Synthesis of a new olefin polymerization catalyst supported by an sp^3-C donor *via* insertion of a ligand-appended alkene into the Hf–C bond of a neutral pyridylamidohafnium trimethyl complex†

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A new living and isoselective propylene polymerization precatalyst was generated *via* the intramolecular insertion of a ligand-appended vinyl group into the Hf–C bond of a neutral pyridylamidohafnium trimethyl complex.

Recent advances in non-metallocene olefin polymerization catalysts[1] allow unprecedented access to new and useful polyolefin architectures. In particular, advances in living olefin polymerization,[2] and more recently, chain shuttling polymerization,[3] have allowed researchers to prepare olefin-based block copolymers that exhibit promising material properties.[3a,4] One of the most exciting classes of catalysts to emerge in the past decade is derived from the C_1-symmetric arylpyridylamidohafnium complexes ((APA)HfMe$_2$, R = 2-^{i}PrC$_6$H$_4$, Fig. 1) developed by Dow and Symyx.[5] For propylene polymerization several catalysts in this family are highly isoselective, thermally robust, and are capable of producing high molecular weight ($M_w > 10^5$ g mol^{-1}) polypropylene (PP). Detailed mechanistic studies of the C_1-symmetric (APA)HfMe$_2$ complex by Froese *et al.* have shown that 1,2-insertion of an olefin into the Hf–C$_{\text{Aryl}}$ bond generates an sp^3-hybridized carbon donor atom that supports the active metal center rather than participating in further olefin insertion.[5b] We have shown that the catalyst derived from a C_s-symmetric (APA)HfMe$_2$ complex (R = H, Fig. 1) furnished moderately isotactic PP (iPP).[6] Statistical analysis of the stereoerrors in the iPP sample *via* ^{13}C{^{1}H} NMR spectroscopy revealed that, quite unexpectedly, an enantiomorphic site control mechanism of isotactic monomer enchainment was operative for this catalyst.[7] These observations suggest that the isoselectivity exhibited by catalysts derived from the C_s-symmetric (APA)HfMe$_2$ complex might result from the 1,2-insertion of an α-olefin into the Hf–C$_{\text{Aryl}}$ bond generating a C_1-symmetric catalyst supported by an sp^3-hybridized carbon donor atom.

With the goal of incorporating an ancillary sp^3-C donor into the ligand framework of an olefin polymerization catalyst, we set out to prepare a pyridylamidohafnium trimethyl complex bearing a vinyl group in the ligand framework. We initially targeted the pyridylamidohafnium trimethyl complex (**1**, Fig. 1) envisioning that methide abstraction with B(C$_6$F$_5$)$_3$ would generate the pyridylamidohafnium dimethyl cation, which would subsequently undergo intramolecular migratory insertion of the vinyl group. Geometry optimization calculations indicate that the pathway leading to 1,2-insertion of this compound is energetically less favorable than 2,1-insertion. A 2,1-insertion would be interesting in its own right since it could lead to the generation of a polymerization catalyst bearing a stable η^2-CR$_2$Ar moiety bound to the active metal center.

Treating the pyridylamidohafnium trichloride complex (Fig. 1) with 3.7 equivalents of MeMgBr furnished the crude product as a yellow-orange foam-like solid. Characterization of the crude product by ^{1}H NMR spectroscopy revealed a 15 : 85 mixture of products formulated as the expected pyridylamidohafnium trimethyl complex (**1**) and a diastereomeric mixture of pyridylamidohafnium dimethyl complexes (*rac*-**2a,b**). Heating a C$_6$D$_6$ solution of this mixture at 80 °C overnight led to the disappearance of the vinyl proton resonances and complete conversion to *rac*-**2a,b**. The ^{1}H NMR spectrum revealed two sets of two singlets corresponding to the Hf–CH_3 groups, which are consistent with the formulation of the product as a mixture of diastereomers. Characterization of the product *via* ^{13}C{^{1}H} NMR reveals 70 resonances, 35 corresponding to each diastereomer. Single crystals suitable for structural determination *via* X-ray crystallography were grown from a saturated, pentane-layered toluene solution over several days at −30 °C. The X-ray structure (Fig. 2) revealed

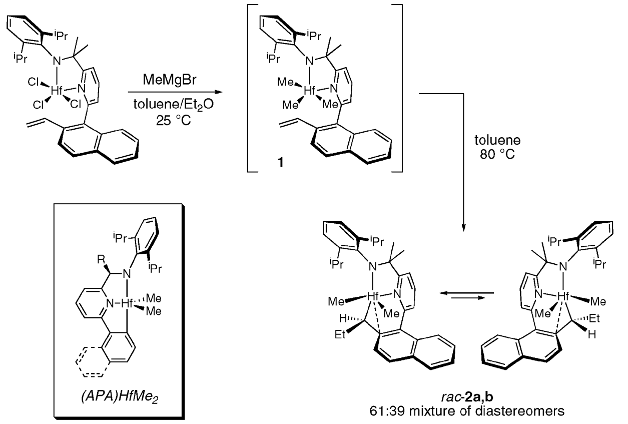

Fig. 1 Synthesis of complexes **2a** and **2b**.

