10746 *J. Am. Chem. Soc.* **2001,** *123,* 10746−10747

Cationic Hafnium Alkyl Complexes that Are Stable toward *β*-Hydride Elimination below 10 °C and Active as Initiators for the Living Polymerization of 1-Hexene

Parisa Mehrkhodavandi and Richard R. Schrock*

Department of Chemistry
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, Massachusetts 02139

Received June 11, 2001

Recently we reported the synthesis and activation of zirconium dialkyl complexes bearing arylated diamido pyridine ligands, $[(MesNCH_2)_2C(CH_3)(2\text{-}C_5H_4N)]^{2-}$ ($[MesNpy]^{2-}$), and their use as initiators for the polymerization of 1-hexene.[1] Use of $\{[MesNpy]ZrMe\}[B(C_6F_5)_4]$ as an initiator was complicated by formation of unreactive $\{[MesNpy]_2Zr_2Me_3\}[B(C_6F_5)_4]$ and by 2,1-insertion into the ZrMe bond followed by *β*-hydride elimination to give inactive species. $\{[MesNpy]Zr(CH_2CHMe_2)\}[B(C_6F_5)_4]$ was found to be an excellent initiator at 0 °C in bromobenzene; only 1,2-insertion of 1-hexene into Zr−C bonds appeared to take place, and cationic intermediates appeared to be stable toward *β*-hydride elimination. However, $\{[MesNpy]Zr(CH_2CHMe_2)\}[B(C_6F_5)_4]$ itself was unstable toward *β*-hydride elimination. We now find that cationic hafnium complexes of the type $\{[MesNpy]HfR\}[B(C_6F_5)_4]$ (R = Et, *n*-Bu, *i*-Bu, *n*-Pr, *i*-Pr) that are formed upon treating $[MesNpy]HfR_2$ with $[Ph_3C][B(C_6F_5)_4]$ can be characterized readily by NMR methods, are stable toward *β*-hydride elimination at 10 °C or below, and are active initiators for the living polymerization of 1-hexene via 1,2-insertion into the Hf−C bond at a rate that is approximately half that estimated for the Zr-catalyzed process.

The dichloride complex, $[MesNpy]HfCl_2$, was prepared by methods analogous to those used to prepare $[MesNpy]ZrCl_2$.[1] Dialkyl complexes of the type $[MesNpy]HfR_2$ (R = Et, *n*-Bu, *i*-Bu, *n*-Pr, *i*-Pr) were prepared by treating $[MesNpy]HfCl_2$ with Grignard reagents. All dialkyl complexes are stable at room temperature in the solid state or in solution (benzene, toluene, ether, etc.). Perhaps the most unusual is $[MesNpy]Hf(i\text{-Pr})_2$, whose structure was shown by X-ray crystallography to be similar to that of $[MesNpy]ZrMe_2$.[1] (The structure will be described later in a full paper.) There is a good deal of evidence in the literature that dialkyl group 4 metal complexes can be relatively resistant toward *β*-hydride abstraction, especially those of hafnium. For example, Cp_2MEt_2 is relatively stable only when M = Hf.[2] A variety of isopropyl complexes are known for metals outside of group 4.[3−8]

Activation of $[MesNpy]Hf(i\text{-Bu})_2$ (**1**) and $[MesNpy]Hf(^{13}CH_2CHMe_2)_2$ (**1***) in C_6D_5Br with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ at −20 °C led to formation of Ph_3CH, isobutene, and the isobutyl cations, $[(MesNpy)Hf(i\text{-Bu})][B(C_6F_5)_4]$ (**2** and **2***; eq 1). The $^{13}C\{^1H\}$ NMR spectrum (0 °C, C_6D_5Br) of activated **1*** shows a singlet at 93.3 ppm corresponding to the isobutyl methylene carbon atom in **2*** along with a resonance for $^{13}CH_2{=}CMe_2$ at 111.1 ppm. The ^1H NMR spectrum (−20 °C, C_6D_5Br) for **2** shows resonances for the isobutyl methyl, methylene, and methine protons at 0.55, 0.44, and 1.73 ppm, respectively. Unlike its zirconium analogue,[1] $[(MesNpy)Hf(i\text{-Bu})][B(C_6F_5)_4]$ shows no sign of decomposition over a period of 2 h at 0 °C.

