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# Nature of the Initiation, Propagation, and Chain Transfer Steps during the Formation of Ethylene Oligomers Catalyzed by $PdMe_2$(*N*,*N*,*N*′*N*′-tetramethylethylenediamine)/$B(C_6F_5)_3$

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*Summary: Reaction of equimolar quantities of $PdMe_2(Me_2NCH_2CH_2NMe_2)$ and $B(C_6F_5)_3$ in the presence of ethylene results in the formation of $[PdMe(C_2H_4)(Me_2NCH_2CH_2NMe_2)]^+[BMe(C_6F_5)_3]^-$; the latter catalyzes the oligomerization of ethylene to highly branched products, which are apparently formed via both reversible β-elimination−reinsertion processes and the incorporation of short chain oligomeric products.*

There is currently great interest in Ziegler catalysts, based on cationic nickel and palladium compounds containing bulky diimine ligands, that polymerize ethylene to polyethylenes containing highly branched microstructures.[1] Although the branching is thought to result from a series of reversible β-H elimination and reinsertion steps, which allow the metal to migrate along the polymer chain (chain walking), there has been, as yet, little research into the mechanism(s) of the overall process.[1,2]

We now report the acquisition of useful mechanistic information via in situ NMR monitoring of a polymerization process; we have also identified end groups and the types of unsaturation in the products of polymerization via detailed NMR analyses of polymers of low molecular weight. Since the presence of bulky ligands in catalyst systems is known to inhibit chain transfer reactions, resulting in the formation of high molecular weight polymers,[1,2] we have utilized the new, sterically undemanding cationic catalytic system obtained when $PdMe_2$(tmeda)[3] (tmeda = *N*,*N*,*N*′*N*′-tetramethylethylenediamine) is activated with $B(C_6F_5)_3$. This catalyst system facilitates β-hydrogen transfer relative to propagation reactions and produces highly branched ethylene oligomers of sufficiently low molecular weights that useful NMR data may be obtained.

Reaction of equimolar quantities of $PdMe_2$(tmeda) and $B(C_6F_5)_3$ in $CD_2Cl_2$ at 193 K was monitored by $^1$H NMR spectroscopy and proceeds cleanly as in eq 1. The Pd−Me resonances of $PdMe_2$(tmeda)[3b] disappeared, giving rise to new methyl resonances at δ 0.48 and 0.33 (br) attributable to $[PdMe(CD_2Cl_2)(tmeda)]^+$ and free $[BMe(C_6F_5)_3]^-$, respectively. Thus, the borate anion does not coordinate to the cationic metal center via the methyl group, as commonly observed in group 4 $d^0$ systems.[4] The NMR spectrum also exhibited broadened resonances at ca. δ 2.32 and 3.18 attributable to nonequivalent $CH_2$ hydrogens and at ca. δ 2.45 (6H), 2.62 (3H), and 2.72 (3H) attributed to the N−Me groups. Since the N−Me groups appeared in at least three environments, the cationic complex is formulated as in eq 1 rather than as the more symmetric μ-methyl complex $[Pd_2(\mu\text{-}Me)_2(tmeda)_2]^{2+}$. The spectrum broadened significantly on raising the temperature over 200 K, consistent with ensuing rapid ring inversion.[3]

$$PdMe_2(tmeda) + B(C_6F_5)_3 \rightarrow [PdMe(CD_2Cl_2)(tmeda)]^+ + [BMe(C_6F_5)_3]^- \quad (1)$$

Ethylene is oligomerized by "$[PdMe(tmeda)][BMe(C_6F_5)_3]$", formed in situ in toluene. In a typical experiment, the oligomer obtained over 2 h at ~7 atm at 298 K (TON = 1250 g of oligomer/mol of catalyst/h) was a low molecular weight ($M_w$ = 265, $M_n$ = 240), highly branched material with low polydispersity (1.1). Consistent with the very narrow molecular weight distribution, lower oligomers were not detected in the crude catalytic mixture by GC-MS analysis, although a large number of compounds in the molecular weight range 250−300 were detected. While molecular ions and cracking patterns showed that the oligomeric products were olefinic rather than saturated, more definitive characterization was achieved by $^1$H and $^{13}C\{^1H\}$NMR spectroscopy.[5]

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[2] Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 6177. (b) Deng, L.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 1094. (c) Froese, R. D. J.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 1581. (d) Strömberg, S.; Zetterberg, K.; Siegbahn, P. E. M. *J. Chem. Soc., Dalton Trans.* **1997**, 4147.