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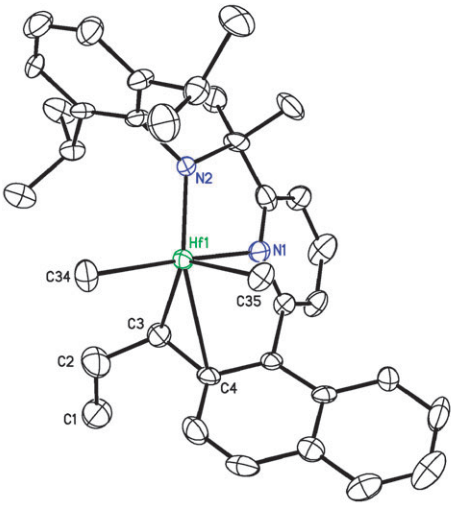

Fig. 2 ORTEP diagram of *rac*-**2a**. Thermal ellipsoids are drawn at the 40% probability level. The unlabelled atoms are carbon.

that the coordination geometry about hafnium is best described as distorted trigonal bipyramidal with C(34) and N(1) occupying the axial positions (C(34)–Hf(1)–N(1) = 167.1(2)°). From the short Hf(1)–C(4) distance (2.684(7) Å), it is apparent that the 1-(naphthalen-2-yl)propyl moiety is bound in an η^2-fashion.[8] Inspection of the extended unit cell revealed the presence of only one diastereomer. However, the ^{1}H NMR spectrum of the redissolved single crystals revealed the presence of both diastereomers in the same ratio (61 : 39) as that observed in the crude product. This result suggests that an equilibrium exists for the mixture of diastereomers in solution; it is possible to envision interconversion of the diastereomers *via* a ring-flip of the six-membered metallacycle.[9] These results represent a rare example of olefin insertion into the metal–alkyl bond of a neutral group IV metal complex,[10–13] and to the best of our knowledge represents the only report of intramolecular insertion of an alkene into a Hf–C$_{\mathrm{Alkyl}}$ bond for a neutral hafnium alkyl compound. Although we cannot rule out Grignard attack of the alkene followed by chloride displacement on the hafnium, it is unlikely, since treating the 15 : 85 mixture of **1** : *rac*-**2a,b** with a further 3.7 equivalents of MeMgBr led to no decrease in the intensity of the ^{1}H NMR resonances corresponding to the vinyl protons of **1**. Additionally, the formation of **1** in the crude reaction mixture and subsequent conversion to *rac*-**2a,b** upon heating as monitored by ^{1}H NMR spectroscopy suggests a migratory insertion of the alkene.

Addition of $B(C_6F_5)_3$ to a solution of *rac*/**2a,b** and 1-hexene (1 : 1 : 580) in toluene at 25 °C led to the formation of 0.48 g of poly(1-hexene) (62% conversion) in 30 minutes. The polymer possessed an M_n = 49 000 g mol^{-1} and a relatively narrow molecular weight distribution (M_w/M_n = 1.85). Analysis of the poly(1-hexene) microstructure *via* ^{13}C{^{1}H} NMR spectroscopy revealed that the polymer was regioregular and highly isotactic; the spectrum revealed no resonances corresponding to stereoerrors (see ESI†). It is likely that the high degree of stereoselectivity observed for this catalyst is due to the chiral structure of *rac*-**2a,b**. Analysis of the organic residues isolated after a 1-hexene polymerization revealed that the protonated ligand derived from *rac*-**2a,b** was the exclusive small molecule product thereby indicating that the Hf–C(sp^3) bond remains intact throughout the course of polymerization. Therefore, *rac*-**2a,b**/$B(C_6F_5)_3$ represents a new, highly isoselective catalyst for 1-hexene polymerization.

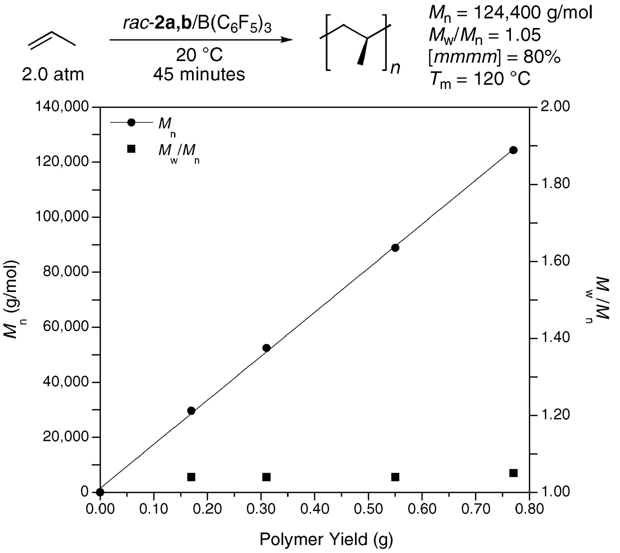

Fig. 3 Plot of M_n (●) and M_w/M_n (■) *versus* polymer yield for propylene polymerization at 20 °C catalyzed by *rac*-**2a,b**/$B(C_6F_5)_3$.

