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Cyclometalated group 4 complexes supported by tridentate pyridine-2-phenolate-6-(σ-aryl) ligands: Catalysts for ethylene polymerization and comparisons with fluorinated analogues

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Dedicated to Prof. Dr. Gerhard Erker for his inspiring research on the occasion of his 60th birthday.

Abstract

An adaptable synthetic methodology for the tridentate dianionic pyridine-2-phenolate-6-aryl [O,N,C] ligand framework, comprising the aromatic σ-carbanion moiety as a chelating component, has been developed. A series of non-fluorinated group 4 bis(benzyl) complexes supported by [O,N,C] auxiliaries, with halogen and alkyl groups at the 'R^1' position *ortho* to the metal-C(σ-aryl) bond, have been prepared by exploiting the cyclometalation of the ligand. All derivatives have been characterized by NMR spectroscopy, and the spectral features concerning the metal-bound diastereotopic methylene groups have been highlighted. The capabilities of these complexes as catalysts for olefin polymerization have been tested, and comparisons with the recently reported fluorine-containing Ti-[O,N,C] analogues and related Hf-[N,N,C] derivatives are discussed. The titanium catalysts, in conjunction with MAO, displayed moderate to high activities for ethylene polymerization (up to 200 g $mmol^{-1}$ h^{-1}).

Keywords: Benzyl complexes; Cyclometalation; Olefin polymerization; Post-metallocenes; σ-Aryl ligand

1. Introduction

The development of new 'post-metallocene' complexes as olefin polymerization catalysts, propelled by the pursuit of novel materials and properties, and superior control over reactivity, have proliferated [1]. The myriad of ancillary ligand combinations that can support an active catalytic species continues to expand, and in the impetus to avoid the cyclopentadienyl group, C-based anionic ligands have largely been overlooked. For group 4 complexes, the limited studies have focused on simple allyl ligands [2] plus tropidinyl [3] and heteroatom analogues [4], but in general their inertness is insufficient and modest catalytic activities are obtained. The σ-aryl moiety has been employed as a chelating unit by Hessen and coworkers [5], although only low to moderate activities in propylene polymerization was reported for Zr(IV) catalysts with tridentate dianionic bis(σ-aryl)amine ligands [6].

We previously presented the first direct observation of weak intramolecular C–H···F–C contacts in Group 4 post-metallocene catalysts bearing tridentate pyridine-2-phenolate-6-(fluorinated σ-aryl) ligands [7]. Moreover, the structural parameters of the controversial [8] C–H···F–C interaction was accurately determined for the first time by a recent neutron diffraction study [9]. The observed C–H···F–C interactions are important with regards to design implications in olefin polymerization catalysts. In particular, they substantiate the DFT-derived ortho-F···H(β) ligand–polymer contacts proposed by Fujita [10] to account for the remarkable living olefin polymerization behavior at elevated temperatures displayed by Group

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4 fluorinated phenoxyimine 'FI' catalysts [11]. Indeed, unlike conventional agostic [12] and metal···cocatalyst contacts [13,14], weak attractive non-covalent interactions between a 'non-innocent' ligand and the polymer chain may be considered as a new concept in polyolefin catalysis. In this work, a new collection of Group 4 catalysts with non-fluorinated substituents in the locality of the metal center has been designed and synthesized from the facile ortho-cyclometalation of pyridine-2-(2′-phenol)-6-(aryl) substrates. The principal aims of the present study is to probe (a) the influence of the metal ion (Ti, Zr, Hf), and (b) the impact of replacing the F or CF_3 group [9] adjacent to the metal–C(σ-aryl) bond (termed the R^1 position; see Scheme 1) with substituents displaying different steric and electronic characteristics, namely Br, Cl and methyl, upon NMR spectroscopic properties and polymerization behavior. The development of bromine-substituted ligands is interesting because this potentially allows further derivatization to novel ligands with a variety of aryl moieties at R^1 using Suzuki/Stille-type C–C coupling reactions. The systematic study of all group 4 metals was deemed appropriate since researchers at Symyx and Dow have very recently observed excellent propylene polymerization activities for related hafnium(IV) catalysts bearing tridentate cyclometalated pyridylamido ligands [15].

2. Results and discussion

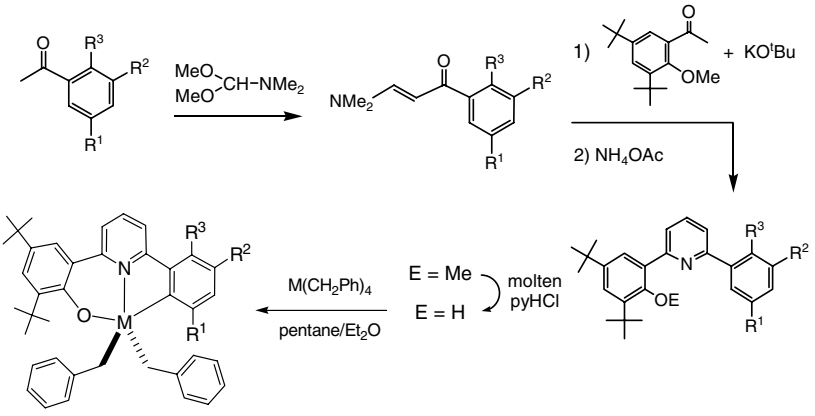
2.1. Design approach

We became attracted to the design and assembly of the tridentate non-symmetric pyridine-2-aryloxide-6-(σ-aryl) [O,N,C] framework as a suitable ligand ensemble in olefin polymerization catalysts: (1) aryloxide- and alkoxide-based chelating ligands have been one of the cornerstones of advances in post-metallocene catalyst design [16]; (2) from our recent work on a family of Zr(IV) catalysts bearing tridentate pyridine-2,6-bis(aryloxide) [O,N,O] auxiliaries, we concluded that strong binding by the central pyridyl moiety is a critical factor in achieving exceptional catalytic efficiencies [17]; (3) aromatic σ-carbanions are predominantly σ-donors with minimal π-donation (in contrast to strong π-donors such as Cp), and can engender a catalytic center with enhanced electrophilicity.

The geometry and rigidity of the [O,N,C] ligand are important features, dictating that the R^1 substituent *ortho* to the metal–C(σ-aryl) bond (Scheme 1) is in close proximity to the metal/catalytic site but is nevertheless 'tied back' to preclude interaction with the metal center. Furthermore, facile modification of the R^1 substituent has been demonstrated through the development of a versatile synthetic methodology for the ligand (see below). Lastly, as noted by Hessen [6], it is a pre-requisite that the resultant metal–C(σ-aryl) bond is more inert compared with aliphatic counterparts [e.g. metal–C(polymer chain)].