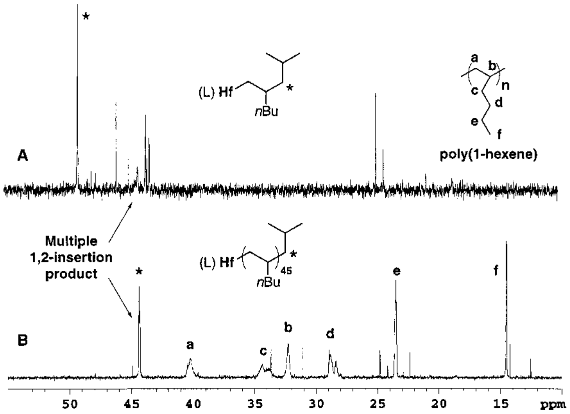
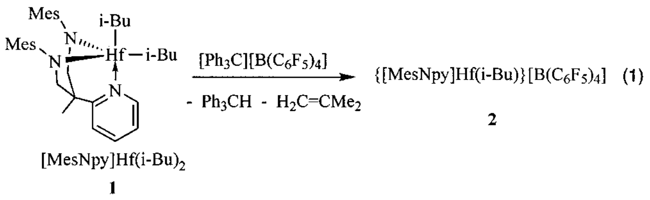


Figure 1. $^{13}C\{^1H\}$ NMR spectra (0 °C, C_6D_5Br) for addition of 1-hexene to **2***; (a) 1−2 equiv of 1-hexene, (b) 45 equiv of 1-hexene.



Addition of 1−2 equiv of 1-hexene to a solution of **2*** led to a decrease in the intensity of the isobutyl methylene resonance in **2*** at 93.3 ppm, appearance of a new $^{13}C\{^1H\}$ NMR resonance at 49.0 ppm for the first insertion product, and appearance of other resonances near 45 ppm for the second, third, and so forth insertion products (Figure 1a). Addition of 44 more equiv of 1-hexene led to the appearance of a resonance at 44.3 ppm for the labeled methylene in the intermediate formed by multiple 1,2-insertions plus the usual resonances (natural ^{13}C abundance) for atactic poly(1-hexene) formed via a 1,2-insertion process (Figure 1b). The living polymer is formed quantitatively (vs Ph_3CH), and there is no sign of decomposition by *β*-hydride elimination over a period of 2−3 hours at 0 °C.

Consumption of 1-hexene by $[(MesNpy)Hf(i\text{-Bu})][B(C_6F_5)_4]$ in C_6D_5Br at 0 °C follows first-order kinetics. Two consecutive additions of 60 equiv of 1-hexene to a solution of **2** (0.015 M) in C_6D_5Br at 0 °C yielded identical linear plots of ln[1-hexene] versus time with $k_{obs} = 0.059$ min^{-1} or $k_p = 0.067$ M^{-1} s^{-1}. No induction period was observed. Addition of 1-hexene to this solution after it had been stored at room temperature for 24 h led to first-order olefin consumption of 1-hexene at 0 °C, but at a rate $\sim{}^1/_3$ of that observed originally. Resonances for vinylic protons at 4.84 and 4.82 ppm indicated that some *β*-hydride elimination had taken place in 24 h at room temperature; we propose to yield catalytically inactive metal-containing products. The value of $k_p = 0.067$ M^{-1} s^{-1} should be compared with $k_p = 0.044$ M^{-1} s^{-1} for polymerization of 1-hexene under identical conditions with the analogous Zr species, *assuming* all Zr is active. However, only $\sim{}^1/_3$ of the Zr was active in that particular run so that the true value for the Zr system is ~0.13 M^{-1} s^{-1}, approximately twice the value for the hafnium catalyst. Polym-

---

[1] Mehrkhodavandi, P.; Bonitatebus, P. J., Jr.; Schrock, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 7841.

[2] Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124.

[3] Chisholm, M. H.; Haitko, D. A.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046−4053.

[4] Jaffart, J.; Mathieu, R.; Etienne, M.; McGrady, J. E.; Eisenstein, O.; Maseras, F. *Chem. Commun.* **1998**, 2011−2012.

[5] Jones, W. D.; Wick, D. D. *Inorg. Chem.* **1997**, *36*, 2723−2729.

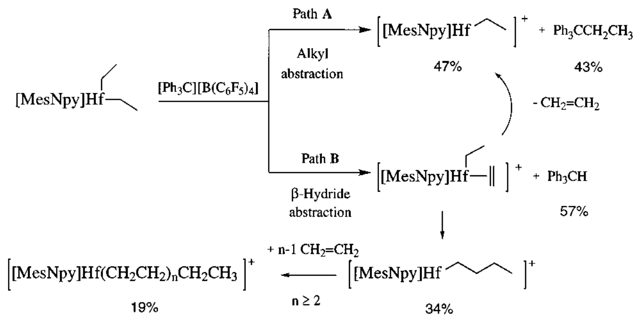
[6] Pahor, N. B.; Dreos-Garlatti, R.; Geremia, S.; Randaccio, L.; Tauzher, G.; Zangrando, E. *Inorg. Chem.* **1990**, *29*, 3437−3441.

[7] Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 7372−7373.

[8] Reger, D. L.; Garza, D. G.; Lebioda, L. *Organometallics* **1991**, *10*, 902−906.