[3] (a) De Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907. (b) The $^1$H NMR spectrum of $PdMe_2$(tmeda) in $CD_2Cl_2$ at 193 K exhibits singlets at δ −0.47 and 2.32 attributable to the Pd−Me and N−Me groups, respectively, and broadened doublets at δ 2.12 and 2.75 attributable to nonequivalent $CH_2$ hydrogens of the puckered five-membered ring.[3a] At higher temperatures, ring inversion becomes rapid on the NMR time scale and exchange of the $CH_2$ hydrogens occurs to give a singlet at δ 2.49 (298 K).

[4] See, for instance: (a) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842. (b) Giardello, M. A.; Eisen, M. S.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 12114. (c) Wang, Q.; Quyoum, R.; Gillis, D. J.; Jeremic, D.; Baird, M. C. *J. Organomet. Chem.* **1997**, *527*, 7. (d) Sarsfield, M. J.; Ewart, S. W.; Tremblay, T. L.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3097.

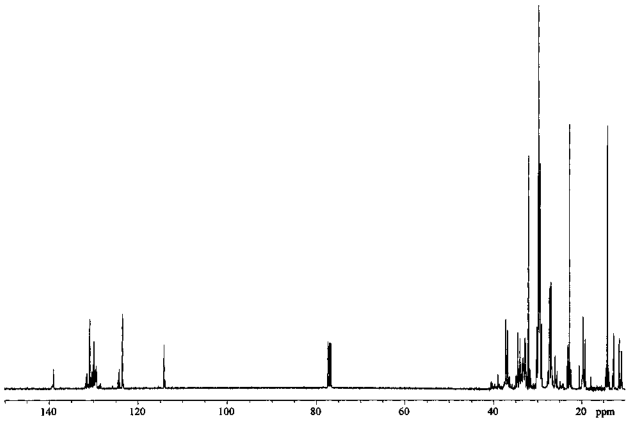

**Figure 1.** $^{13}C\{^1H\}$ NMR spectrum of the ethylene oligomer.

The $^1H$ spectrum exhibited a broad, main chain $CH_2$ resonance at $\delta$ 1.27 (52% of total H) and a somewhat weaker methyl multiplet centered at $\delta$ 0.87 (23% of total H). The presence of internal unsaturation was indicated by the presence of resonances at $\delta$ 2.04 (8% of total H) attributed to allylic methylene groups of the type $-C\mathbf{H}_2$-$CH{=}CH-$, a sharp doublet at $\delta$ 1.61 attributed to the methyl group in $C\mathbf{H}_3HC{=}CH-$ (3% of total H), and a prominent, broad resonance centered at $\delta$ 5.4 attributed to *cis*- and *trans*-$C\mathbf{H}{=}C\mathbf{H}-$ (4% of total H). Much weaker resonances at $\delta$ 5.82 and 4.95 in a 1:2 ratio, respectively, are attributable to vinyl end groups, $-C\mathbf{H}{=}C\mathbf{H}_2$. Thus, the majority of the unsaturated functionalities are internal and involve a methyl group ($CH_3CH{=}CH-$), suggesting that termination processes occur predominantly via $\beta$-H transfer from $Pd-CH(CH_3)CH_2-P$ moieties. It is also likely that less sterically hindered terminal olefins are formed but that these are subsequently incorporated into the growing oligomer, consistent with the GC-MS data discussed above and an ethylene-1-hexene copolymerization study described below. In any case, the high degree of unsaturation, the high termination-to-insertion ratio indicated by the low molecular weights obtained, and the high degree of branching are consistent with the high rate of $\beta$-H elimination and the high degree of branching predicted theoretically for similar catalyst systems.[2]