2.2. Synthesis of Group 4 complexes bearing tridentate pyridine-2-phenolate-6-(σ-aryl) ligands

The 2-(2′-phenol)-6-arylpyridine ligands were prepared by significant modification of a literature synthesis for 2,6-bis(2′-phenol)pyridine [18]. The 1-*N*,*N*-dimethylamino-3-(substituted aryl)-3-oxo-1-propenes were prepared from the reactions of *N*,*N*-dimethylformamide dimethyl acetal with acetophenones bearing functional groups at the R^1/R^2 or R^1/R^3 positions (Scheme 1). Treatment of the oxopropene substrates with 3,5-di-*tert*-butyl-2-methoxyacetophenone/potassium *tert*-butoxide followed by ammo-



R^1	R^2	R^3	Ligand (E = H)	Complex M = Ti	M = Zr	M = Hf
Br	Br	H	H_2L^{Br}	**1**	**4**	**7**
Cl	H	Cl	H_2L^{Cl}	**2**	**5**	**8**
CH_3	H	CH_3	H_2L^{Me}	**3**	**6**	**9**

Scheme 1.

nium acetate yielded the 2-(2′-methoxyaryl)-6-arylpyridines by cyclization, and subsequent demethylation using molten pyridinium chloride afforded the desired ligands. Hence, by exploiting the sequential nature of this route, the use of different substituted acetophenones inherently leads to the formation of non-symmetric ligands.

The proposed ligand design strategy is aided by the accessibility of the synthetic procedure, and in particular, the wide and facile availability of polysubstituted acetophenone precursors. Hence, 2,5-dimethyl- and 2,5-dichloroacetophenone are commercially available, while 3,5-dibromoacetophenone was prepared by the treatment of 1,3,5-tribromobenzene with *n*-butyllithium followed by *N*,*N*-dimethylacetamide/HCl [19]. By considering the cyclometalation process, the judicious incorporation of substituents at selected positions on the acetophenone can yield specific R^1 groups that reside adjacent to the metal center in the resultant complex (see below).

Metalation of ligands $H_2L^{Br,Cl,Me}$ containing acidic *ortho*-aryl and phenol protons proceeded smoothly with the $M(CH_2Ph)_4$ (M = Ti, Zr, Hf) precursors in diethyl ether/pentane mixtures at −78 °C to give complexes **1**–**9** as dark red (Ti), yellow (Zr) and pale yellow (Hf) crystalline solids in moderate (40–60%) yields (Scheme 1). The ^{1}H NMR spectra of "as-prepared" reaction mixtures after removal of volatiles revealed that in each case the predominant species is the desired complex. C–H activation is of course favored over C–Cl and C–C activation respectively, hence the choice of substituent at R^3 ensures that cyclometalation occurs at the designated aryl-H para to R^2. The complexes therefore incorporate a Br, Cl or Me substituent at the R^1 position that is in close proximity to the metal center but without contact, so that comparisons may be drawn with the congeners bearing a CF_3 or F group at R^1 [7,9].

2.3. Characterization by NMR spectroscopy

All complexes have been fully characterized by ^{1}H and ^{13}C NMR spectroscopy, including 135-DEPT and 2D ^{1}H–^{1}H, ^{13}C–^{1}H and NOE correlation experiments (see Supporting information for selected spectra). As a representative example to illustrate the assignment process, the ^{1}H–^{1}H COSY NMR spectrum of **1** is given in Fig. 1. Because the resonances for $H^{4,6}$ are easily identifiable from related complexes, the weak 5-bond correlations detected for $H^6 \leftrightarrow H^8$ and $H^{10} \leftrightarrow H^{13}$ provide good indicators for the assignment of all aryl hydrogens, and these are subsequently confirmed by NOE experiments.

The ^{1}H NMR spectra for the methylene region of the titanium complexes **1**–**3**, and the congeners bearing a F (**10**) or CF_3 (**11**) group respectively at R^1, are displayed in Fig. 2. For **3** ($R^1 = CH_3$), the diastereotopic methylene hydrogens of the benzyl ligands are conventional and appear as two doublets, in contrast to **11** ($R^1 = CF_3$) where the upfield CH_2 resonance appears as a multiplet due to C–H···F–C coupling with three F atoms [7]. While the two methylene doublets for **10** (R^1 = F) are highly symmetric, it is intriguing to note that for **1** and **2** (R^1 = Br, Cl respectively), very slight broadening or 'shortening' of the upfield doublet can apparently be detected (Fig. 2). Such observations are customarily attributed to the steric consequence of a neighboring substituent, although the fact that the impact of the bulkier methyl group in **3** is seemingly negligible appears to contradict this assumption. Nevertheless, without further evidence, we are reluctant to ascribe this minimal broadening to any electronic effects caused by the Br and Cl atoms.

It has been established that the distortion of M–CH_2–Ph groups, which becomes more prevalent at high-valent electrophilic metal ions, can be indicated by ^{1}H and ^{13}C NMR spectroscopy. The M···Ph interaction will reduce the M–C–C angle and concomitantly increase the H–C–H angle, resulting in decreased $^2J_{H,H}$ (<10 Hz) and enlarged $^1J_{C,H}$ (>125 Hz) values [20]. The relevant NMR parameters for complexes **1**–**9** are listed in Table 1. It is apparent that the η^2-coordination mode is observed for all titanium and zirconium complexes, and the M···Ph interactions for the former ($^2J_{H,H}$ *ca.* 8.2 Hz and $^1J_{C,H} \geqslant 135$ Hz) are stronger. In addition, η^2-benzyl groups may also be manifested through a high-field ^{1}H NMR shift for the *ortho*-Ph resonances, although the use of this as a criterion is less reliable because the resonances can also be influenced by the ring currents of ancillary ligands [21]. Indeed, the *ortho*-Ph resonances of all derivatives are observed at around 6.5–6.8 ppm with no clear trends for different metals. The large $^2J_{H,H}$ values for the hafnium complexes suggest that the extent of η^2-coordination by the benzyl groups is minimal.

