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Copolymerization of Silyl Vinyl Ethers with Olefins by (α-diimine)PdR$^+$

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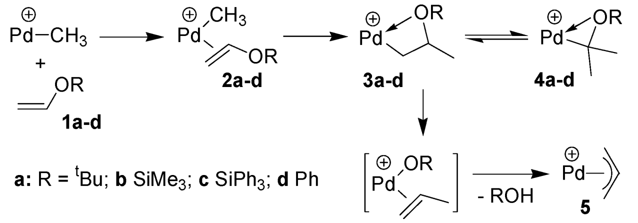
The development of methods for the incorporation of polar $CH_2{=}CHX$ vinyl monomers in metal-catalyzed insertion polymerizations of olefins is a challenging goal.[1] In a key advance, Brookhart discovered that (α-diimine)PdR$^+$ species catalyze the copolymerization of alkyl-acrylates with olefins.[2] Here we report that (α-diimine)PdMe$^+$ (α-diimine = (2,6-^{i}Pr$_2$−C$_6$H$_3$)N═CMeCMe═N(2,6-^{i}Pr$_2$−C$_6$H$_3$)) copolymerizes silyl vinyl ethers with olefins to OSiR$_3$-substituted polyolefins that can be desilylated to yield OH-substituted polyolefins.

Vinyl ethers ($CH_2{=}CHOR$) are attractive potential comonomers for insertion polymerization because their properties can be tuned by variation of the OR group. However, (i) vinyl ethers are susceptible to cationic polymerization by electrophilic metal catalysts,[3] (ii) insertion barriers for L$_n$MR′(CH$_2$═CHOR) species are predicted to be high due to the electron donation by the OR group,[4] and (iii) L$_n$MCH$_2$CH(OR)R′ species generated by insertion may undergo β-OR elimination, which would terminate chain growth. Nevertheless, Wolczanski found that (^{t}Bu$_3$SiO)$_3$TaH$_2$ inserts CH$_2$═CHOR (R = alkyl, Ph) to generate (^{t}Bu$_3$SiO)$_3$TaH(CH$_2$CH$_2$OR) and that subsequent β-OR elimination is slow when R is bulky (e.g.. ^{t}Bu).[5] Reasoning that problems i−iii could be avoided by suitable tuning of the OR group, we investigated the reactions of CH$_2$═CHOR (**1a**−**d**: R = ^{t}Bu (**a**), SiMe$_3$ (**b**), SiPh$_3$ (**c**), Ph (**d**)) with (α-diimine)PdMe$^+$ (as [(α-diimine)PdMe(Et$_2$O)][SbF$_6$] or generated in situ from (α-diimine)PdMeCl and [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$]).[6]

The reaction of (α-diimine)PdMe$^+$ with excess **1a** (10−50 equiv, CH$_2$Cl$_2$, 20 °C) results in rapid quantitative polymerization of **1a** and rapid Pd^0 formation. The −[CH$_2$CHO^{t}Bu]$_n$− polymer contains aldehyde and acetal end groups and internal −CH═CH− units. Very similar polymers are generated by the reaction of **1a** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] or [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$]. These results are consistent with a cationic polymerization mechanism.[7] Addition of 2,6-^{t}Bu$_2$-pyridine does not significantly affect the polymerization of **1a** by (α-diimine)PdMe$^+$, which suggests that (α-diimine)PdR$^+$ species may play a direct role in initiation. The cationic polymerization and Pd^0 formation preclude (α-diimine)PdMe$^+$-catalyzed copolymerization of **1a** with olefins; for example, the reaction with **1a**/ethylene results in **1a** homopolymerization. In contrast, **1b** is only slowly cationically polymerized by (α-diimine)PdMe$^+$, and neither **1c** nor **1d** are polymerized by this catalyst.[8] Thus, cationic polymerization can be minimized or avoided by using silyl or aryl vinyl ethers.

Scheme 1[a]



[a] Pd = (α-diimine)Pd.

Table 1. Reactivity of CH$_2$═CHOR with (α-Diimine)PdMe$^+$

CH$_2$═CHOR	^{t}Bu	SiMe$_3$	SiPh$_3$	Ph
K_{eq} vs ethylene (−60 °C)[a]	1.2(1)	0.17(1)	<0.01	0.04(2)
$t_{1/2}$, conversion of **2** to **3**/**4** (0 °C)[b]	> 1 h	15 min	8.9 min	7.7 min
3/**4** ratio (20 °C)	73/27	0/100	0/100	not obsd
$t_{1/2}$, conversion of **3**/**4** to **5** (20 °C)	88 h	5.5 h	2.2 h	<3 min

[a] K_{eq} = [**2**][CH$_2$═CH$_2$][PdMe(CH$_2$═CH$_2$)$^+$]$^{-1}$[**1**]$^{-1}$. [b] $t_{1/2}$ for insertion of PdMe(CH$_2$═CH$_2$)$^+$ at 0 °C is ca. 8 s.