Detailed assignment of the very complex $^{13}C\{^1H\}$ NMR spectra of the oligomers is beyond the scope of this report, but a typical $^{13}C\{^1H\}$ NMR spectrum exhibited broad, complex multiplet methine, methylene, and methyl resonances (Figure 1). The spectrum is clearly consistent with a highly branched material, including short chain branches of varying lengths (C-2 to C-6)[5] as, in addition to the "main chain" methylene resonance at $\delta$ 29.98, there were resonances of methyl, propyl, butyl, and longer branches.[5] There were also multiple resonances associated with internal double bonds of the types $-H\mathbf{C}{=}\mathbf{C}H-$ ($\delta$ 132.4−129.5, 124.6−123.5),[5] as suggested by the $^1H$ NMR spectra (see above), while the presence of relatively weak resonances at $\delta$ 139.3 and 114.3 indicated the presence of minor amounts of terminal vinyl end groups, consistent again with the $^1H$ NMR data. All $^{13}C$ assignments were confirmed by 2D HETCOR NMR experiments.

The occurrence of predominantly internal olefinic groups of the type $RCH{=}CHR$ is notable, as apparently very similar palladium catalysts containing phosphines rather than TMEDA produce ethylene oligomers containing predominantly trisubstituted ($R_2C{=}CHR$) groups.[6] Perhaps equally striking is a report that the corresponding 1,5-cyclooctadiene complex produces only butenes, the products of ethylene dimerization.[6] These divergent results suggest that in addition to the steric factors mentioned above, subtle, as yet not understood, differences in electronic factors can also greatly influence the mode(s) of insertion and $\beta$-elimination processes in this type of palladium-based catalysts.

Ethylene coordination and oligomerization were also monitored directly by $^1H$ NMR spectroscopy. On addition of 1 equiv of ethylene to a 1:1 mixture of $PdMe_2$(tmeda) and $B(C_6F_5)_3$ in $CD_2Cl_2$ at 193 K, the cationic complex $[PdMe(CD_2Cl_2)(tmeda)]^+$ formed (eq 2), as shown by the $^1H$ NMR spectrum: $\delta$ 0.30 (s, 3H, Pd−Me), 0.33 (3H, br, B−Me), 4.4 (2H, br, $C_2H_4$), 4.7 (2H, br, $C_2H_4$);[7] the tmeda resonances were very complex.

$$[PdMe(CD_2Cl_2)(tmeda)]^+ + C_2H_4 \rightarrow [PdMe(C_2H_4)(tmeda)]^+ + CD_2Cl_2 \quad (2)$$

Upon warming to 213 K, the ethylene resonance weakened and disappeared and was replaced by resonances at $\delta$ 1.25−1.29 ($CH_2$) and 0.82−0.88 (Me) attributable to products of insertion. Thus, migratory insertion of ethylene into the palladium alkyl bond was already occurring at this low temperature, although an absence of olefinic resonances suggests that either $\beta$-elimination was not occurring to a significant extent or low molecular weight, unsaturated products were being incorporated into the growing polymer chains. As a test of the latter possibility, a similar ethylene polymerization reaction, also monitored by $^1H$ NMR spectroscopy, was carried out in the presence of 1-hexene. Interestingly, the olefinic resonances of the 1-hexene weakened and disappeared as the temperature was raised above ~250 K, and thus, lower weight oligomeric products may well be incorporated into the final products and could account for much of the observed branching.