2.4. Ethylene polymerization studies

The complexes herein have been evaluated as ethylene polymerization catalysts in conjunction with MAO in small-scale reactors (conditions: 20 mL toluene, 500 equiv MAO, 1 atm of ethylene, 25 °C, 10 min reaction time). The results (Table 2) show that all hafnium complexes are inactive, which is in stark contrast to the excellent efficiencies reported for the related Hf-[N,N,C] catalysts [15], while the Ti/MAO systems display higher polymerization activities (150–200 g of polymer $mmol^{-1}$ h^{-1}) than the Zr/MAO counterparts. The NMR characterization data indicate that the interaction between the metal and benzyl groups, which reflects the electrophilicity of the metal center, increases in the order Hf < Zr < Ti, and this is consistent with the observed differences in activity between the metals.

For the Ti catalysts, the variations in activity for the Br, Cl or Me substituents at R^1 (**1**–**3** respectively), can be attributed to a combination of steric and electronic factors. Our previous results have indicated that the coordination sphere around the metal center and active site in these catalysts is highly congested [9]. The presence of the bulkier CH_3 substituent adjacent to the active site may therefore hinder

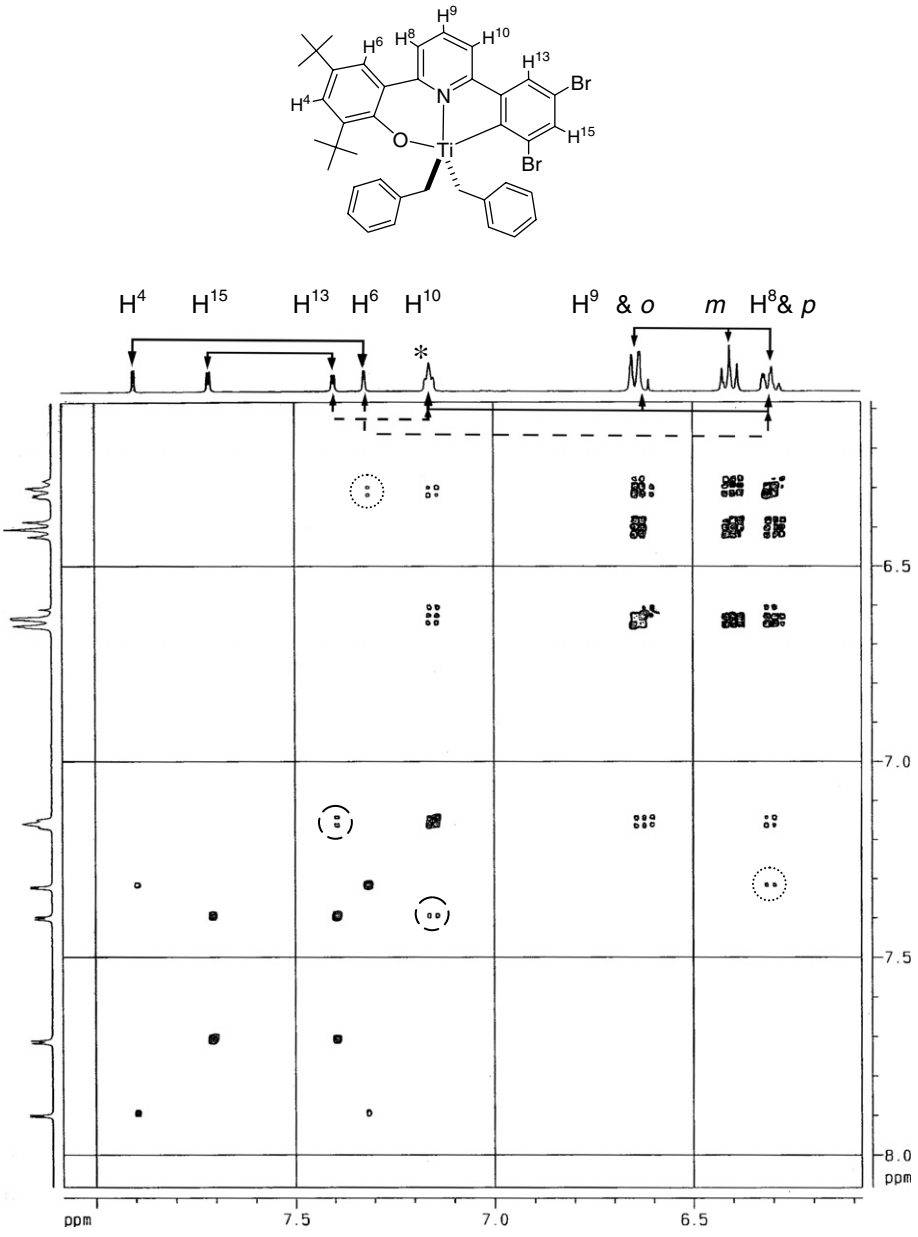


Fig. 1. ^{1}H–^{1}H COSY NMR spectrum of **1** (400 MHz, C_6D_6 [*], 298 K). The weak 5-bond correlations for $H^6 \leftrightarrow H^8$ and $H^{10} \leftrightarrow H^{13}$ (circled) aids the assignment.

the approach and insertion of olefin substrates. In contrast, the electron-withdrawing Cl or Br moiety is anticipated to yield a more electrophilic as well as accessible catalytic site, resulting in superior activities. Although bulky substituents are often advocated for improving catalytic performance by reducing termination processes, we conclude that for the R^1 position of the Ti-[O,N,C] system, the methyl group is ineffective or even detrimental to catalytic efficiency and the impact of R^1 upon the metal electrophilicity is of greater importance. For the Zr derivatives, possibly because of the greater size of the metal center, the effects of steric hindrance exerted by R^1 may be diminished.

The observed activities in this work are of the same magnitude but slightly lower than those for the fluorinated Ti analogues **10** and **11** ($R^1 = F$, CF_3 respectively) [9, Table 2]. Apparently, the enhanced electrophilicity of the Ti catalytic site due to the effects of multiple F atoms becomes the dominant factor. In addition, the T_m values suggest that the nature of the polyethylene materials formed appear to be quite different from those by the fluorinated congeners.