We proceeded to investigate the propylene polymerization behavior of *rac*-**2a,b**/$B(C_6F_5)_3$. Several polymerizations of varying duration were conducted at 20 °C under 2 atm of propylene. The M_n of the PP increased linearly with increasing polymer yield over the course of 45 min while the molecular weight distribution remained narrow ($M_w/M_n \leq 1.05$) (Fig. 3). The average turnover frequency (TOF) was 2800 h^{-1}, which is significantly lower than that observed for the analogous *ortho*-metalated precatalyst under identical conditions (25 000 h^{-1}).[14] Analysis of the PP *via* ^{13}C{^{1}H} NMR spectroscopy revealed that the polymer was isotactic ([m^4] = 80%). The degree of isotacticity was also somewhat lower than that of the iPP produced by the analogous *ortho*-metalated precatalyst ([m^4] = 91%).[14] Statistical analysis of the methyl region revealed a 2 : 2 : 1 ratio of peaks corresponding to [*mmmr*] : [*mmrr*] : [*mrrm*] stereoerrors which indicated that an enantiomorphic site-controlled mechanism of isotactic monomer enchainment was operative.[7] It is unclear at this time whether the rate of interconversion between diastereomers is similar to the rate of propagation, however, if it is, it does not result in a change in the enantiofacial selectivity of the catalyst since no resonance attributable to the *mmrm* stereoerror was observed. The ^{13}C{^{1}H} NMR spectrum (Fig. 4) also revealed resonances due to regioerrors (*ca.* 9 mol%) arising from head-to-head or tail-to-tail misinsertions[5a] which may explain the relatively low melting temperature (T_m = 120 °C relative to 123 °C for a regioregular iPP with a similar degree of isotacticity).[15a] The catalyst *rac*-**2a,b**/$B(C_6F_5)_3$ is a rare example of one that is both living and isoselective for propylene polymerization.[4,6,15]

Since *rac*-**2a,b** contains three hafnium-bound alkyl groups (two methyl groups, and one 2-naphthyl-1-propyl group), it was necessary to determine which of these were being

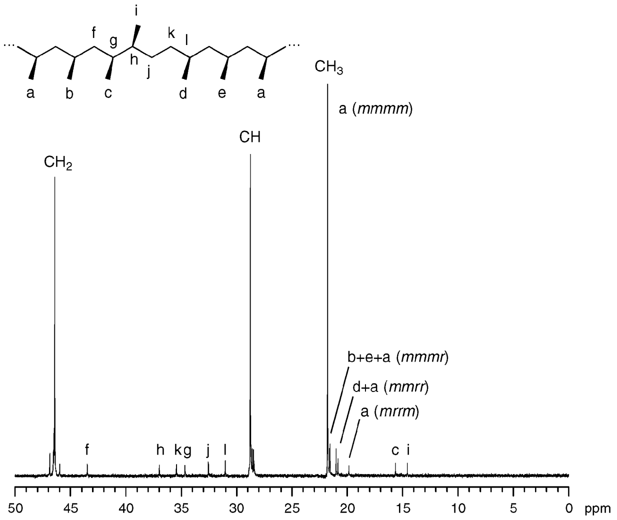

Fig. 4 $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 1,1,2,2-$C_2D_2Cl_4$, 135 °C) of iPP produced by *rac*-**2a,b**/$B(C_6F_5)_3$ at 20 °C.

abstracted by $B(C_6F_5)_3$. The reaction between *rac*-**2a,b** and $B(C_6F_5)_3$ was monitored using ^1H NMR spectroscopy. The spectrum revealed that two of the four resonances corresponding to Hf–CH_3 groups had disappeared. The two remaining Hf–CH_3 resonances appeared at −0.25 and −0.44 ppm in a 70 : 30 ratio. Two broad, overlapping resonances appeared at 1.75 ppm which were assigned to $[(C_6F_5)_3BCH_3]^-$. Importantly, no resonance attributable to $(C_6F_5)_3B$–CH($C_{Naphthyl}$)(Et) was present. These observations suggest that *rac*-**2a,b** reacts with $B(C_6F_5)_3$ *via* methide abstraction to produce a diastereomeric mixture of pyridylamidohafnium methyl cations.

We set out to synthesize **1** and subsequently generate the corresponding pyridylamidohafnium dimethyl cation *via* methide abstraction. Unexpectedly, intramolecular 2,1-insertion of the appended vinyl group into the Hf–CH_3 bond of **1** occurred, thereby furnishing *rac*-**2a,b** in a rare example of olefin insertion into the Hf–C bond of a neutral hafnium–methyl complex. Upon activation with $B(C_6F_5)_3$, *rac*-**2a,b** formed an active polymerization catalyst that isoselectively polymerized propylene in a living fashion. The origin of isoselectivity in these systems remains unclear; current studies focus on modeling the chiral framework of the putative active species. The catalyst derived from methide abstraction of *rac*-**2a,b** represents a rare example of an olefin polymerization catalyst supported by an sp^3-C donor.

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