (m, 12 H, $H^{14,15,17,18,21,22,23}$), 1.21 (d, 6 H, $H^{14,15,17,18}$), 2.41 (s, 6 H, $H^{CH2benzyl}$), 2.77 (t, 4 H, $H^{20,24}$), 3.19 (sept, 2 H, $H^{13,16}$), 5.03 (d, 1 H, H^3), 5.49 (d, 1 H, H^5), 6.77 (t, 1 H, H^4), 6.94 (d, 6 H, $H^{CHbenzyl}$), 6.98–7.22 (m, 12 H, $H^{9,10,11,CHbenzyl}$) ppm.**^{13}C NMR** (100 MHz, C_6D_6, 298 K): δ = 23.98 ($C^{14,15,17,18}$), 24.13 ($C^{14,15,17,18}$), 25.18 ($C^{13,16}$), 25.66 (C^{22}), 28.78 ($C^{21,23}$), 45.20 ($C^{20,24}$), 79.23 ($C^{CH2benzyl}$), 96.25 (C^3), 97.90 (C^5), 122.90 (C^{benzyl}), 128.20 ($C^{9,11}$), 129.20 (C^{benzyl}), 129.62 (C^{10}), 133.50 ($C^{8,12}$), 137.80 (C^4), 142.87 (C^{benzyl}), 143.09 (C^7), 144.14 (C^{benzyl}), 144.67 (C^6), 159.38 (C^2) ppm.

Synthesis of 2d: Aminopyridine **1d** (0.295 g, 1.0 mmol in 20.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 25.0 mL toluene). The color changed from yellow to red. The solution was stirred for 12h at room temperature. The toluene was removed under vacuum and the yellow product was extracted and crystallized with n-hexane at –24 °C. Yield 0.60 g (80 %). $C_{40}H_{45}HfN_3$ (745.85): calcd. C 64.36, H 6.08, N 5.63; found C 64.75, H 5.65, N 5.43 %.



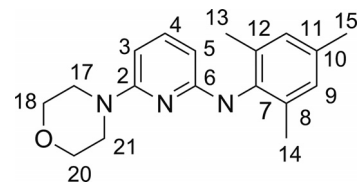
^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.40 (m, 6 H, $H^{18,19,20}$), 2.14 (s, 9 H, $H^{13,14,15}$), 2.43 (s. 6 H, $H^{CH2benzyl}$), 3.44 (t, 4 H, $H^{17,21}$), 5.47 (d, 1 H, H^3), 5.93 (d, 1 H, H^5), 6.79 (s, 2 H, H ^{9,11}), 6.84 (t, 1 H, H^4), 6.95–7.20 (m, 9 H, $H^{CHbenzyl}$) ppm. **^{13}C NMR** (100 MHz, C_6D_6, 298 K): δ = 18.39 ($C^{13,14}$), 20.85 (C^{15}), 25.62 (C^{19}), 28.60 ($C^{18,20}$), 49.50 ($C^{17,21}$), 89.40 ($C^{CH2benzyl}$), 95.40 (C^3), 96.58 (C^5), 122.79 ($C^{9,11}$), 127.60 (C^{benzyl}), 128.90 (C^{10}), 129.22 (C^{benzyl}), 129.40 (C^{benzyl}), 134.20 ($C^{8,12}$), 141.86 (C^{10}), 143.78 (C^4), 143.96 (C^{benzyl}), 156.30 (C^7), 158.78 (C^2) 164.70 (C^6) ppm.

Synthesis of 2e: Aminopyridine **1e** (0.339 g, 1.0 mmol in 15.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 20.0 mL toluene). The color changed from yellow to red. The resultant solution was stirred for 12h at room temperature. The toluene was removed under vacuum and the yellow product was extracted and crystallized with n-hexane at –24 °C. Yield 0.68 g (86 %). $C_{42}H_{49}HfN_3O$ (790.35): calcd. C 63.81, H 6.25, N 5.32; found, C 64.35, H 5.80, N 5.36 %.