3. Conclusion

A new series of Ti, Zr, and Hf complexes supported by cyclometalated [O,N,C] ligands, with substituents appended at the R^1 position *ortho* to the metal–C(σ-aryl) linkage, have been prepared as potential olefin polymerization catalysts. All derivatives have been characterized by NMR spectroscopy. The attention reserved for the R^1

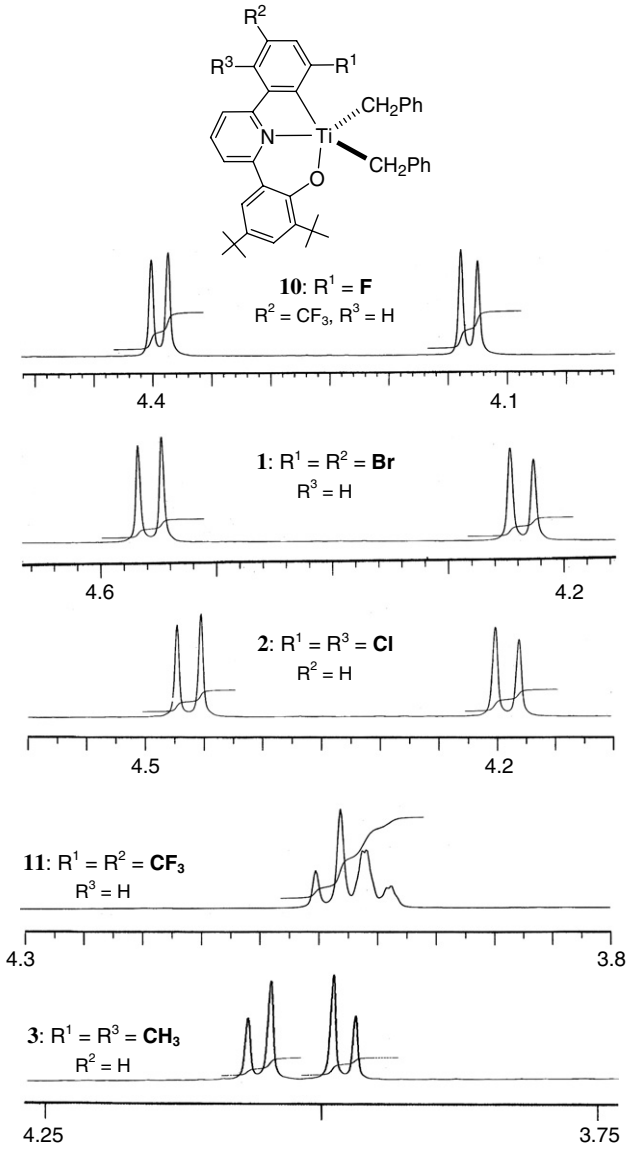


Fig. 2. ^{1}H NMR spectra for diastereotopic CH_2 region of Ti-[O,N,C] complexes (400 MHz [600 MHz for **10**], C_6D_6, 298 K; a 0.5 ppm range is shown to facilitate comparison).

Table 1
NMR parameters associated with M–benzyl coordination (C_6D_6)

Complex		$^2J_{H,H}$ (Hz)	$^1J_{C,H}$ (Hz)	*ortho*-Ph (d)
Ti	**1**	8.2	136.1	6.63
	2	8.2	137.1	6.63
	3	8.3	134.7	6.60
Zr	**4**	9.4	134.5	6.80
	5	9.3	135.1	6.49
	6	9.8	132.7	6.71
Hf	**7**	[a]	130.3	6.76
	8	10.4	131.2	[b]
	9	10.8	129.3	6.70

[a] A virtual singlet is observed.
[b] Aryl-H resonances overlap.

substituent is justified because it is situated directly adjacent to the catalytic center and along the path of the incoming olefin. In this study, it has been possible to make comparisons with fluorinated Ti analogues, and differences in NMR spectroscopic and catalytic properties as a consequence of the R^1 group (Br and Cl cf. F; CH_3 cf. CF_3) have been observed. It is evident that the fluorinated catalysts display elevated activities. With regards to the impact of the R^1 substituent upon catalytic efficiency, the present work indicates that the electrophilicity of the metal center is more important than steric protection for the active site. The inactivity of the Hf congeners is in stark contrast to the exceptional activities reported for seemingly related amido-type [N,N,C]-hafnium(IV) catalysts. The development of the dibromo-substituted σ-aryl fragment within the [O,N,C] framework has been achieved, paving the way for further derivatization towards different aryl groups at the vital R^1 position.

Table 2
Polymerization data

Catalyst (μmol)		Yield (g)	Activity[a]	T_m (°C)
Ti	**1** (6.5)	0.213	202	125
	2 (6.4)	0.187	175	124
	3 (6.3)	0.169	156	128
Zr	**4** (6.5)	0.061	58	122
	5 (6.2)	0	–	–
	6 (6.3)	0.075	70	125
Hf	**7** (6.4)	0	–	–
	8 (6.5)	0	–	–
	9 (6.5)	0	–	–
	10 (6.4)	0.272	255	135
	11 (6.3)	0.569	542	134

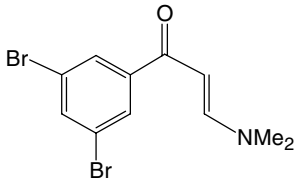
Conditions: 20 mL toluene, 500 equiv MAO, 1 atm p of ethylene, 25 °C, 10 min reaction time.
[a] Activity: g of polymer $mmol^{-1}$ h^{-1}.

4. Experimental

4.1. General considerations

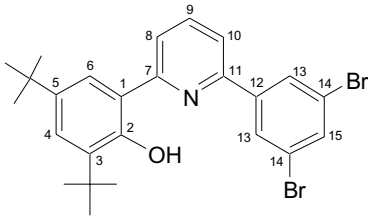
All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques or in a Braun dry-box. All solvents were appropriately dried and distilled then degassed prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 DRX, 400 DRX or 300 FT-NMR spectrometer (ppm) using Me_4Si as internal standard. Peak assignments were based on combinations of DEPT-135, and 2-D ^{1}H–^{1}H, ^{13}C–^{1}H and NOE correlation NMR experiments. Mass spectra (EI) were obtained on a Finnigan MAT 95 mass spectrometer. Elemental analyses were performed by Medac Ltd., UK. Melting points of polymer samples were determined by differential scanning calorimetry on a Perkin–Elmer DSC7. Methylaluminoxane (MAO, 10 wt% solution in toluene) was purchased from Aldrich and used as received. Ethylene (BOC, polymer grade) was passed through Drierite and P_2O_5. 3,5-Dibromoacetophenone [19] and $M(CH_2Ph)_4$ (M = Ti, Zr, Hf) [22] were prepared according to the literature procedure, and the synthesis of H_2L^{Me}, **3** and **6** were given previously [9].