10.1021/ja0114198 CCC: $20.00

Scheme 1. Activation of [MesNpy]HfEt$_2$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$]



erization of 1-hexene at five temperatures between 5 and -20 °C yielded $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values of 10.9(5) kcal mol^{-1} and -23(2) cal mol^{-1} K^{-1} respectively. These values should be compared with those obtained for polymerization of 1-hexene with [(MesNpy)Zr(i-Bu)][B(C$_6$F$_5$)$_4$] ($\Delta H^{\ddagger} = 8.1(7)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -33$(2) cal mol^{-1} K^{-1}). Seven poly(1-hexene) samples (prepared at 0 °C) that contained up to 600 equiv of 1-hexene were found to have polydispersities between 1.02 and 1.05 and molecular weights (as determined by light scattering coupled with a refractive index detector[9]) that were essentially equal to the molecular weights expected for a well-behaved living system (Figure 2, Supporting Information).

Activation of [MesNpy]HfEt$_2$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in C$_6$D$_5$Br at -20 °C led to formation of Ph$_3$CEt and Ph$_3$CH and two major cationic hafnium alkyl species, {[MesNpy]HfEt}[B(C$_6$F$_5$)$_4$] and {[MesNpy]Hf(n-Bu)}[B(C$_6$F$_5$)$_4$], in approximately equal amounts. The first is formed by direct attack on an ethyl ligand to give Ph$_3$CEt, while the second is formed when trityl abstracts a β-hydride from an ethyl ligand to give intermediate "{[MesNpy]HfEt(C$_2$H$_4$)}[B(C$_6$F$_5$)$_4$]" followed by insertion of ethylene into the Hf$-$Et bond (Scheme 1). The assignment of resonances for the two cations was made possible by gCOSY and ^{13}C DEPT experiments. The amounts of {[MesNpy]HfEt}[B(C$_6$F$_5$)$_4$] (47%), Ph$_3$CEt (43%), {[MesNpy]Hf(n-Bu)}[B(C$_6$F$_5$)$_4$] (34%), and Ph$_3$CH (57%) that are formed (with the sum of Ph$_3$CEt and Ph$_3$CH set equal to 100%) suggest that some ethylene is lost from intermediate "{[MesNpy]HfEt(C$_2$H$_4$)}[B(C$_6$F$_5$)$_4$]" to give {[MesNpy]HfEt}[B(C$_6$F$_5$)$_4$] and free ethylene, which is then available to react with {[MesNpy]HfEt}[B(C$_6$F$_5$)$_4$] to form {[MesNpy]Hf(n-Bu)}[B(C$_6$F$_5$)$_4$], and with {[MesNpy]Hf(n-Bu)}[B(C$_6$F$_5$)$_4$] to form higher insertion products, {[MesNpy]Hf(CH$_2$CH$_2$)$_n$Et}[B(C$_6$F$_5$)$_4$] (~19%), where n is greater than or equal to 2. {[MesNpy]HfEt}[B(C$_6$F$_5$)$_4$] and {[MesNpy]Hf(n-Bu)}[B(C$_6$F$_5$)$_4$] can be distinguished from each other by the chemical shift of the ortho pyridyl proton at 8.40 and 8.51 ppm, respectively, although the ortho pyridyl proton resonance in {[MesNpy]Hf(CH$_2$CH$_2$)$_n$Et}[B(C$_6$F$_5$)$_4$] (8.52 ppm) overlaps with that for {[MesNpy]Hf(n-Bu)}[B(C$_6$F$_5$)$_4$] in 500 MHz proton NMR spectra (C$_6$D$_5$Br, -20 °C). Addition of 1$-$2 equiv of 1-hexene to a solution containing {[MesNpy]Hf(CH$_2$CH$_2$)$_n$Et}[B(C$_6$F$_5$)$_4$] ($n = 0, 1, 2, ...$) leads to formation of two major insertion products which can be formulated as 1,2-insertion products, {[MesNpy]HfCH$_2$CH(n-Bu)(Et)}[B(C$_6$F$_5$)$_4$] (if $n = 0$) and {[MesNpy]HfCH$_2$CH(n-Bu)$_2$}[B(C$_6$F$_5$)$_4$] (if $n = 1$), on the basis of ^{13}C DEPT experiments. Only a resonance at 88.7 ppm corresponding to a methylene of the type HfCH$_2$CR′R″ is present, consistent with 1,2-insertion. A resonance for a hafnium-bound methine carbon, HfCHR′R″, was not observed.

