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Synthesis and Structure of Zirconium and Hafnium Polymerisation Catalysts Stabilised by Very Bulky Aminopyridinato Ligands

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Mono(aminopyridinato) complexes of the type [ApM($CH_2C_6H_5$)$_3$] [M = Zr, Hf and Ap = aminopyridinate] were prepared by treating the three different sterically demanding aminopyridines with one equiv. of tetrabenzylzirconium or -hafnium. One of the three benzyl groups is η^2-coordinated in the solid state. However all of the three benzyl substituents are equivalent in solution as evidenced by the ^{1}H NMR spectrum. Treatment of these neutral complexes with B(C_6F_5)$_3$ afforded the corresponding zwitterionic dibenzyl complexes. The η^6-coordination of the phenyl ring of the B-bound benzyl group to the metal centre was supported by ^{1}H NMR spectroscopy and confirmed by single-crystal X-ray diffraction analysis. These zwitterionic complexes show very low activity for ethylene polymerisation at low temperature since the coordination site is blocked by the η^6-coordinated phenyl ring. At elevated temperature, moderate activity with the formation of high molecular weight polyethylene (PE) was observed. An attempted abstraction of the second benzyl group failed when the zwitterionic complexes were treated with an additional equivalent of B(C_6F_5)$_3$. Using one equiv. of [R_2(Me)NH][B(C_6F_5)$_4$] (R = $C_{16}H_{33}$–$C_{18}H_{37}$) instead of B(C_6F_5)$_3$, moderate activities of ethylene polymerisation were observed. Treatment of the aminopyridinato metal tribenzyls with [R_2(Me)NH][B(C_6F_5)$_4$] (R = $C_{16}H_{33}$–$C_{18}H_{37}$) gave active ethylene polymerisation catalysts which produced low molecular weight PE in the case of the zirconium analogues and higher molecular weight PE in the case of the hafnium example. Propylene homopolymerisation under the same conditions failed. Ethylene–propylene copolymers with separated propene units and alternating sequences were observed in the presence of both monomers.

Introduction

Group 4 metal alkyl cations possessing a weakly coordinating anion are one of the most important classes of compounds with regards to coordinative polymerisation of olefins. The Zr/Hf chemistry of dialkyl cations stabilised by anionic polydentate *N*-ligands is rather unexplored but might be unique due to the presence of two metal-alkyl functionalities and the tuneable *N*-ligand environment (Figure 1).

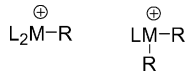

Figure 1. Mono vs. dialkyl cations (L = monoanionic *N*-ligand).

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The starting materials for generating such *N*-ligand stabilised dialkyl cations, namely Zr/Hf trialkyls stabilised by anionic *N*-ligands, are well documented and known for amidinates,[1] guanidinates,[2] diketiminate,[3] macrocyclic amides,[4] tropocoronands[5] and tris(pyrazolyl)borates.[6] Dialkyl cations have been generated from the corresponding tris(pyrazolyl)borates.[6] Unfortunately, these cations are unstable at temperatures above 0 °C and rearrange by ligand degradation.

In recent years the organometallic chemistry of the ancillary aminopyridinato ligands has developed rapidly.[7] Relatively simple and high yield synthesis, combined with easy modification of steric and electronic properties of the precursor aminopyridines has led to a wide variety of mono-, bis-, tris- and tetrakis(aminopyridinato) Zr derivatives.[8] In comparison with zirconium, the chemistry of hafnium with such ligands is much less developed and only homoleptic complexes have been reported so far.[9] In general, aminopyridinato ligands are interesting nonsymmetric versions of bidentate mono anionic *N*-Ligands suited to stabilise early and late transition metals and can be considered as related to amidinate[10] or diketiminate[11] ligands, Figure 2 (middle and right, respectively).

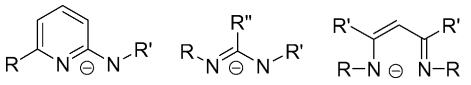


Figure 2. Aminopyridinato ligands (left) and other related bidentate monoanionic *N*-ligands (R, R′ and R′′, for instance, alkyl or aryl substituents).

We have recently reported that bis(aminopyridinato) zirconium catalysts show not only very high activity towards olefin polymerisation but also show selectivity in polymerising ethylene out of ethylene/propylene mixtures and they promote living ethylene polymerisation at elevated temperatures.[8m] The bis(aminopyridinato) complexes discussed in this study were synthesised by salt metathesis. Since the overall yield was only moderate, we became interested in toluene elimination chemistry and observed that the bulky aminopyridinates that selectively gave bis(aminopyridinato) complexes by salt metathesis selectively led to mono(aminopyridinato) tribenzyl Zr/Hf complexes. Mono(aminopyridinates) of these metals are rare[8b,8h,12] and the corresponding trialkyls are unknown. We report here on the synthesis and structures of a series of tribenzyl Hf and Zr aminopyridinates and the corresponding dibenzyl zwitterions as well as some aspects of their ethylene and propylene polymerisation behaviour.

Results and Discussion

Synthesis and Structures of the Zr and Hf Tribenzyl Complexes

The aminopyridine ligands **1**, **2** and **3** (Figure 3) can be synthesised according to published procedures.[13–15]

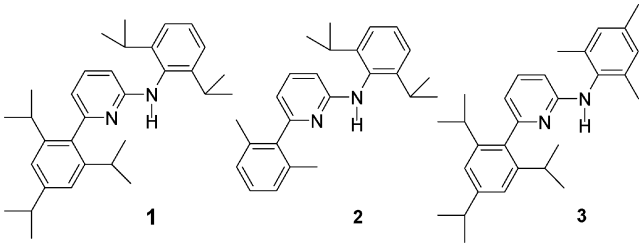
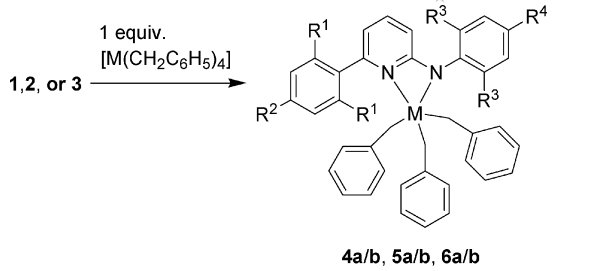


Figure 3. Aminopyridines utilised in this study (**1** = Ap*-H, **2** = Ap^{+}-H and **3** = Ap^{9Me}-H).

Treatment of one equiv. of $[Zr(CH_2C_6H_5)_4]$ or $[Hf(CH_2C_6H_5)_4]$ with **1** in toluene leads to the mono substituted complexes **4a** and **4b**, respectively, due to clean elimination of one toluene molecule (Scheme 1).

NMR scale reactions were found to show complete conversion to the desired products. X-ray quality crystals of complex **4a** were grown from a concentrated pentane solution and details of the X-ray crystal structure analysis are summarised in Table 4. The molecular structure of **4a** is shown in Figure 4. Two of the benzyl groups are bound to the metal in an η^1 manner [Zr1–C40–C41 116.4(3)° and



Scheme 1. Synthesis of tribenzyl complexes [**4**: $R^1 = R^2 = R^3 = CH(CH_3)_2$, R^4 = H, 5: $R^1 = CH_3$, $R^2 = R^4$ = H, $R^3 = CH(CH_3)_2$, **6**: $R^1 = R^2 = CH(CH_3)_2$, $R^3 = R^4 = CH_3$; **a**: M = Zr; **b**: M = Hf].

Zr1–C47–C48 102.5(3)°] while the third displays an acute Zr–C–C_{ipso} angle consistent with η^2-coordination [Zr1–C33–C34 89.3(3)°]. Distances between the metal and the *ipso*-C atoms of the two benzyl groups are 2.921(4) and 3.222(4) Å while a short distance of 2.664(4) Å observed for the third is consistent with an η^2-coordinated benzyl group. The average Zr–CH_2 distance is 2.252 Å which is slightly shorter than the corresponding distances in the closely related guanidinate [{CyNC[$N(SiMe_3)_2$]NCy}$Zr(CH_2C_6H_5)_3$ (Cy = cyclohexyl) 2.273(6) Å][2] or diketiminate complexes [(TTP)$Zr(CH_2C_6H_5)_3$ (TTP = 2-(*p*-tolylamino)-4-(*p*-tolylimino)-2-pentenato) 2.290(5) Å].[3]

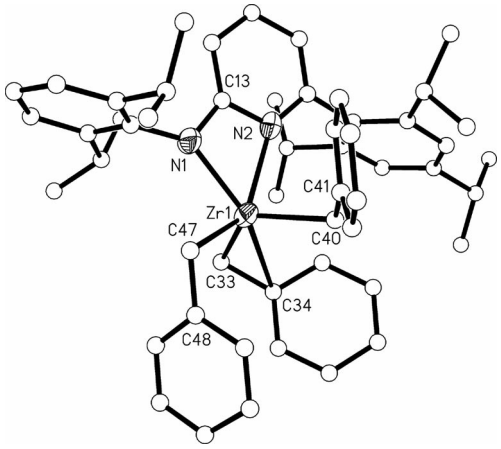


Figure 4. Molecular structure of **4a**, Hydrogen atoms have been omitted for clarity; selected bond lengths [A°] and angles [°]: C33–Zr1 2.243(5), C34–Zr1 2.664(4), C40–Zr1 2.275(5), C47–Zr1 2.236(5), N1–Zr1 2.167(3), N2–Zr1 2.379(4); C34–C33–Zr1 89.3(3), N1–Zr1–C47 82.81(17), C47–Zr1–C33 106.4(2), C47–Zr1–C40 96.7(2), C33–Zr1–C40 126.91(18), N1–Zr1–N2 58.37(12), C47–Zr1–C13 109.33(16), C33–Zr1–C13 109.32(16), C40–Zr1–C13 106.70(16).