4.2. Synthesis of 1-N,N-dimethylamino-3-(3,5-dibromophenyl)-3-oxo-1-propene



A mixture of 3,5-dibromoacetophenone (8.7 g, 31.3 mmol) and *N*,*N*-dimethylformamide dimethyl acetal (10 mL, 75 mmol) was refluxed for 18 h to give a red solution, after which dichloromethane (100 mL) was added. The organic layer was washed with water and brine, dried over sodium sulphate and the solvent was removed to give a red oil. Purification was performed by silica gel flash chromatography using *n*-hexane:ethyl acetate (20:1) as eluent to give a red solid. Yield: 7.2 g, 69%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.94 (br s, 3H, N–Me), 3.16 (br s, 3H, N–Me), 5.55 (d, $J = 20.4$ Hz, 1H, C=CH), 7.71 (s, 1H, H^4), 7.80 (d, $J = 20.4$ Hz, 1H, C=CH), 7.92 (s, 2H, H^2).

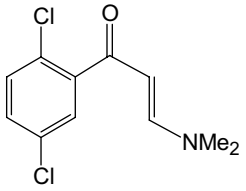
4.3. Synthesis of H_2L^{Br}



A solution of 3,5-di-*tert*-butyl-2-methoxyacetophenone (5.70 g, 22 mmol) and potassium *tert*-butoxide (5.00 g, 45 mmol) in THF (30 mL) was stirred for 2 h at room temperature to give a yellow suspension. A solution of 1-*N*, *N*-dimethylamino-3-(3,5-dibromophenyl)-3-oxo-1-propene (7.22 g, 22 mmol) in THF (20 mL) was then added and the mixture was stirred for 12 h at room temperature to give a dark red solution. A solution of ammonium acetate (16 g, 208 mmol) in acetic acid (100 mL) was added to the mixture. THF was removed by distillation over 2 h and the residue was dried under vacuum. After extraction by dichloromethane, purification was performed by silica gel flash chromatography using *n*-hexane:ethyl acetate (20:1) as eluent to give the 2-(2′-methoxyaryl)-6-arylpyridine precursor (E = Me; Scheme 1) as a pale yellow solid. Yield: 3.8 g, 32%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 9H, ^{t}Bu), 1.45 (s, 9H, ^{t}Bu), 3.37 (s, 3H, OCH_3), 7.43 (d, $J = 2.5$ Hz, 1H), 7.59 (d, $J = 2.5$ Hz, 1H), 7.64 (dd, $J = 5.7$, 3.0 Hz, 1H), 7.71 (s, 1H), 7.80–7.81 (m, 2H), 8.21 (d, $J = 1.6$ Hz, 2H).

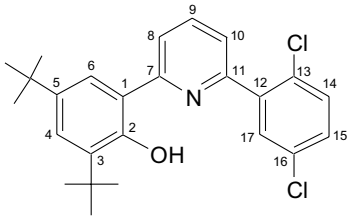
Demethylation of the 2′-methoxy precursor (1.87 g, 3.52 mmol) in molten pyridinium chloride (4.0 g, 34.6 mmol) under N_2 at 220 °C for 10 h according to the procedure described by Dietrich-Buchecker et al. [23] gave H_2L^{Br} as a pale yellow solid which was recrystallized in *n*-hexane. Yield: 0.68 g, 37%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (s, 9H, ^{t}Bu), 1.54 (s, 9H, ^{t}Bu), 7.47 (d, $J = 2.9$ Hz, 1H, H^4), 7.53 (dd, $J = 6.9$, 3.8 Hz, 1H, H^{10}), 7.68 (d, $J = 2.9$ Hz, 1H, H^6), 7.76 (t, $J = 2.0$ Hz, 1H, H^{15}), 7.88–7.91 (m, 2H, H^8 and H^9), 7.99 (d, $J = 2.1$ Hz, 2H, H^{13}), 14.07 (s, 1H, OH). ^{13}C NMR (126 MHz, C_6D_6): δ 29.78 (CMe_3), 31.76 (CMe_3), 34.51 (CMe_3), 35.51 (CMe_3); methine carbons: 118.61, 119.79, 121.32, 126.77, 128.95, 134.81, 138.73; 4° carbons: 118.09, 123.77, 137.89, 140.32, 141.92, 151.80, 156.57, 159.61. EI-MS (+ve, *m*/*z*): 517 [M^+].

4.4. Synthesis of 1-N,N-dimethylamino-3-(2,5-dichlorophenyl)-3-oxo-1-propene



The procedure described in Section 4.2 was followed using 2,5-dichloroacetophenone (10 g, 52.9 mmol) and *N*,*N*-dimethylformamide dimethyl acetal (14 mL, 100 mmol) to give a red solid. Yield: 7.5 g, 58%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.89 (br s, 3H, N–Me), 3.12 (br s, 3H, N–Me), 5.32 (d, $J = 12.88$ Hz, 1H, C=CH), 7.23–7.26 (m, 1H), 7.30–7.39 (m, 2H).

4.5. Synthesis of H_2L^{Cl}

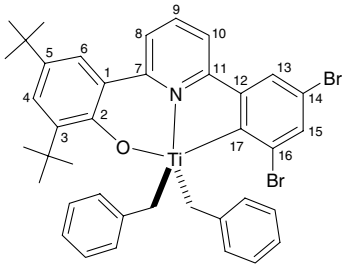


The procedure described in Section 4.3 was followed using 1-*N*,*N*-dimethylamino-3-(2,5-dichlorophenyl)-3-oxo-1-propene to give the 2-(2′-methoxyaryl)-6-arylpyridine precursor as a pale yellow solid. Yield: 6.0 g, 44%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (s, 9H, ^{t}Bu), 1.45 (s, 9H, ^{t}Bu), 3.37 (s, 3H, OMe), 7.31 (dd, $J = 8.6$, 2.5 Hz, 1H, H^{15}), 7.40–7.44 (s, 2H, H^{14} and H^{17}), 7.56–7.59 (m, 2H, H^4 and H^{10}), 7.72 (d, $J = 2.5$ Hz, 1H, H^6), 7.79–7.81 (m, 2H, H^8 and H^9).