^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.11 (d, 6 H, $H^{14,15,17,18}$), 1.21 (d, 6 H, $H^{14,15,17,18}$), 2.41 (s, 6 H, $H^{CH2benzyl}$), 2.64 (t, 4 H, $H^{19,23}$), 2.71 (t, 4 H, $H^{20,22}$), 3.19 (sept, 2 H, $H^{13,16}$), 5.10 (d, 1 H, H^3), 5.49 (d, 1 H, H^5), 6.77 (t, 1 H, H^4), 6.88 (d, 6 H, H^{benzyl}), 6.94–7.20 (m, 12 H, $H^{9,10,11,CHbenzyl}$) ppm. **^{13}C NMR** (75 MHz, C_6D_6, 298 K): δ = 23.98 ($C^{14,15,17,18}$), 24.13 ($C^{14,15,17,18}$), 25.18 ($C^{13,16}$), 48.25 ($C^{19,23}$), 66.20 ($C^{20,22}$), 79.23 ($C^{CH2benzyl}$), 96.25 (C^3), 97.90 (C^5), 122.90 (C^{benzyl}), 128.20 ($C^{9,11}$), 129.20 (C^{benzyl}), 129.62 (C^{10}), 133.50 ($C^{8,12}$), 137.80 (C^4), 142.87 (C^{benzyl}), 143.09 (C^7), 144.14 (C^{benzyl}), 144.67 (C^6), 159.38 (C^2) ppm.

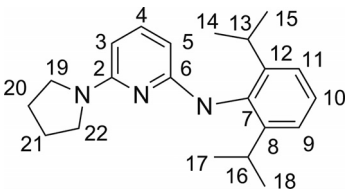
Synthesis of 2f: Aminopyridine **1f** (0.296 g, 1.0 mmol in 20.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 20.0 mL toluene). The resultant solution was stirred for 12h at room temperature. The toluene was removed and the yellow product was extracted and crystallized with n-hexane at –24 °C. Yield 0.63 g (84 %). $C_{39}H_{43}HfN_3O$ (747.83): calcd. C 62.58, H 5.79, N 5.62; found C 63.15, H 5.24, N 5.33 %.



^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 2.04 (s, 6 H, $H^{CH2benzyl}$), 2.19 (s, 6 H, $H^{13,14}$), 2.26 (s, 3 H, H^{15}), 2.64 (t, 4 H, $H^{17,21}$), 3.28 (t, 4 H, $H^{18,20}$), 5.16 (d, 1 H, H^3), 5.40 (d, 1 H, H^5), 6.80 (t, 6 H, H^{benzyl}), 6.84 (t, 1 H, H^4), 6.95–7.20 (m, 11 H, $H^{9,11,CHbenzyl}$) ppm. **^{13}C NMR** (100 MHz, C_6D_6, 298K): δ = 18.39 ($C^{13,14}$), 20.85 (C^{15}), 48.02 ($C^{17,21}$), 65.86 ($C^{18,20}$), 89.52 ($C^{CH2benzyl}$), 95.51 (C^3), 96.66 (C^5), 122.79 ($C^{9,11}$), 127.60 (C^{benzyl}), 128.90 (C^{10}), 129.22 (C^{benzyl}), 129.40 (C^{benzyl}), 134.20 ($C^{8,12}$), 141.86 (C^{10}), 143.78 (C^4), 143.96 (C^{benzyl}), 156.30 (C^7), 158.78 (C^2), 164.70 (C^6) ppm.

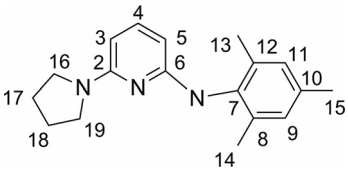
Zeitschrift für anorganische und allgemeine Chemie ZAAC Journal of Inorganic and General Chemistry

Synthesis of 2g: Aminopyridine **1g** (0.323 g, 1.0 mmol in 20.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 20.0 mL toluene). The resultant solution was stirred for 12h at room temperature. The toluene was removed and the yellow product was extracted and crystallized with n-hexane at –24 °C. Yield 0.60 g (77 %). $C_{42}H_{49}HfN_3$ (773.88): calcd. C 65.13, H 6.38, N 5.43; found C 64.78, H 6.12, N 5.90 %.