Complex **4b** was crystallised from toluene solution along with incorporation of a solvated toluene molecule and it is the first structurally characterised heteroleptic Hf aminopyridinate known to date. The molecular structure is shown in Figure 5. The bonding pattern for the three benzyls is similar to that observed for **4a**, two of them being η^1-coordinated and the third one being η^2-bonded making an acute angle [Hf1–C8–C9 = 88.06 (19)°] which is comparatively smaller than that seen in **4a**. This angle as well as the η^1 or η^2 binding mode is quite sensitive to packing forces.[2b] The

average Hf–C bond length of 2.236 Å is, as expected, slightly shorter than the corresponding bond length observed for the analogous Zr complex.[16]

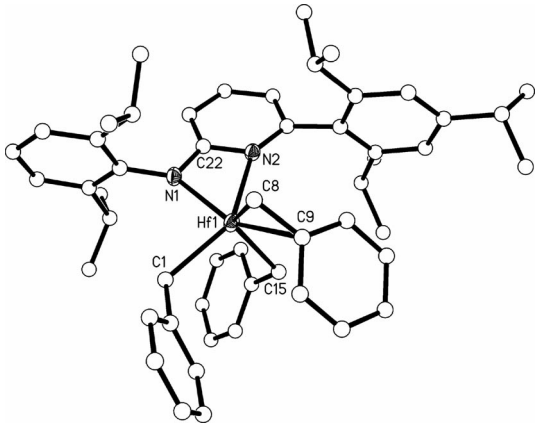


Figure 5. Molecular structure of **4b**, hydrogen atoms and one toluene molecule have been omitted for clarity; selected bond lengths [Å] and angles [°]: C1–Hf1 2.236(3), C8–Hf1 2.228(3), C9–Hf1 2.632(3), C15–Hf1 2.245(3), N1–Hf1 2.132(2), N2–Hf1 2.360(2); C9–C8–Hf1 88.06(19), C8–Hf1–C1 102.91(13), C8–Hf1–C15 124.01(12), C1–Hf1–C15 96.73(13), N1–Hf1–N2 58.85(9), C15–Hf1–C9 89.93(11), C15–Hf1–C22 103.99(10).

The ^{1}H NMR spectra display sharp single peaks at δ = 2.08 ppm and 1.85 ppm for all CH_2 protons of **4a** and **4b**, respectively, indicating the equivalency of all CH_2 protons in solution.

Addition of **2** to $[Zr(CH_2C_6H_5)_4]$ or $[Hf(CH_2C_6H_5)_4]$ in toluene leads to immediate precipitation of the desired mono(aminopyridinato)tribenzylzirconium (**5a**) or hafnium (**5b**) complex (Scheme 1) in quantitative yield. X-ray quality crystals of **5a** were grown from C_6D_6 and those of **5b** were obtained from the cold solution of the filtered mother liquor. The molecular structure of **5a** is shown in Figure 6 and that of **5b** in Figure 7. Again, as in the case of **4a**, one of the three benzyls is η^2-coordinated and the other two benzyl ligands show η^1-coordination.

The η^2-coordinated benzyl group makes an acute angle of 86.74(9)° in **5a** which is smaller than the equivalent angle observed in **4a**. The same angle in **5b** is 90.2(2)° which is slightly larger than that of **4a**. The average Zr–CH_2 distance of 2.267 Å is comparable to that of 2.252 (5) Å in **4a** but the Hf–CH_2 distance of 2.233(4) Å is comparatively shorter than that in **4a**. Similarly, the Zr–C_{ipso} distance of 2.629(15) Å in **5a** is comparatively shorter than that in **5a** but the Hf–C_{ipso} distance of 2.669(4) Å in **5b** involving the η^2-coordinated benzyl is comparable to that of 2.664(4) Å in **4a**. The differences in the Zr–N_{amido} [2.167(3)/2.180(12) Å] and Zr–$N_{pyridine}$ [2.379(4)/2.359(11) Å] distances of **4/5a**, respectively, and the Hf–N_{amido} [2.132(2)/2.136(3) Å] and Hf–$N_{pyridine}$ [2.360(2)/2.340(3) Å] distances in **4/5b**, respectively, indicate a localised binding mode. The anionic charge of the N-ligand is localised at the N_{amido} atom which means a classic donor functionalised amido metal bond rather than an aminopyridinate is observed.[17]

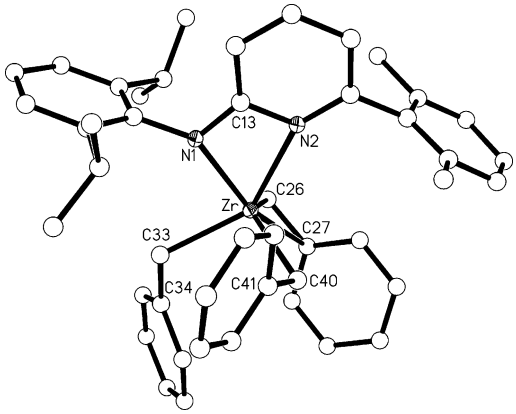


Figure 6. Molecular structure of **5a**; hydrogen atoms and a C_6D_6 molecule have been omitted for clarity. Selected bond lengths [Å] and angles [°]:N1–Zr 2.180(12), N2–Zr 2.359(11), C26–Zr 2.268(16), C27–Zr 2.629(15), C33–Zr 2.260(16), C40–Zr 2.273(15); N1–Zr–N2 58.70(4), C26–Zr–C33 101.16(6), C26–Zr–C40 125.85 (6), C33–Zr–C40 96.53 (6), C27–C26–Zr 86.74 (9).

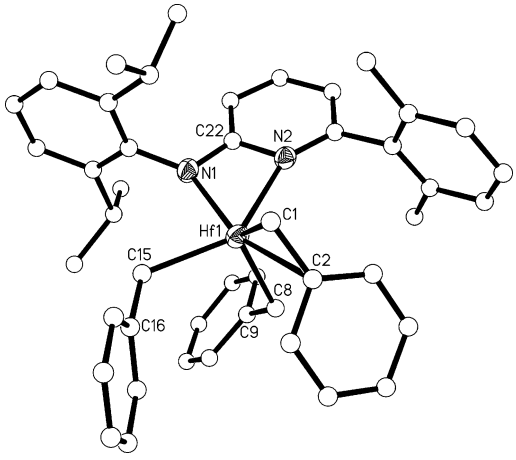
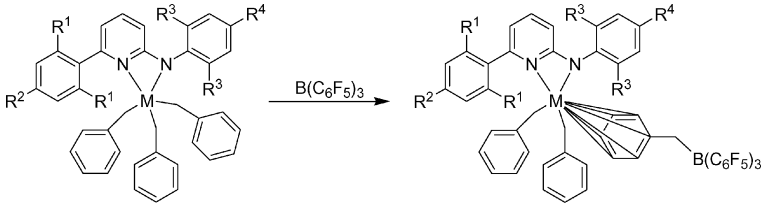


Figure 7. Molecular structure of **5b**; Selected bond lengths [A°] and angles [°]: C1–Hf1 2.223(4), C2–Hf1 2.669(4) C8–Hf1 2.233(4), C15–Hf1 2.243(4), N1–Hf1 2.136(3), N2–Hf1 2.340(3); C2–C1–Hf1 90.2(2), C1–Hf1–C8 120.81(15), C1–Hf1–C15 99.24(18), C8–Hf1–C15 101.16(18), C1–Hf1–C22 117.43(13), C8–Hf1–C22 105.57(13), C15–Hf1–C22 111.02(14).

Mono(aminopyridinato)tribenzylzirconium or hafnium complexes **6a/b** could be obtained when **3** was treated with an equimolar quantity of the corresponding tetrabenzyl complex in toluene. Cooling of the solvent leads to the desired complexes in good yields (Scheme 1).

Synthesis and Structures of the Zwitterionic Complexes

The reaction of **4a** with 1 equiv. of $B(C_6F_5)_3$ in toluene (Scheme 2) at room temperature afforded a red-orange crystalline solid after the addition of pentane. It was identified by ^{1}H and ^{13}C NMR spectroscopy to be the zwitterionic complex, $[Ap^*Zr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ **7a**. of particular note, in the ^{1}H NMR spectrum, are two doublets of an AB system observed at δ = 2.42 and 2.80 ppm for nonequivalent Zr–CH_2Ph methylene protons. The chemical



Scheme 2. Synthesis of the zwitterionic complexes [**7**: $R^1 = R^2 = R^3 = CH(CH_3)_2$, R^4 = H, **8**: $R^1 = CH_3$, $R^2 = R^4$ = H, $R^3 = CH(CH_3)_2$, **9**: $R^1 = R^2 = CH(CH_3)_2$, $R^3 = R^4 = CH_3$, **a**: M = Zr; **b**: M = Hf].