Demethylation of the 2′-methoxy precursor (7.0 g, 15.8 mmol) in molten pyridinium chloride (18 g, 155.8 mmol) under N_2 at 220 °C for 10 h gave H_2L^{Cl} as a pale

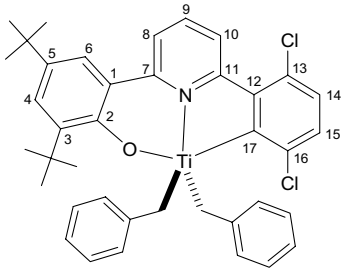
yellow solid which was recrystallized in *n*-hexane. Yield: 4.32 g, 64%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.37 (s, 9H, 5-^{t}Bu), 1.48 (s, 9H, 3-^{t}Bu), 7.36 (dd, $J = 10.7$, 3.2 Hz, 1H, H^{15}), 7.42 (d, $J = 3.0$ Hz, 1H, H^4), 7.46 (d, $J = 10.6$ Hz, 1H, H^{14}), 7.48 (dd, $J = 10.4$, 1.5 Hz, 1H, H^{10}), 7.59 (d, $J = 3.2$ Hz, 1H, H^{17}), 7.69 (d, $J = 3.0$ Hz, 1H, H^6), 7.91 (t, $J = 9.8$ Hz, 1H, H^9), 7.95 (dd, $J = 10.4$, 1.4 Hz, 1H, H^8), 13.99 (s, 1H, OH). EI-MS (+ve, *m*/*z*): 428 [M^+].

4.6. Synthesis of titanium complex **1**



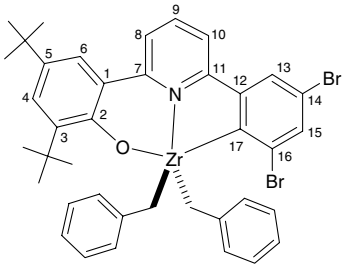
A solution of H_2L^{Br} (0.260 g, 0.50 mmol) in pentane (20 mL) and diethyl ether (8 mL) was slowly added at −78 °C to $Ti(CH_2Ph)_4$ (0.208 g, 0.50 mmol) in pentane (15 ml) and diethyl ether (5 mL). The resultant dark red solution was stirred for 1 h at −78 °C and for 12 h at room temperature. Filtration and concentration of the mixture gave a dark red solid at −78 °C. Yield: 0.17 g, 46%. ^{1}H NMR (500 MHz, C_6D_6): δ 1.35 (s, 9H, 5-^{t}Bu), 1.82 (s, 9H, 3-^{t}Bu), 4.23 (d, $J = 8.2$ Hz, 2H, CH_2), 4.55 (d, $J = 8.2$ Hz, 2H, CH_2), 6.30 (m, 3H, H^8 and *p*-Ph), 6.41 (t, $J = 7.7$ Hz, 4H, *m*-Ph), 6.63 (m, 5H, H^9 and *o*-Ph), 7.16 (s, 1H, H^{10}), 7.32 (d, $J = 1.4$ Hz, 1H, H^6), 7.40 (d, $J = 2.3$ Hz, 1H, H^{13}), 7.71 (d, $J = 2.3$ Hz, 1H, H^{15}), 7.90 (d, $J = 1.4$ Hz, 1H, H^4). ^{13}C NMR (126 MHz, C_6D_6): δ 31.04 (3-C*Me*$_3$), 31.74 (5-C*Me*$_3$), 34.68 (*C*Me$_3$), 35.75 (*C*Me$_3$), 98.19 (CH_2), 116.23 (C^8), 122.92 (C^{10}), 124.04 (*p*-Ph), 124.39 (C^{13}), 124.79 (C^6), 127.22 (C^{15}), 127.58 (*m*-Ph), 130.84 (*o*-Ph), 135.62 (C^4), 139.01 (C^9); 4° carbons: 122.17, 127.27, 128.35, 132.54, 136.87, 137.01, 142.73, 145.93, 157.01, 161.48, 193.48. Anal. Calc. for $C_{39}H_{39}NOTiBr_2$ (745.45): C, 62.84; H, 5.27; N, 1.88. Found: C, 62.74; H, 5.43; N, 1.99%.

4.7. Synthesis of titanium complex **2**



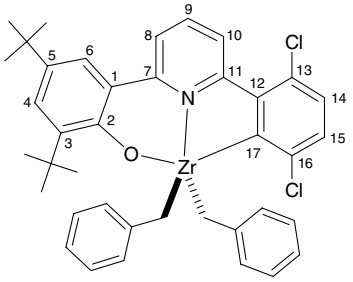
The procedure described in Section 4.6 was followed using H_2L^{Cl} (0.260 g, 0.61 mmol) and $Ti(CH_2Ph)_4$ (0.250 g, 0.61 mmol) to give a dark red solid. Yield: 0.21 g, 52%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.36 (s, 9H, 5-^{t}Bu), 1.84 (s, 9H, 3-^{t}Bu), 4.20 (d, $J = 8.2$ Hz, 2H, CH_2), 4.47 (d, $J = 8.2$ Hz, 2H, CH_2), 6.31 (t, $J = 7.3$ Hz, 2H, *p*-Ph), 6.45 (t, $J = 7.8$ Hz, 4H, *m*-Ph), 6.63 (d, $J = 7.3$ Hz, 4H, *o*-Ph), 6.71 (t, $J = 8.0$ Hz, 1H, H^9), 6.98 (d, $J = 8.3$ Hz, 1H, H^{14}), 7.10 (dd, $J = 8.0$, 0.6 Hz, 1H, H^8), 7.15 (d, $J = 8.2$ Hz, 1H, H^{15}), 7.37 (d, $J = 2.3$ Hz, 1H, H^6), 7.69 (dd, $J = 8.0$, 1.1 Hz, 1H, H^{10}), 7.73 (d, $J = 2.4$ Hz, 1H, H^4). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 31.11 (3-C*Me*$_3$), 31.75 (5-C*Me*$_3$), 34.71 (*C*Me$_3$), 35.75 (*C*Me$_3$), 97.41 (CH_2), 121.77 (C^8), 123.06 (C^{10}), 124.10 (*p*-Ph), 124.86 (C^6), 126.99 (C^4), 127.62 (*m*-Ph), 130.84 (*o*-Ph), 131.07 (C^{15}), 132.39 (C^{14}); 138.68 (C^9); 4° carbons: 128.35, 128.49, 136.74, 136.90, 139.15, 141.91, 142.96, 156.95, 158.05, 161.74, 195.04. Anal. Calc. for $C_{39}H_{39}NOTiCl_2$ (656.55): C, 71.35; H, 5.99; N, 2.13. Found: C, 71.60; H, 6.11; N, 2.22%.