^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.17 (m, 10 H, $H^{14,15,17,18,20,21}$), 1.30 (d, 6 H, $H^{14,15,17,18}$), 2.45 (t, 4 H, $H^{19,22}$), 2.67 (s, 6 H, $H^{CH2benzyl}$), 3.41 (sept, 2 H, $H^{13,16}$), 4.96 (d, 1 H, H^3), 5.27 (d, 1 H, H^5), 6.75 (t, 1 H, H^4), 6.86 (d, 6 H, H^{benzyl}), 6.94–7.20 (m, 12 H, $H^{9,10,11,CHbenzyl}$) ppm. **^{13}C NMR** (100 MHz, C_6D_6, 298 K): δ = 24.42 ($C^{14,15,17,18}$), 24.13 ($C^{14,15,17,18}$), 25.57 ($C^{13,16}$), 28.95 ($C^{20,21}$), 47.81 ($C^{19,22}$), 89.65 ($C^{CH2benzyl}$), 91.39 (C^3), 96.19 (C^5), 122.08 (C^{benzyl}), 124.02 ($C^{9,11}$), 126.47 (C^{benzyl}), 128.38 (C^{10}), 133.50 ($C^{8,12}$), 134.30 (C^7), 142.20 (C^4), 142.87 (C^{benzyl}), 143.09 (C^7), 144.14 (C^{benzyl}), 154.49 (C^6), 165.32 (C^2) ppm.

Synthesis of 2h: Aminopyridine **1h** (0.281 g, 1.0 mmol in 15.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 20.0 mL toluene). The resultant solution was stirred for 12h at room temperature. The toluene was removed and the yellow product was extracted and crystallized with n-hexane at –24 °C. Yield 0.560 g (76 %). $C_{39}H_{43}HfN_3$ (732.27): calcd. C 63.97, H 5.92, N 5.74; found C 63.85, H 5.72, N 5.62 %.



^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.20 (t, 4 H, $H^{17,18}$), 2.25 (s, 6 H, $H^{13,14}$), 2.26 (s, 3 H, H^{15}), 2.41 (s, 6 H, $H^{CH2benzyl}$), 2.70 (t, 4 H, $H^{17,18}$), 5.06 (d, 1 H, H^3), 5.28 (d, 1 H, H^5), 6.80 (t, 6 H, H^{benzyl}), 6.84 (t, 1 H, H^4), 6.95–7.20 (m, 11 H, $H^{9,11,CHbenzyl}$) ppm. **^{13}C NMR** (400 MHz, C_6D_6, 298K): δ = 18.54 ($C^{13,14}$), 20.82 (C^{15}), 24.79 ($C^{17,18}$), 47.87 ($C^{16,19}$), 89.39 ($C^{CH2benzyl}$), 90.41 (C^3), 96.25 (C^5), 122.20 ($C^{9,11}$), 127.03 (C^{benzyl}), 128.90 (C^{10}), 129.46 (C^{benzyl}), 133.91 ($C^{8,12}$), 134.60 (C^7), 142.60 (C^{10}), 143.78 (C^4), 142.71 (C^{benzyl}), 154.84 (C^2), 163.38 (C^6) ppm.

NMR Tube Reactions with TMA

A NMR tube was charged with **2c** (20 mg, 0.025 mmol), deutero-benzene (0.5 mL) together with TMA (54 mg, 0.750 mmol). Afterwards, the tube was sealed, shaken for 5 min and measured.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (DFG) SFB 840 for supporting this work. M. H. thanks the University of Azad Jammu & Kashmir and the HEC (Higher Education Commission) Pakistan for a scholarship. We thank *T. Bauer* for his help in the X-ray lab.

References

[1] For review articles on aminopyridinato ligands see: a) R. Kempe, H. Noss, T. Irrgang, *J. Organomet. Chem.* **2002**, *647*, 12–20; b) R. Kempe, *Eur. J. Inorg. Chem.* **2003**, 791–803.

[2] For discussion of the binding modes see: S. Deeken, G. Motz, R. Kempe, *Z. Anorg. Allg. Chem.* **2007**, *633*, 320–325.

[3] For the general applicability of the ligands see: G. Glatz, S. Demeshko, G. Motz, R. Kempe, *Eur. J. Inorg. Chem.* **2009**, 1385–1392.

[4] For the synthesis of aminopyridines via Pd catalyzed aryl amination see: a) S. Wagaw, S. L. Buchwald, *J. Org. Chem.* **1996**, *61*, 7240–7241; b) T. Schareina, G. Hillebrand, H. Fuhrmann, R. Kempe, *Eur. J. Inorg. Chem.* **2001**, 2421–2426.