shifts of the B*CH*$_2$Ph methylene moiety appear as a broad singlet at δ = 3.13 ppm. The *ortho*, *meta* and *para* H atoms of the B-bonded benzyl group appear at δ = 6.22, 5.89 and 5.77 ppm, respectively, suggesting the coordination of the phenyl ring to Zr. An analogous reaction of **4b** with $B(C_6F_5)_3$ in an NMR tube led to a similar ^{1}H NMR spectrum for **7b** (two doublets of an AB system observed at δ = 2.12 and 2.24 ppm for nonequivalent Zr–*CH*$_2$Ph methylene protons and a broad doublet at δ = 3.31 ppm for the B*CH*$_2$Ph methylene protons). The B-bound benzyl group shows a doublet-triplet-triplet pattern of resonances with chemical shifts of 5.85, 6.14 and 6.42 ppm for the *ortho*, *meta* and *para* hydrogen atoms, respectively, suggesting coordination of the phenyl ring of the borate moiety to the Hf metal centre. The formation of these zwitterionic complexes through benzyl coordination was also reflected by the large $\Delta\delta$[(*p*-F) – (*m*-F)] value of 3.9 ppm.[18] Complexes **8a/b** were prepared in an analogous way to **7a/b** by treating **5a/b** with $B(C_6F_5)_3$ (Scheme 2). Complex **8a** was crystallised in good yield (81%) by layering a toluene solution with pentane. The molecular structure of **8a** was established by single-crystal X-ray diffraction analysis of its toluene solvate. Details of the X-ray crystal structure analyses are summarised in Table 5. As shown in Figure 8, the molecular structure of **8a** consists of an $[Ap^+Zr(CH_2C_6H_5)_2]^+$ cation π-coordinated to the $BCH_2C_6H_5$ moiety of the $[B(CH_2C_6H_5)(C_6F_5)_3]^-$ anion. The two benzyl groups of the "cation" behave as normal, undistorted η^1 ligands, without significant Zr···C_{ipso} interactions. Zr–CH_2 distances [2.258(5) and 2.267(5) Å] are in the typical range of values observed for Zr benzyl compounds. The six Zr–C metal–arene distances are slightly different. In particular, the *ipso* carbon is significantly further from Zr [2.844(5) Å] whereas the *m*- and *p*-C atoms are found closer to Zr. The four B–C bonds in $[B(CH_2C_6H_5)(C_6F_5)_3]^-$ are tetrahedrally arranged. ^{1}H NMR spectroscopy shows that the zwitterionic structure of **8a** found in the solid state is maintained in solution. An NMR tube reaction was carried out for **5b** with $B(C_6F_5)_3$ to form **8b** in C_6D_6. Noteworthy in the ^{1}H NMR spectrum are broad signals, especially two broad singlets at δ = 2.10 and 2.21 ppm for the Zr-C*H*$_2$Ph protons, one broad singlet for the protons of the isopropyl group of the ligands and one broad singlet for the B–CH_2 protons. The two broad singlets for C*H*$_2$Ph were seen to become converted into two sharp doublets of an AB system when a C_7D_8 solution was cooled to 253 K. This low temperature measurement also leads to a well resolved septet for the protons of the isopropyl group and sharp signals for the aromatic protons of the aminopyridinato ligand. The large $\Delta\delta$[(*p*-F)-(*m*-F)] values of 4.1 and 4.0 ppm found for **8a** and **8b**, respectively, are indicative of the formation of zwitterionic complexes.[18]

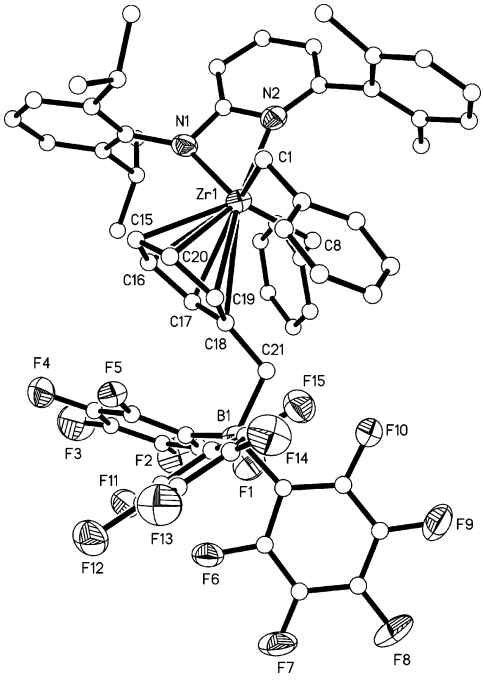


Figure 8. Molecular structure of **8a**. Hydrogen atoms and two toluene molecules have been omitted for clarity; selected bond lengths [Å] and angles [°]: C1–Zr1 2.258(5), C8–Zr1 2.267(5), C15–Zr1 2.616(5), C16–Zr1 2.614(5), C17–Zr1 2.705(5), C19–Zr1 2.762(5), C18–Zr1 2.844(5), C19–Zr1 2.762(5), C20–Zr1 2.668(5); C1–Zr1–C8 113.7(2), N1–Zr1–N2 59.00(14), C1–Zr1–C22 101.85(17), C8–Zr1–C22 99.24(17).

The reaction of **6a** (in toluene) or **6b** (in C_6D_6) with $B(C_6F_5)_3$ at room temperature results in the formation of **9a** or **9b**, respectively, in quantitative yield (Scheme 2). Complex **9a** was isolated as orange crystals when a concentrated toluene solution was layered with pentane. The molecular structure of **9a** as a solvate with two toluene molecules was determined by single-crystal X-ray diffraction analysis. The molecular structure consists of an $[Ap^{9Me}Zr(CH_2C_6H_5)_2]^+$ cation π-coordinated to the $BCH_2C_6H_5$ moiety of the $[B(CH_2C_6H_5)(C_6F_5)_3]^-$ anion (Figure 9). The two benzyl ligands are η^1-coordinated with Zr–CH_2 distances of 2.235(5) and 2.264(5) Å. The phenyl ring of the anion is η^6-coordinated to the Zr centre. The Zr–C_{ipso} dis-

tance of 2.816(5) Å is comparable to that of 2.844(5) Å in **8a**. The *m*-, *p*-C atoms were found closer to Zr with bond lengths of 2.650(5) Å and 2.667(5) Å, respectively, compared with the *o*-C atoms with an average distance of 2.720(5) Å from Zr.

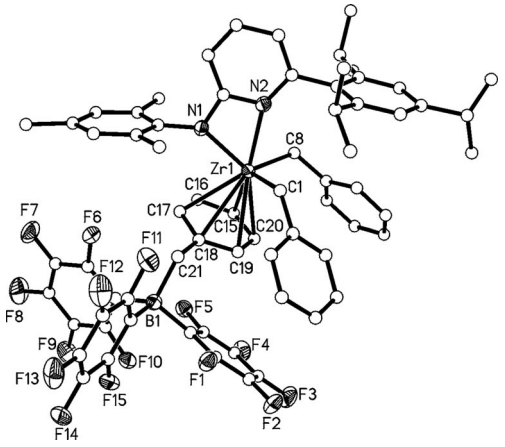


Figure 9. Molecular structure of **9a**. Hydrogen atoms and toluene molecules have been omitted for clarity; selected bond lengths [Å] and angles [°]: C1–Zr1 2.235(5), C8–Zr1 2.264(5), C15–Zr1 2.651(5), C16–Zr1 2.667(5), C17–Zr1 2.731(5), C18–Zr1 2.816(5), C19–Zr1 2.708(5), C20–Zr1 2.650(5), N1–Zr1 2.123(4), N2–Zr1 2.401(4); C1–Zr1–C8 108.70(2), N1–Zr1–N2 59.01(16), C1–Zr1–C22 97.75(18), C8–Zr1–C22 99.37(18).

Of particular note, in the ^{1}H NMR spectra, are two doublets of an AB system at δ = 2.37 and 2.76 ppm for **9a** and at δ = 2.01 and 2.22 ppm for **9b** for the nonequivalent Zr–CH_2 protons and broad singlets at δ = 3.22 and 3.30 ppm for the B–CH_2 protons of **9a** and **9b**, respectively. Moreover a doublet, triplet and triplet pattern for the *o*-, *m*- and *p*-protons of the B-bound benzyl was observed at 6.09, 5.81 and 5.71 ppm for **9a** and at 6.22, 6.00 and 5.92 ppm for **9b**. The large $\Delta\delta$[(*p*-F) – (*m*-F)] values of 4.0 and 3.9 ppm for **9a** and **9b**, respectively, reflect the formation of these zwitterionic complexes.[18] The different Zr–N_{amido} [2.143(4)/2.123(4) Å] and Zr–$N_{pyridine}$ [2.334(4)/2.401(4) Å] distances for **8a**/**9a**, respectively, indicate a localised binding mode of the aminopyridinato ligand. We studied the formation of the dicationic species by NMR spectroscopy using $[R_2MeNH][BC_6F_5]_4$. The NMR spectra are not indicative of a clear formation of the dicationic species. We also studied, by NMR spectroscopy, the stability and possible abstraction of the second benzyl group by treating the zwitterionic complex **7a** with one equiv. of $B(C_6F_5)_3$. However this complex was quite stable and did not undergo any noticeable change.

Polymerisation Studies

The activities of the catalyst precursors **4a**–**6a** and **4b** were studied for the polymerisation of ethylene and the catalysts have been explored in terms of the cocatalyst used for the generation of the cationic species, Table 1. It was observed that activating **4a** with $B(C_6F_5)_3$ produces very low activity towards ethylene at 50 °C even if H_2 was introduced into the system to generate more active hydride species (entries 1 and 3). This might be understandable as **4a** forms the zwitterionic complex which essentially blocks the coordination site and leads to an inactivated catalyst. At higher temperatures, the dormant catalyst could be forced to achieve a moderate single site polymerisation activity (M_w/M_n = 1.9) with the formation of high molecular weight polyethylene. To get more insight into this behaviour and to study the possible blockage of the coordination sites of the catalyst, we switched to ammonium borate as the activator. The abstraction of one of the benzyls of **4a** leads to a quite active polymerisation system (entry 4) and the catalyst is stable even at high temperature. However the single site behaviour observed above was replaced by different active sites producing a trimodal distributed PE. Introduction of H_2 into the system doesn′t have a pronounced effect on the catalytic activity (entry 5) but leads to a strong drop-down in the average molecular weight of the polymer. For the less sterically crowded systems **5a** and **6a**, comparatively low activities were observed under identical conditions. It is also worth noting that for the Hf system **4b**, which has the same steric demand as **4a**, yields much longer PE chains with a broad but mono modal distribution (runs 10 and 11). Since we did not observe clear formation of the dicat-

Table 1. Activator dependence of the ethylene polymerisation catalysed by tribenzyl-Zr and -Hf complexes.[a]

Entry	pre-Cat. [μmol]		Activator [μmol]		T / °C	$m_{Pol.}$ [g]	Activity [$kg_{PE}\,mol_{cat}^{-1}\,h^{-1}\,bar^{-1}$]	M_w [$g\,mol^{-1}$]	M_w/M_n
			$B(C_6F_5)_3$	$B(C_6F_5)_4^-$ [c]					
1	**4a**	2	2.2		50	0.05	20	–	–
2	**4a**[b]	2	2.2		80	0.30	120	1130000	1.9
3	**4a**[d]	2	2.2		50	0.05	20	–	–
4	**4a**	2		2.2	30	0.70	280	70000	19.9
5	**4a**	2		2.2	50	2.30	920	72900	21.1
6	**4a**	2		2.2	80	2.80	1120	71800	21.6
7	**4a**[d]	2		2.2	80	2.70	1080	16100	6.4
8	**5a**	2		2.2	50	1.60	640	328000	62.3
9	**6a**	2		2.2	50	1.20	480	45200	14.2
10	**4b**	1.8		2.2	80	1.20	533	212000	5.5
11	**4b**[b]	1.8		2.2	80	2.70	1200	108000	3.1

[a] Toluene: 260 mL, p = 5 bar, t = 15 min, scavenger: TIBAO (50 μmol). [b] TIBA (110 μmol); pre-catalyst and activator premixed before injection. [c] Ammonium borate, $[R_2(CH_3)NH]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$). [d] 80 mL H_2 added.

ionic species we did not investigate the polymerisation chemistry of the dicationic species generated by adding two equiv. of $[R_2MeNH][BC_6F_5]_4$.