4.8. Synthesis of zirconium complex **4**



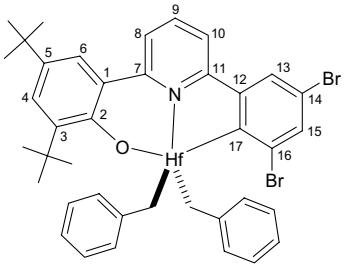
A solution of H_2L^{Br} (0.250 g, 0.48 mmol) in pentane (20 mL) and diethyl ether (5 mL) was slowly added at −78 °C to $Zr(CH_2Ph)_4$ (0.225 g, 0.49 mmol) in pentane (15 ml) and diethyl ether (5 mL). The resultant yellow solution was stirred for 1 h at −78 °C and for 12 h at room temperature. Filtration and concentration of the mixture gave a yellow solid at −78 °C. Yield: 0.18 g, 48%. ^{1}H NMR (500 MHz, C_6D_6): δ 1.35 (s, 9H, 5-^{t}Bu), 1.70 (s, 9H, 3-^{t}Bu), 3.42 (d, $J = 9.4$ Hz, 2H, CH_2), 3.56 (d, $J = 9.4$ Hz, 2H, CH_2), 6.26 (t, $J = 7.3$ Hz, 2H, *p*-Ph), 6.37 (t, $J = 7.7$ Hz, 4H, *m*-Ph), 6.49 (d, $J = 7.7$ Hz, 1H, H^8), 6.75 (t, $J = 8.0$ Hz, 1H, H^9), 6.80 (d, $J = 7.5$ Hz, 4H, *o*-Ph), 7.16 (d, $J = 4.4$ Hz, 1H, H^{10}), 7.32 (d, $J = 0.8$ Hz, 1H, H^6), 7.37 (d, $J = 2.2$ Hz, 1H, H^{13}), 7.60 (d, $J = 1.2$ Hz, 1H, H^4), 7.66 (d, $J = 2.3$ Hz, 1H, H^{15}). ^{13}C NMR (126 MHz, C_6D_6): δ 30.81 (3-C*Me*$_3$), 31.77 (5-C*Me*$_3$), 34.61 (*C*Me$_3$), 35.68 (*C*Me$_3$), 71.18 (CH_2), 117.64 (C^8), 123.64 (C^{10}), 123.69 (*p*-Ph), 125.08 (C^6), 125.20 (C^{13}), 127.00 (C^{15}), 129.05 (*m*-Ph), 129.51 (*o*-Ph), 134.02 (C^4), 138.87 (C^9); 4° carbons: 122.08, 126.63, 132.39, 136.22, 137.54, 142.30, 145.81, 154.99, 158.85, 161.42, 187.37. Anal. Calc. for $C_{39}H_{39}NOZrBr_2$ (788.77): C, 59.39; H, 4.98; N, 1.77. Found: C, 59.63 H, 5.12; N, 1.95%.

4.9. Synthesis of zirconium complex **5**



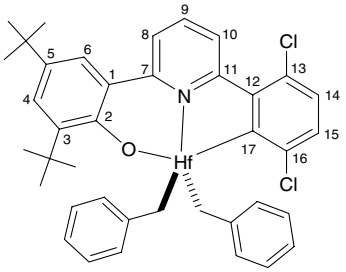
The procedure described in Section 4.8 was followed using H_2L^{Cl} (0.220 g, 0.51 mmol) and $Zr(CH_2Ph)_4$ (0.235 g, 0.52 mmol) to give a yellow solid. Yield: 0.17 g, 48%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.37 (s, 9H, 5-^{t}Bu), 1.66 (s, 9H, 3-^{t}Bu), 2.99 (d, $J = 9.3$ Hz, 2H, CH_2), 3.07 (d, $J = 9.3$ Hz, 2H, CH_2), 6.37 (t, $J = 7.2$ Hz, 2H, *p*-Ph), 6.41 (t, $J = 7.4$ Hz, 4H, *m*-Ph), 6.49 (d, $J = 7.5$ Hz, 4H, *o*-Ph), 7.10 (d, $J = 8.3$ Hz, 1H, H^{14}), 7.13 (d, $J = 8.2$ Hz, 1H, H^{15}), 7.39 (d, $J = 2.4$ Hz, 1H, H^6), 7.54 (d, $J = 9.0$ Hz, 1H, H^8), 7.56 (d, $J = 2.4$ Hz, 1H, H^4), 7.66 (t, $J = 8.0$ Hz, 1H, H^9), 7.80 (dd, $J = 8.0$, 1.2 Hz, 1H, H^{10}). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 30.04 (3-C*Me*$_3$), 30.92 (5-C*Me*$_3$), 34.03 (*C*Me$_3$), 34.87 (*C*Me$_3$), 68.76 (CH_2), 122.63 (C^{10}), 122.75 (*p*-Ph), 123.49 (C^8), 124.96 (C^6), 126.16 (C^4), 128.18 (*m*-Ph), 128.40 (*o*-Ph), 128.61 (C^{15}), 131.32 (C^{14}); 137.99 (C^9); 4° carbons: 126.11, 127.74, 128.14, 128.22, 128.56, 135.03, 136.37, 142.16, 159.10, 160.51, 187.25. Anal. Calc. for $C_{39}H_{39}NOZrCl_2$ (699.87): C, 66.93; H, 5.62; N, 2.00. Found: C, 67.17; H, 5.42; N, 2.24%.

4.10. Synthesis of hafnium complex **7**



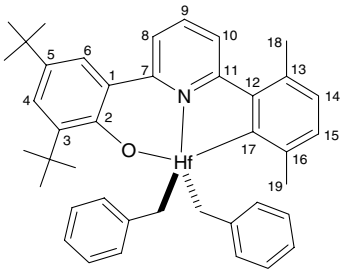
A solution of H_2L^{Br} (0.210 g, 0.41 mmol) in pentane (20 mL) and diethyl ether (5 mL) was slowly added at −78 °C to $Hf(CH_2Ph)_4$ (0.230 g, 0.42 mmol) in pentane (15 ml) and diethyl ether (5 mL). The resultant pale yellow solution was stirred for 1 h at −78 °C and for 12 h at room temperature. Filtration and concentration of the mixture gave a pale yellow solid at −78 °C. Yield: 0.14 g, 39%. ^{1}H NMR (500 MHz, C_6D_6): δ 1.35 (s, 9H, 5-^{t}Bu), 1.74 (s, 9H, 3-^{t}Bu), 3.21 (virtual s, 4H, CH_2), 6.31 (t, $J = 7.3$ Hz, 2H, *p*-Ph), 6.39 (t, $J = 7.5$ Hz, 4H, *m*-Ph), 6.43 (d, $J = 7.4$ Hz, 1H, H^8), 6.70 (t, $J = 8.0$ Hz, 1H, H^9), 6.76 (d, $J = 8.0$ Hz, 4H, *o*-Ph), 7.19 (d, $J = 7.7$ Hz, 1H, H^{10}), 7.33 (d, $J = 2.3$ Hz, 1H, H^{13}), 7.36 (d, $J = 1.3$ Hz, 1H, H^6), 7.69 (d, $J = 2.4$ Hz, 1H, H^{15}), 7.76 (d, $J = 1.3$ Hz, 1H, H^4). ^{13}C NMR (126 MHz, C_6D_6): δ 30.77 (3-C*Me*$_3$), 31.79 (5-C*Me*$_3$), 34.57 (*C*Me$_3$), 35.64 (*C*Me$_3$), 79.08 (CH_2), 117.55 (C^8), 123.61 (C^{10}), 123.76 (*p*-Ph), 124.91 (C^{13}), 125.65 (C^6), 127.26 (C^{15}), 128.47 (*m*-Ph), 129.85 (*o*-Ph), 135.09 (C^4), 139.22 (C^9); 4° carbons: 122.48, 126.18, 133.24, 135.83, 138.05, 142.12, 146.82, 155.45, 158.83, 161.26, 195.99. Anal. Calc. for $C_{39}H_{39}NOHfBr_2$ (876.04): C, 53.47; H, 4.49; N, 1.60. Found: C, 53.85; H, 4.43; N, 1.71%.