[5] For selected reviews on amidinate coordination chemistry see: a) J. Barker, M. Kilner, *Coord. Chem. Rev.* **1994**, *133*, 219–300; b) F. T. Edelmann, *Coord. Chem. Rev.* **1994**, *137*, 403–481; c) N. Nagashima, H. Kondo, T. Hayashida, Y. Yamaguchi, M. Gondo, S. Masuda, K. Miyazaki, K. Matsubara, K. Kirchner, *Coord. Chem. Rev.* **2003**, *245*, 177–190.

[6] For selected reviews on NacNac coordination chemistry see: a) L. Kakaliou, W. J. Scanlon IV, B. Qian, S. W. Baek, M. R. Smith III, D. H. Motry, *Inorg. Chem.* **1999**, *38*, 5964–5977; b) B. Qian, W. J. Scanlon IV, M. R. Smith III, D. H. Motry, *Organometallics* **1999**, *18*, 1693–1698; c) L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031–3065.

[7] a) R. Kempe, P. Arndt, *Inorg. Chem.* **1996**, *35*, 2644–2649; b) M. Polamo, M. Leskela, *Acta Crystallogr., Sect. C* **1996**, *52*, 2975–2977; c) H. Fuhrmann, S. Brenner, P. Arndt, R. Kempe, *Inorg. Chem.* **1996**, *35*, 6742–6745; d) R. Kempe, *Z. Kristallogr. New Cryst. Struct.* **1997**, *212*, 477–478; e) G. Hillebrand, A. Spannenberg, P. Arndt, R. Kempe, *Organometallics* **1997**, *16*, 5585–5588; f) M. Oberthür, G. Hillebrand, P. Arndt, R. Kempe, *Chem. Ber./Recueil* **1997**, *130*, 789–794; g) A. Spannenberg, A. Tillack, P. Arndt, R. Kirmse, R. Kempe, *Polyhedron* **1998**, *17*, 845–850; h) I. Westmoreland, I. J. Munslow, P. N. O'Shaughnessy, P. Scott, *Organometallics* **2003**, *22*, 2972–2976; i) C. Jones, P. C. Junk, S. G. Leary, N. A. Smithies, *Inorg. Chem. Commun.* **2003**, *6*, 1126–1128; j) M. Talja, M. Klinga, M. Polamo, E. Aitola, M. Leskela, *Inorg. Chim. Acta* **2005**, *358*, 1061–1067; k) R. Fandos, C. Hernandez, A. Otero, A. Rodriguez, M. J. Ruiz, *J. Organomet. Chem.* **2005**, *690*, 4828–4834; l) E. Smolensky, M. Kapon, J. D. Woollins, M. S. Eisen, *Organometallics* **2005**, *24*, 3255–3265; m) E. Smolensky, M. Kapon, M. S. Eisen, *Organometallics* **2005**, *24*, 5495–5498; n) H. Shen, H.-S. Chan, Z. Xie, *Organometallics* **2007**, *26*, 2694–2704; o) V. Bertolasi, R. Boaretto, M. R. Chierotti, R. Gobetto, S. Sostero, *Dalton Trans.* **2007**, 5179–5189; p) M. Talja, T. Luhtanen, M. Polamo, M. Klinga, T. Pakkanen, M. Leskela, *Inorg. Chim. Acta* **2008**, *361*, 2195–2202; q) A. Noor, R. Kempe, *Eur. J. Inorg. Chem.* **2008**, 2377–2381; r) G. Zi, F. Zhang, X. Liu, L. Ai, H. Song, *J. Organomet. Chem.* **2010**, *695*, 730–739; s) A. Noor, W. P. Kretschmer, G. Glatz, R. Kempe, *Inorg. Chem.* **2011**, *50*, 4598–4606; t) M. Hafeez, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **2011**, published online, DOI: 10.1002/ejic.201100843.

[8] a) R. Kempe, S. Brenner, P. Arndt, *Organometallics* **1996**, *15*, 1071–1074; b) M. Polamo, M. Leskelä, *J. Chem. Soc., Dalton Trans.* **1996**, *23*, 4345–4349; c) C. Morton, P. N. O'Shaughnessy, P. Scott, *Chem. Commun.* **2000**, *21*, 2099–2100; d) P. N. O'Shaughnessy, K. M. Gillespie, C. Morton, I. Westmoreland, P. Scott, *Organometallics* **2002**, *21*, 4496–4504; e) H. M. Hoyt, F. E. Michael, R. G. Bergman, *J. Am. Chem. Soc.* **2004**, *126*, 1018–1019; f) E. J. Crust, I. J. Munslow, C. Morton, P. Scott, *Dalton Trans.* **2004**, *15*, 2257–2266; g) E. J. Crust, A. J. Clarke, R. J. Deeth, C. Morton, P. Scott, *Dalton Trans.* **2004**, *23*, 4050–4058; h) E. J. Crust, I. J. Munslow, P. Scott, *J. Organomet. Chem.* **2005**,