Since, in case of tribenzyl systems, the coordination of the abstracted benzyl seems to interfere with the polymerisation process we became interested in a possible double activation of these catalysts, Table 2. The results show that these species can be converted into active catalysts especially if premixing of the zwitterionic complexes **7a**–**9a** is carried out with ammonium borate before injection into the autoclave. Nevertheless the broad molecular weight distribution of the produced polymers, the similar average molecular weights and activities compared with those in Table 1 entries 8 and 9 suggests that this is, rather, the result of an anion exchange than formation of a well defined dicationic catalyst.

The catalyst systems based on **4a/b** are not active towards propylene polymerisation, Table 3 (entries 1 and 4). However, presence of ethylene reactivates the catalysts and leads to copolymerisation. NMR spectroscopic analysis of the copolymers based on **4a/b** reveals quite a different nature for the resultant copolymers. Zirconium complex **4a** gives long chain α-olefins for which one can detect the resonances for the olefinic and methyl end groups at 14, 114 and 139 ppm, Figure 10. In contrast, hafnium complex **4b** based on the same steric bulk gives a long chain copolymer with isolated/

Table 2. Ethylene polymerisation catalysed by zwitterionic Zr complexes.[a]

Entry	pre-Cat. [μmol]		Activator [μmol] $B(C_6F_5)_3$	$B(C_6F_5)_4^-$ [b]	$m_{Pol.}$ [g]	Activity $[kg_{PE}\,mol_{cat}^{-1}\,h^{-1}]$	M_w $[g\,mol^{-1}]$	M_w/M_n
1	**4a**	2	2.2		0.30	120	1130000	1.9
2	**4a**	2	2.2	2.2	1.30	520	1256000	1.9
3	**8a**	2			0.07	28	–	–
4	**8a**	2		2.2	1.70	680	455000	102.9
5	**9a**	2			0.08	32	534000	23.9
6	**9a**	2		2.2	1.50	600	13700	7.1

[a] Toluene: 260 mL, p = 5 bar, t = 15 min, T = 80 [°C], scavenger: TIBA (110 μmol), pre-catalyst and activator premixed before injection. [b] Ammonium borate, $[R_2(CH_3)NH]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$).

Table 3. Propylene homo- and ethylene/propylene co-polymerisation using **4a/b**.[a]

Entry	pre-Cat. [μmol]		Pressure [bar] ethene	propene	$m_{Pol.}$ [g]	Activity $[kg_{PE}\,mol_{cat}^{-1}\,h^{-1}]$	M_w $[g\,mol^{-1}]$	M_w/M_n
1	**4a**	2		5	0.05	100	–	–
2	**4a**	2	5	3	3.10	6200	14700	11.6
3	**4a**	2	5	4	2.50	5000	14300	8.0
4	**4b**	1.80		5	0.05	110	–	–
5	**4b**	1.80	5	3	2.20	4889	94600	2.4
6	**4b**	1.80	5	4	2.20	4889	76000	2.4

[a] Toluene: 260 mL, t = 15 min, T = 80 °C, scavenger: TIBA (110 μmol), activator: ammonium borate, $[R_2(CH_3)NH]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$); pre-catalyst and activator premixed before injection.

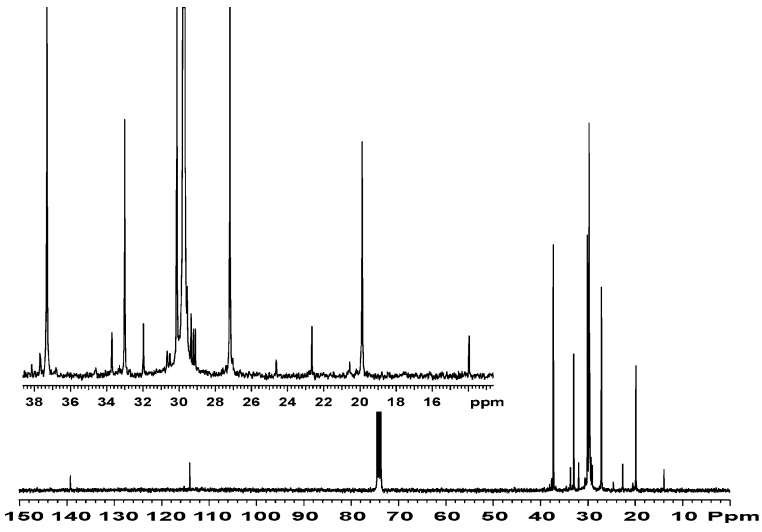


Figure 10. ^{13}C NMR spectrum of poly(ethylene-co-propene) obtained with **4a**/$[R_3NH][B(C_6F_5)_4]$ (Table 3, entry 2).

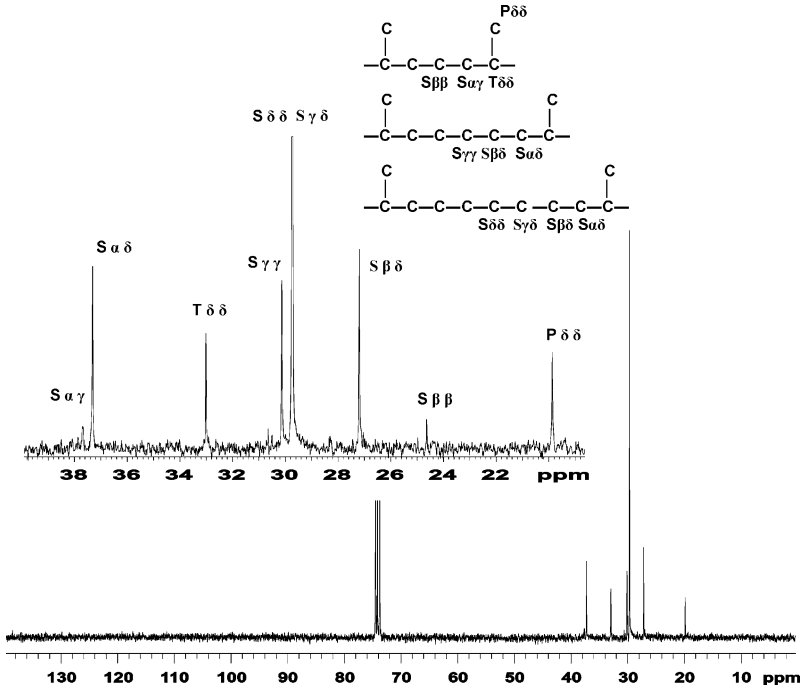


Figure 11. ^{13}C NMR spectrum of poly(ethylene-co-propene) obtained with **4b**/$[R_3NH][B(C_6F_5)_4]$ (Table 3, entry 5).

alternating propene units with no evidence of PP sequences, Figure 11. It is noteworthy that the resultant EP-copolymer has a much smaller molecular weight distribution than the ethylene homopolymer observed under similar conditions.

Conclusions

Mono(aminopyridinato) tribenzyl complexes of zirconium and hafnium can be prepared by toluene elimination in high yield if the tetrabenzyl metal precursor is treated with one equivalent of the corresponding aminopyridine. In the solid state, one of the three benzyls is η^2-coordinated and rest are η^1-coordinated to the electron deficient metal centres. Moreover, one of the three benzyls has been partially abstracted using $B(C_6F_5)_3$, the phenyl ring of B-bounded benzyl shows an η^6-coordination fashion. These zwitterionic complexes do not react with a second equiv. of $B(C_6F_5)_3$ which would allow abstraction of a second benzyl. Polymerisation studies revealed that the B-bounded benzyl is too strongly bound to the metal to generate the active catalyst systems. If activation of the tribenzyls occurs with ammonium borate instead of borane, a quite high ethylene polymerisation activity was observed but the multimodal distribution of the polymer suggests that the catalyst is rather ill defined. However, if one applies this system to ethylene-propylene copolymerisation, a high regioselectivity including alternating EP units was detected.

Experimental Section

Synthesis and Structure Analysis: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in a nitrogen-filled glove box (mBraun 120-G) with a high-capacity recirculator (< 0.1 ppm O_2). Nonhalogenated solvents were dried by distillation from sodium/benzophenone. Deuterated solvents were obtained from Cambridge Isotope Laboratories. $[D_6]$Benzene and $[D_8]$toluene were dried with sodium/potassium alloy and $[D_5]$bromobenzene was dried over molecular sieves, degassed and distilled prior to use. Toluene for polymerisation (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), a BASF R3–11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). Ethylene (AGA polymer grade) was passed over a BASF R3–11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). *N*,*N*,*N*-Trialkylammonium tetrakis(pentafluorophenyl)borate ($[R_2NMeH][B(C_6F_5)_4]$, R = $C_{16}H_{33}$–$C_{18}H_{37}$, 6.2 wt.-% $B(C_6F_5)_4^-$ in Isopar, DOW Chemicals) and tri-isobutylaluminium (TIBA, 2.0 M in toluene, Aldrich) were used as received. Tetra-isobutylaluminoxane ($[i Bu_2Al]_2O$, TIBAO) was prepared according to a published procedure.[19] Commercial $ZrCl_4$ (Strem) and $HfCl_4$ (Across Organics) were used as received. $[Zr(CH_2C_6H_5)_4]$ and $[Hf(CH_2C_6H_5)_4]$ were prepared according to the literature procedures.[20] NMR spectra were recorded on Bruker ARX 250 MHz and Varian Inova 400 MHz spectrometers. The chemical shifts are reported in ppm referenced to internal TMS for ^1H and ^{13}C. Elemental analyses (C,H,N) were determined using a Vario EL III instrument. X-ray crystal structure analyses were performed by using a STOE-IPDS II instrument equipped with an Oxford Cryostream low-temperature unit and a Bruker[21] SMART APEX CCD diffractometer (platform with full three-circle goniometer). Structure solution and refinement were accomplished using SIR97,[22] SHELXL97[23] and WinGX.[24] Crystallographic details are summarised in Tables 4 and 5.