4.11. Synthesis of hafnium complex **8**



The procedure described in Section 4.10 was followed using H_2L^{Cl} (0.220 g, 0.51 mmol) and $Hf(CH_2Ph)_4$ (0.280 g, 0.52 mmol) to give a pale yellow solid. Yield: 0.17 g, 42%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.39 (s, 9H, 5-^{t}Bu), 1.69 (s, 9H, 3-^{t}Bu), 2.69 (d, $J = 10.4$ Hz, 2H, CH_2), 2.79 (d, $J = 10.4$ Hz, 2H, CH_2), 6.39–6.45 (m, 10H, *p*-, *m*- and *o*-Ph), 7.17 (d, $J = 8.2$ Hz, 1H, H^{14}), 7.29 (d, $J = 2.4$ Hz, 1H, H^6), 7.31 (d, $J = 8.3$ Hz, 1H, H^{15}), 7.56 (dd, $J = 8.0$, 1.0 Hz, 1H, H^8), 7.58 (d, $J = 2.4$ Hz, 1H, H^4), 7.64 (t, $J = 8.0$ Hz, 1H, H^9), 7.82 (dd, $J = 8.0$, 1.2 Hz, 1H, H^{10}). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 30.00 (3-C*Me*$_3$), 30.94 (5-C*Me*$_3$), 33.99 (*C*Me$_3$), 34.83 (*C*Me$_3$), 76.86 (CH_2), 122.54 (C^{10}), 122.84 (*p*-Ph), 123.53 (C^8), 124.73 (C^6), 126.40 (C^4), 127.60 (*m*-Ph), 128.69 (*o*-Ph), 129.56 (C^{15}), 134.67 (C^{14}); 138.43 (C^9); 4° carbons: 125.59, 129.22, 131.78, 136.83, 139.40, 141.91, 142.22, 154.28, 159.02, 160.52, 195.66. Anal. Calc. for $C_{39}H_{39}NOHfCl_2$ (787.14): C, 59.51; H, 4.99; N, 1.78. Found: C, 59.56; H, 4.93; N, 1.85%.

4.12. Synthesis of hafnium complex **9**



The procedure described in Section 4.10 was followed using H_2L^{Me} (0.214 g, 0.55 mmol) and $Hf(CH_2Ph)_4$ (0.300 g, 0.55 mmol) to give a pale yellow solid. Yield: 0.20 g, 49%. ^1H NMR (500 MHz, C_6D_6): δ 1.36 (s, 9H, 5-^{t}Bu), 1.81 (s, 9H, 3-^{t}Bu), 2.15 (s, 3H, Me^{18}), 2.980(d, $J = 10.8$ Hz, 2H, CH_2), 3.05 (s, 3H, Me^{19}), 3.09 (d, $J = 10.8$ Hz, 2H, CH_2), 6.35 (t, $J = 7.4$ Hz, 2H, *p*-Ph), 6.47 (t, $J = 7.7$ Hz, 4H, *m*-Ph), 6.70 (d, $J = 7.6$ Hz, 4H, *o*-Ph), 6.75 (dd, $J = 7.9$, 1.0 Hz, 1H, H^{10}), 6.83 (t, $J = 7.9$ Hz, 1H, H^9), 6.97 (d, $J = 7.6$ Hz, 1H, H^{14}), 7.16 (m, 2H, H^{15} and H^8), 7.35 (d, $J = 2.4$ Hz, 1H, H^6), 7.71 (d, $J = 2.4$ Hz, 1H, H^4). ^{13}C NMR (126 MHz, C_6D_6): δ 22.63 (Me^{18}), 25.07 (Me^{19}), 30.91 (3-CMe_3), 31.84 (5-CMe_3), 34.58 (CMe$_3$), 35.67 (CMe$_3$), 77.78 (CH_2), 121.65 (C^8), 122.04 (C^{10}), 123.24 (*p*-Ph), 125.08 (C^6), 126.72 (C^4), 128.13 (*m*-Ph), 129.91 (*o*-Ph), 130.70 (C^{15}), 132.73 (C^{14}); 138.41 (C^9); 4° carbons: 126.59, 130.66, 136.01, 137.90, 141.68, 142.11, 145.59, 156.27, 159.43, 165.65, 203.01. Anal. Calc. for $C_{45}H_{41}NOHf$ (746.32): C, 65.99; H, 6.08; N, 1.88. Found: C, 65.74; H, 5.95; N, 2.04%.

4.13. Polymerization procedure

Schlenk-line ethylene polymerization runs were carried out under atmospheric pressure in toluene in a 100 mL glass reactor containing a magnetic stir bar. The stirred solution containing the catalyst was thermostated to the required temperature and purged with ethylene for 15 minutes. Polymerization was initiated by adding a toluene solution of methylaluminoxane (MAO), and the reactor was maintained under 1 atmosphere of ethylene for the duration of the polymerization. After the prescribed time, HCl-acidified methanol (40 mL) was added to terminate the polymerization, and the ethylene gas feed was stopped. The resultant solid polymer was collected by filtration, washed with acidified methanol and dried under vacuum at 80 °C for 12 h.

Acknowledgements

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Appendix A. Supplementary material

As a representative example of the assignment process for each complex, the ^1H, ^1H–^1H COSY, NOESY and ^{13}C–^1H COSY NMR spectra of Ti complex **3** are presented in Figs. S1–S5. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.05.040.

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