690, 3373–3382; i) W. P. Kretschmer, B. Hessen, A. Noor, N. M. Scott, R. Kempe, *J. Organomet. Chem.* **2007**, *692*, 4569–4579; j) E. Smolensky, M. Kapon, M. S. Eisen, *Organometallics* **2007**, *26*, 4510–4527; k) A. L. Gott, G. J. Clarkson, R. J. Deeth, M. L. Hammond, C. Morton, P. Scott, *Dalton Trans.* **2008**, 2983–2990; l) A. Noor, W. P. Kretschmer, G. Glatz, A. Meetsma, R. Kempe, *Eur. J. Inorg. Chem.* **2008**, *32*, 5088–5098.

[9] M. Polamo, M. Leskela, *Acta Chem. Scand.* **1997**, *51*, 69–72.

[10] For selected key papers see a) N. M. Scott, R. Kempe, *Eur. J. Inorg. Chem.* **2005**, 1319–1324; b) S. M. Guillaume, M. Schappacher, N. M. Scott, R. Kempe, *J. Polym. Sci. Part A* **2007**, *45*, 3611–3619; c) G. G. Skvortsov, G. K. Fukin, A. A. Trifonov, A. Noor, C. Döring, R. Kempe, *Organometallics* **2007**, *26*, 5770–5773; d) W. P. Kretschmer, B. Hessen, A. Noor, N. M. Scott, R. Kempe, *J. Organomet. Chem.* **2007**, *692*, 4569–4579; e) D. M. Lyubov, C. Döring, G. K. Fukin, A. V. Cherkasov, A. V. Shavyrin, R. Kempe, A. A. Trifonov, *Organometallics* **2008**, *27*, 2905–2907; f) A. Noor, F. R. Wagner, R. Kempe, *Angew. Chem.* **2008**, *120*, 7356–7359; *Angew. Chem. Int. Ed.* **2008**, *47*, 7246–7259; g) A. Noor, G. Glatz, R. Müller, M. Kaup, S. Demeshko, R. Kempe, *Nature Chem.* **2009**, *1*, 322–325; h) C. Döring, R. Kempe, *Eur. J. Inorg. Chem.* **2009**, 412–413; i) W. P. Kretschmer, T. Bauer, B. Hessen, R. Kempe, *Dalton Trans.* **2010**, *39*, 6847–6852; j) C. Döring, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **2010**, 2853–2860.

[11] K. Kincaid, C. P. Gerlach, G. R. Giesbrecht, J. R. Hagadorn, G. D. Whitener, A. Shafir, J. Arnold, *Organometallics* **1999**, *18*, 5360–5366.

[12] a) D. Wood, G. P. A. Yap, D. S. Richeson, *Inorg. Chem.* **1999**, *38*, 5788–5794; b) G. R. Giesbrecht, G. D. Whitener, J. Arnold, *Organometallics* **2000**, *19*, 2809–2812.

[13] B. Qian, W. J. Scanlon IV, M. R. Smith III, D. H. Motry, *Organometallics* **1999**, *18*, 1693–1698.

[14] G. R. Giesbrecht, A. Shafir, J. Arnold, *Chem. Commun.* **2000**, *21*, 2135–2136.

[15] M. J. Scott, S. J. Lippard, *Inorg. Chim. Acta* **1997**, *263*, 287–299.

[16] H. Lee, R. F. Jordan, *J. Am. Chem. Soc.* **2005**, *127*, 9384–9385.

[17] 2.2696 Å is the mean value of 86 Hf–C bond lengths of Hf–Bn moieties taken from the Cambridge Structural Database version 5.32.

[18] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.

[19] U. Zucchini, E. Abizzati, U. Giannini, *J. Organomet. Chem.* **1971**, *26*, 357–372.

[20] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[21] G. M. Sheldrick, *SHELX-97*, Program for Crystal Structure Analysis (Release 97–2), Institut für Anorganische Chemie der Universität, Göttingen, Germany, **1998**.

[22] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

Received: October 28, 2011
Published Online: January 09, 2012