CCDC-681000 (for **4a**), -681001 (for **4b**), -681005 (for **5a**), -681002 (for **5b**), -681003 (for **8a**) and -681004 (for **9a**) 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.

Table 4. Details of the X-ray crystal structure analyses.

Compound	**4a**	**4b+C_7H_8**	**5a+C_6D_6**	**5b**
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	*Cc*	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a [Å]	18.2613(14)	11.6990(6)	11.1891(7)	12.8690(7)
b [Å]	16.9597(12)	31.2140(7)	12.6619(8)	14.3510(5)
c [Å]	15.8685(11)	18.4030(9)	15.981(1)	21.4180(10)
α [°]		110.893(4)	83.967(1)	
β [°]	111.438(6)	102.505(4)	72.555(1)	101.687(4)
γ [°]		92.733(4)	83.492(1)	
V [Å^3]	4574.5(6)	2570.4(2)	2140.0(2)	3873.5(3)
Crystal size [mm]	0.30 × 0.25 × 0.20	0.76 × 0.33 × 0.12	0.51 × 0.43 × 0.37	0.30 × 0.22 × 0.21
ρ_{calcd} [g cm^{-3}]	1.191	1.292	1.242	1.388
μ [mm^{-1}] (Mo-K_α)	0.276	2.068	0.294	2.726
T [K]	193(2)	133(2)	100(1)	173(2)
θ range [°]	1.70–25.75	1.65–25.69	2.40–29.60	1.71–25.75
No. of reflections unique	8615	9681	9153	7319
No. of reflections obsd. [$I > 2\sigma(I)$]	5454	8685	8604	5718
No. of parameters	505	569	720	448
wR_2 (all data)	0.0895	0.0699	0.0707	0.0664
R value [$I > 2\sigma(I)$]	0.0507	0.0245	0.0275	0.0326

Table 5. Details of the X-ray crystal structure analyses.

Compound	**8a+C_7H_8**	**9a+2C_7H_8**
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a [Å]	10.0540(11)	12.4160(6)
b [Å]	14.7200(18)	24.1090(12)
c [Å]	22.042(3)	22.8350(12)
α [°]	77.993(10)	
β [°]	77.251(10)	99.396(4)
γ [°]	72.677(9)	
V [Å^3]	3001.7(6)	6743.7(6)
Crystal size [mm]	0.26 × 0.20 × 0.18	0.25 × 0.17 × 0.09
ρ_{calcd} [g cm^{-3}]	1.467	1.413
μ, [mm^{-1}] (Mo-K_α)	0.276	0.252
T [K]	133(2)	133(2)
θ range [°]	1.47 to 25.74	1.69–25.79
No. of reflections unique	11035	12608
No. of reflections obsd. [$I > 2\sigma(I)$]	4883	7937
No. of parameters	814	838
wR_2 (all data)	0.1356	0.1925
R value [$I > 2\sigma(I)$]	0.0615	0.0778

General Description of Ethylene Polymerisation Experiments: The catalytic ethylene polymerisation reactions were performed in a stainless steel 1 L autoclave (Medimex) in semi-batch mode (ethylene was added by replenishing flow to keep the pressure constant). The reactor was temperature and pressure controlled and equipped with separated toluene, catalyst and co-catalyst injection systems and a sample outlet for continuous reaction monitoring. Up to 15 bar of ethylene pressure and multiple injections of the catalyst with a pneumatically operated catalyst injection system were used. During a polymerisation run the pressure, ethylene flow, inner and the outer reactor temperature and the stirrer speed were monitored continuously. In a typical semi-batch experiment, the autoclave was evacuated and heated for 1 h at 125 °C prior to use. The reactor was then brought to the desired temperature, stirred at 600 rpm and charged with 230 mL of toluene together with 1 mL of a 0.05 M solution of TIBAO (tetra-isobutylaluminoxan, Zr/Al = 1/100) or 0.1 mL of a 1.1 M solution of TIBA (tri-isobutylaluminum, Zr/Al = 1:110) in toluene as mentioned in the text. After pressurising with ethylene to reach 5 bar total pressure, the autoclave was equilibrated for 5 min. Subsequently, 1 mL of a 0.002 M catalyst stock solution in toluene was injected together with 30 mL of toluene to start the reaction. The catalyst mixture was prepared by successively adding 1 mL of toluene and 1 mL of a 0.002 M catalyst stock solution in toluene to 25 mg of $[R_2NMeH][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$, 6.2 wt.-% $B(C_6F_5)_4^-$ in Isopar, Zr/B = 1:1.1). During the run the ethylene pressure was kept constant to within 0.2 bar of the initial pressure by replenishing the flow. After 15 min of reaction time, the reactor was vented and the residual aluminium alkyls were destroyed by addition of 100 mL of ethanol. The polymeric product was collected, stirred for 30 min in acidified ethanol and rinsed with ethanol and acetone on a glass frit. The polymer was initially dried in air and subsequently in vacuo at 80 °C.

The polymer samples for NMR spectroscopic measurements were prepared by dissolving 15 mg of the polymer in 0.5 mL CD_2Cl_2 at 100 °C for 3 h before measuring. Gel permeation chromatography (GPC) analysis was carried out on a Polymer Laboratories Ltd (PL-GPC210) chromatograph, equipped with a capillary differential viscometer (Viscotek), a refractive index (RI) detector and a two-angle (15° and 90°) light scattering photometer at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.1% w/v) in the mobile phase solvent in an external oven and were run without filtration. The molecular weight was referenced to polyethylene (M_w = 50000 g mol^{-1}) and polystyrene (M_w = 100000–500000 g mol^{-1}) standards. The reported values are the average of at least two independent determinations.

General Description of Ethylene/Propylene Co-Polymerisation Experiments: The general procedure and conditions as described above were followed, using successively 3 bar or 4 bar propylene and 5 bar ethylene to pressurise the reactor (Figure 12).

Synthesis of 4a: Toluene (20 mL) was added to **1** (0.456 g, 1 mmol) and $[Zr(CH_2(C_6H_5))_4]$ (0.456 g, 1 mmol) at room temperature. The solution was stirred overnight in the absence of light at room temperature. The solvent was then evaporated and the product was extracted with pentane (10 mL). The filtrate was cooled to –25 °C affording a yellow crystalline material of the product. Yield 0.603 g (74%). $C_{53}H_{64}N_2Zr$ (820.31): calcd. C 77.60, H 7.86, N 3.41; found

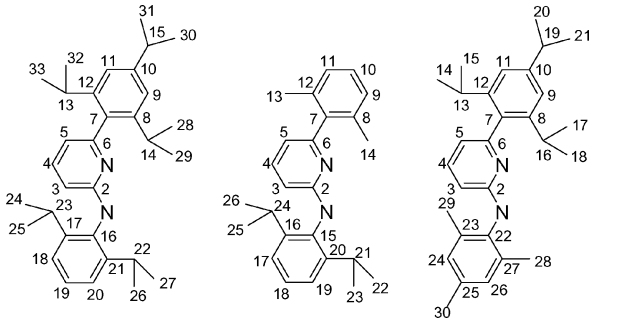


Figure 12. NMR signal labels of the synthesised metal complexes.

C 76.74, H 7.81, N 3.76. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 1.06–1.30 (m, 30 H, $H^{24,25,26,27,28,29,30,31,32,33}$), 2.08 (s, 6 H, $H^{CH2(benzyl)}$), 2.87 (m, 3 H, $H^{13,14,15}$), 3.60 (sept, 2 H, $H^{22,23}$), 5.72 (d, 1 H, H^3), 6.13 (d, 1 H, H^5), 6.46 (dd, 6 H, $H^{CH(benzyl)}$), 6.73 (t, 1 H, H^4), 6.86–7.24 (m, 14 H, $H^{9,11,18,19,20,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 22.3 ($C^{28,29,32,33}$), 24.1 ($C^{24,25,26,27}$), 24.2 ($C^{30,31}$), 25.5 ($C^{24,25,26,27}$), 26.7 ($C^{28,29,32,33}$), 29.1 ($C^{22,23}$), 31.0 ($C^{13,14}$), 34.9 (C^{15}), 80.6 ($C^{CH2(benzyl)}$), 106.2 (C^3), 114.2 (C^5), 121.4 ($C^{9,11}$), 123.2 (C^{benzyl}), 124.7 ($C^{18,20}$), 126.7 (C^{19}), 127.8 (C^{benzyl}), 129.9 (C^{benzyl}), 134.3 (C^7), 141.0 (C^4), 143.2 (C^{benzyl}), 143.5 (C^{16}), 144.0 ($C^{17,21}$), 147.0 ($C^{8,12}$), 150.7 (C^{10}), 155.7 (C^6), 173.0 (C^2) ppm.