Activation of [MesNpy]Hf(i-Pr)$_2$ with 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] led to formation of Ph$_3$CH (only) and two major cationic species in solution, [(MesNpy)Hf(i-Pr)][B(C$_6$F$_5$)$_4$], and the product of 1,2-insertion of propene into the Hf$-$C bond, [(MesNpy)HfCH$_2$CH(CH$_3$)(i-Pr)][B(C$_6$F$_5$)$_4$]. (Pyridyl ortho proton resonances belonging to what we propose to be multiple insertion products were also observed in the aromatic region of the ^{1}H NMR spectrum of this solution.) A ^{13}C DEPT experiment reveals a resonance at 88.5 ppm corresponding to the hafnium methylene carbon in [(MesNpy)HfCH$_2$CH(CH$_3$)(i-Pr)]$^+$ and a resonance at 79.0 ppm corresponding to the hafnium methine carbon in [(MesNpy)Hf(i-Pr)]$^+$. The ratio of [(MesNpy)HfCH$_2$CH(CH$_3$)(i-Pr)]$^+$ to [(MesNpy)Hf(i-Pr)]$^+$ is 4.2:1 if activation is carried out at -20 °C. Formation of [(MesNpy)Hf(n-Pr)]$^+$ was not observed over a period of 1 h at 0 °C. Storage of the same solution at 10 °C for 24 h led to the disappearance of the resonances for [(MesNpy)Hf(i-Pr)]$^+$ and the appearance of two new ^{1}H NMR resonances at 4.68 and 4.73 ppm corresponding to vinylic protons of a β-hydride elimination product. In contrast only about half of the [(MesNpy)HfCH$_2$CH(CH$_3$)(i-Pr)]$^+$ had disappeared during this time period. Therefore, we can say with confidence that [(MesNpy)Hf(i-Pr)]$^+$ is significantly less stable than [(MesNpy)HfCH$_2$CH(CH$_3$)(i-Pr)]$^+$. The greater instability of an internal alkyl toward β-hydride elimination has been postulated for some time in Zr and Hf olefin polymerization systems.[10,11] We believe these results to be the first direct demonstration of that proposal in cationic group 4 alkyl complexes.

It is becoming clear that in several of the cationic zirconium diamido donor systems that we have been investigating β-hydride elimination is slow in part for steric reasons.[12−14] We now believe that in the (MesNpy)$^{2-}$ systems, in particular, the [B(C$_6$F$_5$)$_4$]$^-$ anion itself contributes significantly to steric crowding by interacting with the metal in as yet undefined ways,[15] probably *trans* to the nitrogen donor. This viewpoint is inspired by recent theoretical[16,17] and experimental[18,19] results on cationic metallocene catalysts, which suggest that especially in solvents such as toluene, even the [B(C$_6$F$_5$)$_4$]$^-$ anion is a weakly bound ligand, and therefore one must consider the *ion pair* as the reactive entity, not the cation alone. Although we will now be able to measure a variety of polymerization rates in these well-behaved systems, it is not clear what process is actually being measured. We will try to resolve some of these issues by varying the nature of the aryl group on nitrogen and by measuring relative decomposition rates for terminal and internal cationic alkyl complexes and relative rates of reaction of cationic terminal and internal alkyl complexes with olefins. The results of these experiments will be reported in due course.

Acknowledgment. We thank the Department of Energy (DE-FG02-86ER13564) for supporting this research and Exxon Corporation for a gift of [Ph$_3$C][B(C$_6$F$_5$)$_4$].

Supporting Information Available: Experimental procedures and Figure 2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0114198

---

(9) Molecular weights were determined by light scattering in THF with a Wyatt Minidawn system using a dn/dc value of 0.076. The dn/dc value was determined by Wyatt on poly(1-hexene) samples prepared with the hafnium catalysts.

(10) Busico, V.; Cipullo, R.; Monaco, G.; Vacatello, M.; Bella, J.; Segre, A. L. *Macromolecules* **1998**, *31*, 8713−8719.

(11) Moscardi, G.; Piemontesi, F.; Resconi, L. *Organometallics* **1999**, *18*, 5264.

(12) Schrock, R. R.; Bonitatebus, P. J., Jr.; Schrodi, Y. *Organometallics* **2001**, *20*, 1056.

(13) Baumann, R.; Schrock, R. R. *J. Organomet. Chem.* **1998**, *557*, 69.

(14) Schrock, R. R.; Baumann, R.; Reid, S. M.; Goodman, J. T.; Stumpf, R.; Davis, W. M. *Organometallics* **1999**, *18*, 3649.

(15) The only interaction that has been elucidated through X-ray studies is in a thorium species in which the anion is bound in the solid state to the metal through the meta and para fluorides in perfluorotetraphenylborate; Yang. X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840.

(16) Vanka, K.; Chan, M. S. W.; Pye, C. C.; Ziegler, T. *Organometallics* **2000**, *19*, 1841.

(17) Vanka, K.; Ziegler, T. *Organometallics* **2001**, *20*, 905.

(18) Beck, S.; Lieber, S.; Schaper, F.; Geyer, A.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **2001**, *123*, 1483.

(19) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842.