Polymerization catalysts containing $^{13}C$-enriched methyl ligands have been used extensively[8] to gain mecha-

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(6) (a) Wojcinski, L. M.; Getzie, J.; Sen, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (2), 273. (b) The $^1H$ NMR spectra exhibit broad olefinic resonances at ca. $\delta$ 5.2. Wojcinski, L. M.; Getzie, J.; Sen, A. *Abstracts of Papers*, 214th National Meeting of the American Chemical Society, Las Vegas, NV, Fall 1997; *Div. of Polym. Sci.*, paper 0096. (c) Aspects of this work were reported after submission of this communication, see: Kim, J. S.; Pawlow, J. H.; Wojcinski, L. M.; Murtuza, S.; Kacker, S.; Sen, A. *J. Am. Chem. Soc.* **1998**, *120*, 1932.

(7) For similar cationic ethylene complexes, see: (a) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (b) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809. (c) On addition of 2.5/1 ethylene/Pd at 193 K, the NMR spectrum of the TMEDA complex exhibited only a single, exchange-broadened olefin resonance at $\delta$ 4.65.

nistic insight into the nature of polymerization processes, and a $^1$H NMR study of ethylene polymerization, utilizing $^{13}$C-enriched Pd($^{13}$Me$_2$)(tmeda), was carried out. The Pd−$^{13}$Me ($\delta$ 0.32, br d, $J_{HC}$ 136 Hz) and B−$^{13}$Me ($\delta$ 0.34, br d, $J_{HC}$ 118 Hz) resonances of [Pd($^{13}$Me)(C$_2$H$_4$)(tmeda)][B($^{13}$Me)(C$_6$F$_5$)$_3$] were particularly notable, and on addition of ethylene at 193 K, careful monitoring of the $^1$H NMR spectrum revealed the appearance of a weak double triplet centered at $\delta$ 0.86 ($J_{HC}$ 126 Hz). This resonance is attributable to a $^{13}$C-enriched methyl chain end resulting from the initial migratory insertion of ethylene into the Pd−$^{13}$Me bond to give a Pd−CH$_2$CH$_2$$^{13}$CH$_3$ group.[9] As the temperature was raised to 263 K, the reaction proceeded further and the $^{13}$C-coupled resonance gained both in intensity and in complexity, indicating the formation of a number of new $^{13}$C-enriched enriched sites. Interestingly, similar coupling of the broad CH$_2$ resonance ($\sim\delta$ 1.24) to $^{13}$C was not observed in these early stages, and thus, any enrichment of CH$_2$ groups must be secondary in nature. Eventually rather broad oligomer methyl resonances at ca. $\delta$ 0.87 grew sufficiently intense that the $^{13}$C-coupled resonances were obscured. On warming to 283 K, ethylene was no longer present in solution.

Surprisingly, while an in situ $^{13}$C{$^1$H} NMR spectrum at 298 K exhibited a very intense [B($^{13}$Me)(C$_6$F$_5$)$_3$]$^-$ quartet at $\delta$ 10.7, none of the resonances of the polymer formed at this temperature (methyl at $\delta$ 11.2−22.9, methylene at $\delta$ 27.2−40.0, methine at $\delta$ 38.0−39.5) exhibited an even remotely comparable intensity. Enriched oligomer was, therefore, prepared utilizing $^{13}$C-enriched catalyst at 298 K under 10 atm of ethylene, but again, we observed *no resonances* with enhanced intensities indicative of specific $^{13}$C-enrichment in the $^{13}$C{$^1$H} NMR spectrum. Indeed, the relative intensities of all CH$_2$ and CH$_3$ resonances in the region $\delta$ 10−40 were similar to those observed in the $^{13}$C{$^1$H} NMR spectrum of the oligomer formed using unlabeled catalyst (Figure 1). Thus, it would seem that the combination of product incorporation and a chain-walking process at higher temperatures must result in random redistribution of the original palladium-bonded methyl group to a large number of sites in the oligomeric product.

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[9] The presence of a small amount of $^{13}$C-enriched methane ($\delta$ 0.17, d, $J_{HC}$ 125 Hz), resulting from decomposition, was also observed, but the intensity of this resonance remained constant during warming of the sample to 263 K.