Synthesis of 4b: $[Hf(CH_2(C_6H_5))_4]$ (0.543 g, 1 mmol) was added to **1** (0.456 g, 1 mmol) in toluene (15 mL) at room temperature. A sudden colour change to orange-yellow was observed. The reaction mixture was stirred for 4 h. The volume was reduced and the product was allowed to crystallise at –25 °C. Yield 0.56 g (78%, NMR scale 100%). $C_{53}H_{64}HfN_2$ (908.45): calcd. C 70.14, H 7.11, N 3.09; found C 69.84, H 7.42, N 3.09. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 1.06 (d, 6 H, $H^{28,29,32,33}$), 1.14 (d, 6 H, H, $H^{30,31}$), 1.17 (d, 6 $H^{24,25,26,27}$), 1.22 (d, 6 H, $H^{24,25,26,27}$), 1.31 (d, 6 H, $H^{28,29,32,33}$), 1.85 (s, 6 H, $H^{CH2(benzyl)}$), 2.89 (m, 3 H, $H^{13,14,15}$), 3.47 (sept, 2 H, $H^{22,23}$), 5.64 (d, 1 H, H^3), 6.24 (d, 1 H, H^5), 6.46 (d, 6 H, $H^{CH(benzyl)}$), 6.74 (dd, 1 H, H^4), 6.86 (dd, 3 H, $H^{CH(benzyl)}$), 7.04 (dd, 6 H, $H^{CH(benzyl)}$), 7.18 (s, 2 H, $H^{9,11}$), 7.22 (m, 3 H, $H^{18,19,20}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 22.3 ($C^{28,29,32,33}$), 24.1 ($C^{24,25,26,27}$), 24.2($C^{30,31}$), 25.5 ($C^{24,25,26,27}$), 26.6 ($C^{28,29,32,33}$), 29.1 ($C^{22,23}$), 31.1 ($C^{13,14}$), 34.9 (C^{15}), 86.8 ($C^{CH2–benzyl}$), 106.2 (C^3), 115.3 (C^5), 121.5 ($C^{9,11}$), 123.1 (C^{benzyl}), 124.6 ($C^{18,20}$), 129.3 (C^{19}), 129.4 (C^{benzyl}), 134.2 (s, C^7), 141.4 (C^4), 142.6 ($C^{16/benzyl}$), 143.6 ($C^{17,21}$), 145.1 (C^{benzyl}), 147.0 ($C^{8,12}$), 150.9 (C^{10}), 155.9 (C^6), 170.1 (C^2) ppm.

Synthesis of 5a: $[Zr(CH_2(C_6H_5))_4]$ (0.456 g, 1 mmol) was added to a solution of **2** (0.358 g, 1 mmol) in toluene (15 mL) with stirring at room temperature. A yellow coloured product quickly precipitated. The reaction mixture was stirred for a further 4 h and then filtered leaving behind a yellow product. The filtrate was concentrated under vacuum and allowed to crystallise at low temperature to give yellow crystals suitable for X-ray analysis. Yield 0.6 g (83%, NMR scale 100%). $C_{46}H_{50}N_2Zr$ (722.13): calcd. C 76.51, H 6.98, N 3.88; found C 76.15, H 6.85, N 3.52. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 1.21 (d, 12 H, $H^{22,23,25,26}$), 1.24 (d, 6 H, $H^{22,23,25,26}$), 2.04 (s, 6 H, $H^{CH2(benzyl)}$), 2.06 (s, 6 H, $H^{13,14}$), 3.63 (sept, 2 H, $H^{21,24}$), 5.64 (dd, 1 H, H^3), 5.71 (dd, 1 H, H^5), 6.45 (d, 6 H, $H^{CH(benzyl)}$), 6.74 (t, 1 H, H^4), 6.83–6.93 (m, 5 H, $H^{17,19,CH(benzyl)}$), 7.01–7.24 (m, 10 H, $H^{9,10,11,18,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 20.1 ($C^{13,14}$), 24.1 ($C^{22,23,25,26}$), 25.5 ($C^{22,23,25,26}$), 29.0 ($C^{21,24}$), 80.2 ($C^{CH2–benzyl}$), 105.7 (C^3), 111.9 (C^5), 123.2 (C^{benzyl}), 124.7 ($C^{17,19}$), 126.7 (C^7), 127.8 ($C^{9,11}$), 128.2 (C^{18}), 129.1 (C^{10}), 129.9 (C^{benzyl}), 136.1 ($C^{16,20}$), 138.6 (C^4), 142.2 (C^{benzyl}), 143.0 (C^{15}), 143.2 ($C^{8,12}$), 144.8 (C^{benzyl}), 155.9 (C^6), 172.8 (C^2) ppm.

Synthesis of 5b: $[Hf(CH_2(C_6H_5))_4]$ (0.543 g, 1 mmol) was added to a solution of **2** (0.358 g, 1 mmol) in toluene (15 mL) with stirring at room temperature. A yellow coloured product quickly precipitated. The reaction mixture was stirred for a further 4 h and then filtered leaving behind a yellow coloured product. The filtrate was reduced under vacuum and allowed to crystallise at low temperature to give yellow crystals suitable for X-ray analysis. Yield 0.78 g (96%, NMR scale 100%). $C_{46}H_{50}HfN_2$ (810.34): calcd. C 68.26, H 6.23, N 3.46; found C 67.68, H 6.50, N 3.42. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 1.15 (d, 12 H, $H^{22,23,25,26}$), 1.18 (d, 6 H, $H^{22,23,25,26}$), 1.83 (s, 6 H, $H^{CH2(benzyl)}$), 2.05 (s, 6 H, $H^{13,14}$), 3.49 (sept, 2 H, $H^{21,24}$), 5.57 (dd, 1 H, H^3), 5.81 (dd, 1 H, H^5), 6.47 (d, 6 H, $H^{CH(benzyl)}$), 6.74 (t, 1 H, H^4), 6.85–6.90 (m, 5 H, $H^{17,19,CH(benzyl)}$), 7.00–7.22 (m, 10 H, $H^{9,10,11,18,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 20.1 ($C^{13,14}$), 24.0 ($C^{22,23,25,26}$), 25.4 ($C^{22,23,25,26}$), 29.0 ($C^{21,24}$), 87.0 ($C^{CH2(benzyl)}$), 105.6 (C^3), 112.8 (C^5), 123.1 (C^{benzyl}), 124.6 ($C^{17,19}$)), 128.2 ($C^{9,11}$), 128.5 (C^{18}), 128.9 (C^{10}), 129.3 (C^{benzyl}), 136.0 ($C^{16,20}$), 137.8 (C^7), 138.5 (C^4), 142.2 (C^{benzyl}), 142.5 (C^{15}), 143.4 ($C^{8,12}$), 145.0 (C^{benzyl}), 156.0 (C^6), 170.2(C^2) ppm.

Synthesis of 6a: Toluene (20 mL) was added to **3** (0.3 g, 0.72 mmol) and $Zr(CH_2(C_6H_5))_4$ (0.33 g, 0.72 mmol) at room temperature. The reaction mixture was stirred overnight in the absence of light. The solution was evaporated to dryness and the product was extracted with pentane (10 mL). The filtrate was cooled to –25 °C affording yellow needle like crystals of the product. Yield 0.285 g (50%). $C_{50}H_{58}N_2Zr$ (778.3): calcd. C 77.17, H 7.51, N 3.60; found C 76.63, H 7.69, N 3.65. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 1.08 (d, 6 H, $H^{14,15,17,18}$), 1.22 (d, 6 H, $H^{14,15,17,18}$), 1.30 (d, 6 H, $H^{20,21}$), 2.10 (s, 6 H, $H^{CH2(benzyl)}$), 2.19 (s, 3 H, H^{30}), 2.23 (s, 6 H, $H^{28,29}$), 2.90 (m, 3 H, $H^{13,16,19}$), 5.67 (d, 1 H, H^3), 6.17 (d, 1 H, H^5), 6.45 (d, 6 H, $H^{CH(benzyl)}$), 6.78 (t, 1 H, H^4), 6.85–7.26 (m, 13 H, $H^{9,11,26,24,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz C_6D_6, 298 K): δ = 18.7 ($C^{28,29}$), 20.7 (C^{30}), 22.1 ($C^{14,15,17,18}$), 24.0 ($C^{14,15,17,18}$), 26.5 ($C^{20,21}$), 30.8 ($C^{13,16}$), 34.6 (C^{19}), 79.5 ($C^{CH2(benzyl)}$), 103.9 (C^3), 114.1 (C^5), 120.5 ($C^{9,11}$), 121.1 ($C^{9,11}$), 122.8 ($C^{24,26}$), 127.5 (C^{benzyl}), 129.6 (C^{benzyl}), 129.5 (C^{benzyl}), 133.5 ($C^{23,27}$), 134.4 (C^7), 141.1 (C^{25}), 142.8 ($C^{8,12}$), 143.0 (C^{10}), 146.5 (C^4), 146.8 (C^{benzyl}), 150.3 (C^{22}), 155.7 (C^6), 170.6 (C^2) ppm.

Synthesis of 6b: $[Hf(CH_2(C_6H_5))_4]$ (0.543 g, 1 mmol) was added to **3** (0.441 g, 1 mmol) in toluene (15 mL) at room temperature. The resultant clear yellow solution was stirred for four hours. The volume of the solution was reduced and the reaction mixture was cooled to –25 °C affording yellow needle-like crystals of the product. Yield 0.518 g (60%, NMR scale 100%). $C_{50}H_{58}HfN_2$ (865.50): calcd. C 69.39, H 6.75, N 3.24; found C 69.15, H 7.42, N 3.02. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 1.07 (d, 6 H, $H^{14,15,17,18}$), 1.23 (d, 6 H, $H^{14,15,17,18}$), 1.33 (d, 6 H, $H^{20,21}$), 1.88 (s, 6 H, $H^{CH2(benzyl)}$), 2.15 (s, 6 H, $H^{28,29}$), 2.20 (s, 3 H, H^{30}), 2.90 (m, 3 H, $H^{13,16,19}$), 5.63 (dd, 1 H, H^3), 6.27 (dd, 1 H, H^5), 6.47 (d, 6 H, $H^{CH(benzyl)}$), 6.78 (t, 1 H, H^4), 6.83–6.90 (m, 5 H, $H^{24,26,CH(benzyl)}$), 7.04 (dd, 6 H, $H^{CH(benzyl)}$), 7.19 (s, 2 H, $H^{9,11}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 18.7 ($C^{28,29}$), 20.9 (C^{30}), 22.4 ($C^{14,15,17,18}$), 24.3 ($C^{14,15,17,18}$), 26.8 ($C^{20,21}$), 31.1 ($C^{13,16}$), 34.9 (C^{19}), 86.7 ($C^{CH2(benzyl)}$), 104.2 (C^3), 115.2 (C^5), 121.4 ($C^{9,11}$), 123.0 ($C^{(benzyl)}$), 129.3 ($C^{CH(benzyl)}$), 129.7 ($C^{24,26}$), 134.1 ($C^{23,27}$), 134.2 (C^7), 135.1 (C^{25}), 141.8 (C^{10}), 142.4 (C^4), 143.5 ($C^{CH(benzyl)}$), 147.0 ($C^{8,12}$), 150.8 (C^{22}), 156.0 (C^6), 168.4 (C^2) ppm.

Synthesis of 7a: $B(C_6F_5)_3$ (0.064 g, 0.125 mmol) was added to **4a** (0.1 g, 0.125 mmol) in toluene (2 mL). A colour change from yellow

to red was observed. The reaction mixture was stirred briefly, resulting in a clear oily solution which was layered with pentane and was cooled to –25 °C affording orange crystals over two weeks. Yield 0.099 g (60%). $C_{71}H_{64}BF_{15}N_2Zr{\cdot}C_{3.5}H_4$ (1378.36): calcd. C 64.92, H 4.97, N 2.03; found C 64.92, H 5.22, N 2.36. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.89 (d, 6 H, $H^{28,29,32,33}$), 0.94 (d, 6 H, $H^{30,31}$), 1.04 (d, 12 $H^{24,25,26,27}$), 1.12 (d, 6 H, $H^{28,29,32,33}$), 2.42 (d, 2 H, H^{CH2}), 2.68 (m, 5 H, $H^{13,14,15,22,23}$), 2.80 (d, 2 H, H^{CH2}), 3.15 (br. s, 2 H, H^{CH2}), 5.33 (d, 1 H, H^3), 5.77 (br., 1 H, $H^{CH(benzyl}$), 5.89 (br. t, 2 H, $H^{CH(benzyl)}$), 6.22 (br. d, 2 H, $H^{CH(benzyl)}$), 6.36 (d, 1 H, H^5), 6.46 (d, 4 H, $H^{CH(benzyl)}$), 6.66 (t, 1 H, H^4), 6.88 (t, 2 H, $H^{CH(benzyl)}$), 7.00–7.20 (m, 9 H, $H^{9,11,18,19,20,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 21.8 ($C^{28,29,32,33}$), 23.0 ($C^{24,25,26,27}$), 24.1 ($C^{30,31}$), 26.0 ($C^{24,25,26,27}$), 27.1 ($C^{28,29,32,33}$), 28.4 ($C^{22,23}$), 31.8 ($C^{13,14}$), 34.7 (C^{15}), 76.6 ($C^{CH2(benzyl)}$), 106.5 (C^3), 118.8 (C^5), 121.6 ($C^{9,11}$), 124.6 ($C^{18,20}$), 125.5 (C^{benzyl}), 125.7 (C^{19}), 128.6 (C^{benzyl}), 129.3 (C^7), 129.8 (C^{benzyl}), 135.4 (br., C^{BC6F5}), 141.8 (C^4), 142.7 (C^{benzyl}), 143.0 (C^{16}), 143.5 ($C^{17,21}$), 146.8 (br., C^{BC6F5}), 147.2 ($C^{8,12}$), 150.7 (br., C^{BC6F5}), 151.8 (C^{10}), 156.2 (C^6), 168.2 (C^2) ppm. ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ = –164.97 (t, *m*-F), –160.70 (t, *p*-F), –131.51 (d, *o*-F) ppm.

Synthesis of 7b: An NMR tube was charged with **1** (23 mg) and $[Hf(CH_2(C_6H_5))_4]$ (27 mg) in C_6D_6 (0.5 mL). $B(C_6F_5)_3$ (26 mg) was added to this solution. Afterwards the tube was shaken for 5 min to form a clear solution before measurements were made. $C_{71}H_{64}BF_{15}HfN_2$ (1419.56): calcd. C 60.07, H 4.54, N 1.97; found C 60.01, H 5.26, N 2.21. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.89–1.03 (m, 12 H, $H^{28,29,32,33}$), 1.12 (d, 12 $H^{24,25,26,27}$), 1.12 (d, 6 H, $H^{30,31}$), 2.12 (d, 2 H, H^{CH2}), 2.24 (d, 2 H, H^{CH2}), 2.69 (m, 5 H, $H^{13,14,15,22,23}$), 3.31 (br. d, 2 H, H^{CH2}), 5.28 (d, 1 H, H^3), 5.85 (br. t, 1 H, $H^{CH(benzyl}$), 6.14 (br. t, 2 H, $H^{CH(benzyl}$), 6.21 (d, 1 H, H^5), 6.42 (d, 2 H, $H^{CH(benzyl}$), 6.51 (d, 4 H, $H^{CH(benzyl)}$), 6.70 (t, 1 H, H^4), 6.85–7.23 (m, 11 H, $H^{9,11,18,19,20,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 22.7 ($C^{28,29,32,33}$), 23.0 ($C^{24,25,26,27}$), 24.0 ($C^{30,31}$), 25.9 ($C^{24,25,26,27}$), 27.0 ($C^{28,29,32,33}$), 28.6 ($C^{22,23}$), 31.9 ($C^{13,14}$), 34.7 (C^{15}), 83.9 ($C^{CH2(benzyl)}$), 106.3 (C^3), 119.1 (C^5), 121.5 ($C^{9,11}$), 124.4 ($C^{18,20}$), 126.3 (C^{benzyl}), 129.0 (C^{19}), 129.0 (C^{benzyl}), 133.4 (s, C^7), 135.4 (br., C^{BC6F5}), 139.4 (br., C^{BC6F5}), 142.2 (C^4), 143.9 (C^{benzyl}), 144.3 ($C^{17,21}$), 146.8 (C^{16}), 147.1 (C^{benzyl}), 150.5 (br., C^{BC6F5}), 151.8 (C^{10}), 156.1 ($C^{8,12}$), 162.2 (C^6), 166.6 (C^2) ppm. ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ = –165.30 (t, *m*-F), –161.37 (t, *p*-F), –130.17 (d, *o*-F) ppm. ^{11}B NMR (80 MHz, C_6D_6, 298 K): δ = –11.35 (s, $B^{C6H5CH2B(C6F5)3}$) ppm.

Synthesis of 8a: $[Zr(CH_2(C_6H_5))_4]$ (0.255 g, 0.56 mmol) and **2** (0.2 g, 0.56 mmol) were stirred together in toluene (5 mL) and **5a** soon precipitated as yellow material. $B(C_6F_5)_3$ (0.286 g, 0.56 mmol) was added to this suspension. A colour change from yellow to dark red was observed. The mixture was stirred briefly, resulting in clear oily solution which was layered with pentane and cooled to –25 °C affording orange crystals overnight. Yield 0.56 g (81%). $C_{64}H_{50}BF_{15}N_2Zr$ (1234.11): calcd. C 62.29, H 4.08, N 2.27; found C 62.27, H 3.76, N 1.93. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.88 (d, 6 H, $H^{22,23,25,26}$), 0.98 (d, 6 H, $H^{22,23,25,26}$), 1.93 (s, 6 H, $H^{13,14}$), 2.44 (br. d, 2 H, $H^{CH2(benzyl)}$), 2.63 (sept, 2 H, $H^{21,24}$), 2.76 (d, 2 H, H^{CH2}), 3.21 (br. s, 6 H, $H^{B–CH2}$), 5.21 (d, 1 H, H^3), 5.71 (br. s, 1 H, $H^{CH(benzyl)}$), 5.81 (d, 1 H, H^5), 5.95 (br. s, 2 H, $H^{CH(benzyl)}$), 6.24 (br. s, 2 H, $H^{CH(benzyl)}$), 6.52 (d, 4 H, $^{HCH(benzyl)}$), 6.60 (t, 1 H, H^4), 6.74 (d, 2 H, $H^{17,19}$), 6.87–7.18 (m, 11 H, $H^{9,10,11,18,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 21.4 ($C^{13,14}$), 23.0 ($C^{22,23,25,26}$), 25.9 ($C^{22,23,25,26}$), 28.4 ($C^{21,24}$), 77.8 (br., $C^{CH2(benzyl)}$), 106.0 (C^3), 116.7 (C^5), 124.6 (C^{18}), 125.4 ($C^{17,19}$), 125.6 (C^{benzyl}), 127.8 ($C^{9,11}$), 129.3 (C^{benzyl}), 129.7 (C^{benzyl}), 129.8 (C^{10}), 133.2 (br., C^{BC6F5}), 136.1 ($C^{16,20}$), 136.2 (C^7), 137.8 (C^4), 142.7 (C^{benzyl}), 143.2 (C^{15}), 142.9 ($C^{8,12}$), 143.5 (C^{benzyl}), 145.2 (C^6), 146.8 (br., C^{BC6F5}), 150.7 (br., C^{BC6F5}), 156.3 (C^2) ppm. ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ = –165.30 (t, *m*-F), –161.2 (br., *p*-F), –130.30 (br., *o*-F) ppm. ^{11}B NMR (80 MHz, C_6D_6, 298 K): δ = –11.44 (s, $BC_6H_5CH_2B(C_6F_5)_3$) ppm.

Synthesis of 8b: An NMR tube was charged with **2** (16 mg) and $[Hf(CH_2(C_6H_5))_4]$ (25 mg) in C_6D_6 (0.5 mL). $B(C_6F_5)_3$ (24 mg) was added to this deuterated solution. Afterwards the tube was shaken for 5 min to form a clear solution before recording NMR spectra. $C_{64}H_{50}BF_{15}HfN_2$ (1321.37): calcd. C 58.17, H 3.81, N 2.12; found C 57.98, H 4.28, N 2.34. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.90 (d, 6 H, $H^{22,23,25,26}$), 0.97 (d, 6 H, $H^{22,23,25,26}$), 1.9 (s, 6 H, $H^{13,14}$), 2.10 (br. s, 2 H, $H^{CH2(benzyl)}$), 2.24 (br. s, 2 H, $H^{CH2(benzyl)}$), 2.65 (br. s, 2 H, $H^{21,24}$), 3.38 (br. s, 2 H, $H^{B–CH2}$), 5.19 (br. d, 1 H, H^3), 5.84 (d, 1 H, H^5), 6.13 (br. t, 2 H, $H^{CH(benzyl)}$), 6.42 (br. d, 2 H, $H^{CH(benzyl)}$), 6.54 (d, 4 H, $H^{CH(benzyl)}$), 6.63 (t, 1 H, H^4), 6.74 (br. d, 2 H, $H^{CH(benzyl)}$), 6.88 (t, 2 H, $H^{CH(benzyl)}$), 7.00–7.20 (m, 10 H, $H^{9,10,11,17,18,19,CH(benzyl)}$) ppm. ^{1}H NMR (400 MHz, C_7D_8, 296 K): δ = 0.92 (d, 6 H, $H^{22,23,25,26}$), 1.00 (d, 6 H, $H^{22,23,25,26}$), 1.99 (s, 6 H, $H^{13,14}$), 2.10 (br. s, 2 H, $H^{CH2(benzyl)}$), 2.22 (br. s, 2 H, $H^{CH2(benzyl)}$), 2.66 (br. s, 2 H, $H^{21,24}$), 3.30 (br. s, 2 H, $H^{B–CH2}$), 5.20 (br. s, 1 H, H^3), 5.92 (br. d, 1 H, H^5), 6.14 (br. t, 2 H, $H^{CH(benzyl)}$), 6.38 (br. d, 2 H, $H^{CH(benzyl)}$), 6.54 (d, 4 H, $H^{CH(benzyl)}$), 6.75 (t, 1 H, H^4), 6.88 (t, 2 H, $H^{CH(benzyl)}$), 6.97–7.17 (m, 10 H, $H^{9,10,11,17,18,19,CH(benzyl)}$) ppm. ^{1}H NMR (400 MHz, C_7D_8, 253 K): δ = 0.89 (d, 6 H, $H^{22,23,25,26}$), 0.94 (d, 6 H, $H^{22,23,25,26}$), 1.95 (s, 6 H, $H^{13,14}$), 2.11 (d, 2 H, $H^{CH2(benzyl)}$), 2.26 (d, 2 H, $H^{CH2(benzyl)}$), 2.57 (sept, 2 H, $H^{21,24}$), 3.38 (br. s, 2 H, $H^{B–CH2}$), 5.13 (d, 1 H, H^3), 5.70 (t, 1 H, $H^{CH(benzyl)}$), 5.80 (d, 1 H, H^5), 6.07 (t, 2 H, $H^{CH(benzyl)}$), 6.36 (d, 2 H, $H^{CH(benzyl)}$), 6.54 (d, 4 H, $H^{CH(benzyl)}$), 6.60 (t, 1 H, H^4), 6.70 (d, 2 H, $H^{CH(benzyl)}$), 6.88–7.20 (m, 10 H, $H^{9,10,11,17,18,19,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 20.3 ($C^{13,14}$), 24.6 ($C^{22,23,25,26}$), 25.8 ($C^{22,23,25,26}$), 28.6 ($C^{21,24}$), 85.9 (br., $C^{CH2(benzyl)}$), 106.0 (C^3), 117.0 (C^5), 124.5 ($C^{17,19)}$), 125.4 ($C^{9,11}$), 125.6 (C^{18}), 126.5 ($C^{(benzyl)}$), 128.6 (C^{benzyl}), 129.1 (C^{benzyl}), 129.3 ($C^{16,20}$), 129.9 (C^{10}), 133.6 (C^7), 136.1 (C^{benzyl}), 137.8 (C^4), 139.3 (br., C^{BC6F5})143.5 (C^{15}), 144.0 ($C^{8,12}$), 144.4 (br., C^{benzyl}), 146.8 (br., C^{BC6F5}),150.5 (br., C^{BC6F5}), 156.1 (C^6), 162.2 ppm. (C^2). ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ = –165.3 (*m*-F), –161.3 (*p*-F), –130.25 (*o*-F) ppm. ^{11}B NMR (80 MHz, C_6D_6, 298 K): δ = –11.32 (s, $B^{C6H5CH2B(C6F5)3}$) ppm.

Synthesis of 9a: $[Zr(CH_2(C_6H_5))_4]$ (0.248 g, 0.54 mmol) and **3** (0.225 g, 0.54 mmol) were stirred together in toluene (5 mL). $B(C_6F_5)_3$ (0.279 g, 0.54 mmol) was then added to the clear yellow solution. A colour change to dark red was observed. The mixture was stirred briefly, resulting in clear oily solution which was layered with pentane and kept at low temperature –25 °C to afford orange crystals overnight. Yield 0.624 g (84%). $C_{68}H_{58}BF_{15}N_2Zr{\cdot}C_7H_8$ (1382.35): calcd. C 65.16, H 4.81, N 2.03; found C 65.12, H 4.45, N 1.84. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.96 (d, 6 H, $H^{14,15,17,18}$), 1.00 (d, 6 H, $H^{14,15,17,18}$), 1.15 (d, 6 H, $H^{20,21}$), 1.87 (s, 6 H, $H^{28,29}$), 2.31 (s, 3 H, H^{30}), 2.37 (d, 2 H, H^{CH2}), 2.67 (sept, 3 H, $H^{13,16,19}$), 2.76 (d, 2 H, $H^{CH2(benzyl)}$), 3.22 (br. s, 2 H, H^{CH2}), 5.32 (d, 1 H, H^3), 5.71 (br. t, 2 H, $H^{CH(benzyl)}$), 5.81 (br. t, 1 H, $H^{CH(benzyl)}$), 6.09 (br. d, 2 H, $H^{CH(benzyl)}$), 6.41 (d, 1 H, H^5), 6.45 (d, 4 H, $H^{CH(benzyl)}$), 6.72–6.90 (m, 5 H, $H^{4,24,26,CH(benzyl)}$), 7.01–7.07 (m, 6 H, $H^{9,11,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 18.4 ($C^{28,29}$), 20.7 (C^{30}), 21.7 ($C^{14,15,17,18}$), 24.0 $C^{14,15,17,18}$), 27.3 ($C^{20,21}$), 31.9 ($C^{13,16}$), 34.7 (C^{19}), 78.5 ($C^{CH2(benzyl)}$), 103.6 (C^3), 118.7 (C^5), 121.5 ($C^{9,11}$), 124.3 ($C^{24,26}$), 125.6 (C^{benzyl}), 129.6 (C^{benzyl}), 132.6 (C^{benzyl}), 137.6 ($C^{23,27}$), 137.8 (C^7), 135.3 (br., C^{BC6F5}), 139.2 (br., C^{BC6F5}), 142.5 (C^{25}), 143.0 (C^{10}), 144.2 ($C^{8,12}$), 146.8 (br., C^{BC6F5}), 147.3 (C^{benzyl}), 150.3 (br.,

C^{BC6F5}), 151.5 (C^4), 156.1 (C^{22}), 160.2 (C^6), 166.5 (C^2) ppm. ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ = –165.35 (t, *m*-F), –161.32 (t, *p*-F), –130.70 (br., *o*-F) ppm. ^{11}B NMR (80 MHz, C_6D_6, 298 K): δ = –11.53 (s, $B^{C6H5CH2B(C6F5)3}$) ppm.

Synthesis of 9b: An NMR tube was charged with **3** (83 mg) and $[Hf(CH_2(C_6H_5))_4]$ (109 mg) in C_6D_6 (0.5 mL). $B(C_6F_5)_3$ (102 mg, mmol) was then added to this solution. Afterwards the tube was shaken for 5 min to form a clear solution before measurement. $C_{68}H_{58}BF_{15}HfN_2$ (1377.48): calcd. C 59.29, H 4.24, N 2.03; found C 58.43, H 4.46, N 2.15. ^1H NMR (250 MHz, C_6D_6, 298 K): δ = 0.95 (d, 6 H, $H^{14,15,17,18}$), 1.00 (d, 6 H, $H^{14,15,17,18}$), 1.14 (d, 6 H, $H^{20,21}$), 1.92 (s, 6 H, $H^{28,29}$), 2.01 (d, 2 H, $H^{CH2benzyl}$), 2.22 (d, 2 H, $H^{CH2(benzyl)}$), 2.34 (s, 3 H, H^{30}), 2.68 (sept, 3 H, $H^{13,16,19}$), 3.30 (br. s, 2 H, $H^{CH2–B}$), 5.30 (d, 1 H, H^3), 5.92 (br. t, 2 H, $H^{CH(benzyl)}$), 6.00 (br. t, 1 H, $H^{CH(benzyl)}$), 6.22 (br. d, 2 H, $H^{CH(benzyl}$), 6.45 (m, 5 H, $H^{5,CH(benzyl)}$), 6.83 (t, 3 H, $H^{4,CH(benzyl)}$), 6.92 (s, 2 H, $H^{,24,26}$), 7.03 (s, 2$H^{9,11}$), 7.12 (t, 4 H, $H^{CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 18.3 ($C^{28,29}$), 20.7 (C^{30}), 21.7 ($C^{14,15,17,18}$), 24.1 $C^{14,15,17,18}$), 27.3 ($C^{20,21}$), 32.2 ($C^{13,16}$), 35.8 (C^{19}), 87.1 ($C^{CH2(benzyl)}$), 103.7 (C^3), 119.1 (C^5), 121.5 ($C^{9,11}$), 124.3 ($C^{24,26}$), 125.1 (C^{benzyl}), 129.1 (C^{benzyl}), 133.0 (C^{benzyl}), 134.0 ($C^{23,27}$), 135.4 (br., C^{BC6F5}), 137.7 (C^7), 139.2 (br., C^{BC6F5}), 142.4 (C^{25}), 143.0 (C^{10}), 145.6 ($C^{8,12}$), 146.8 (br., C^{BC6F5}), 147.3 (C^{benzyl}), 150.8 (br., C^{BC6F5}), 151.6 (C^4), 156.0 (C^{22}), 160.7 (C^6), 165.0 (C^2) ppm. ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ = –165.34 (t, *m*-F), –161.41 (t, *p*-F), –130.57 (br., *o*-F) ppm. ^{11}B NMR (80 MHz, C_6D_6, 298 K): δ = –11.46 (s, $B^{C6H5CH2B(C6F5)3}$) ppm.

Attempted Abstraction of the Second Benzyl: In an NMR tube 1 equiv. of $B(C_6F_5)_3$ was added to the zwitterionic complex **7a** and the reaction was studied by NMR spectroscopy. No conversion was observed.

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