The reactions of (α-diimine)PdMe$^+$ with 1−2 equiv of **1a**−**d** were investigated to probe for insertion reactivity under conditions where the vinyl ether concentration is low and cationic polymerization is slow. As shown in Scheme 1, (α-diimine)PdMe$^+$ reacts with **1a**−**d** by C═C π-complexation to form (α-diimine)PdMe(CH$_2$═CHOR)$^+$ (**2a**−**d**), followed by 1,2 insertion to produce (α-diimine)Pd(CH$_2$CHMeOR)$^+$ (**3a**−**d**) and reversible isomerization to (α-diimine)Pd(CMe$_2$OR)$^+$ (**4a**−**d**) by chain-walking (i.e., β-H elimination and reinsertion). Complexes **3** and **4** interconvert rapidly on the lab time scale at 20 °C and react with MeCN to form (α-diimine)Pd(CH$_2$CHMeOR)(NCMe)$^+$ (**3**·NCMe) at −40 °C. NMR and DFT results show that **3** and **4** are O-chelated. No evidence for the 2,1 insertion product (α-diimine)Pd{CH(OR)CH$_2$Me}$^+$ or its chain-walk isomers was observed for **1a**−**d**. The **3**/**4** mixtures react further at 20 °C to generate (α-diimine)Pd(η^3-C$_3$H$_5$)$^+$ (**5**) and ROH, presumably by β-OR elimination of **3** to form (α-diimine)Pd(OR)(CH$_2$═CHMe)$^+$ (not observed) and allylic C−H activation.[9] The viability of the allylic activation was established by the model reaction of [(tmeda)Pd(OPh)]$_n^{n+}$ with propylene to yield (tmeda)Pd(η^3-C$_3$H$_5$)$^+$ and HOPh quantitatively.

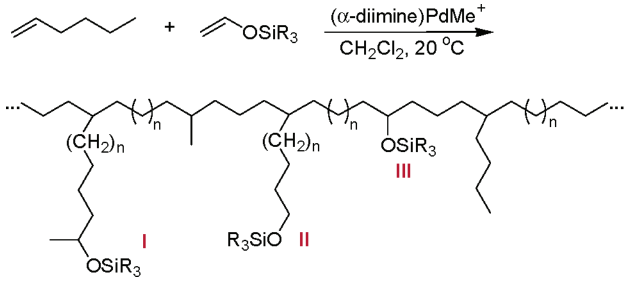
The binding strength of **1a**−**d** to (α-diimine)PdMe$^+$ was assessed by competitive binding experiments with ethylene. The K_{eq} data (Table 1) show that **1a** binds with similar strength as ethylene but **1b**−**d** bind more weakly. The kinetics of key steps in Scheme 1 were measured by NMR, and $t_{1/2}$ data are listed in Table 1. **2a**−**d** insert more slowly than does (α-diimine)PdMe(ethylene)$^+$. The trends in binding strength and insertion rates reflect a balance of steric effects (bulky OR groups inhibit binding and insertion) and electronic effects (strong donor OR groups enhance binding but inhibit insertion).[4] The conversion of **3**/**4** to **5** is slow, except in the case of phenyl vinyl ether, for which **3d**/**4d** react faster than they are formed from **2d** and hence were not directly observed.

The cationic polymerization trends and the results in Table 1 suggested that **1c** and possibly **1b** would be viable comonomers for olefin polymerization with (α-diimine)PdMe$^+$. As **1b**,**c** are much less reactive than ethylene, reactions with the less reactive olefin 1-hexene were explored.

The reaction of (α-diimine)PdMe$^+$ with 1-hexene/**1c** mixtures (CH$_2$Cl$_2$, 20 °C) produces copolymers containing up to 20 mol % silyl vinyl ether (Scheme 2). The copolymers were isolated and purified by washing with acetone and extracting into hexane. The yields are similar and the molecular weights (M_n = 18,000, PDI =

10.1021/ja064398w CCC: $33.50

Scheme 2



1.7) are lower compared to results for hexene homopolymerization under identical conditions. The copolymers contain 90−100 branches/1000 C (60% Me, 20% Bu > long > Et > Pr), which is similar to what is observed in control hexene homopolymerizations.[10] NMR data establish that the major comonomer units in the copolymers are $CH_3CH(OSiPh_3)CH_2-$ (**I**, 85%) and $CH_2(OSiPh_3)CH_2-$ (**II**, 6%).

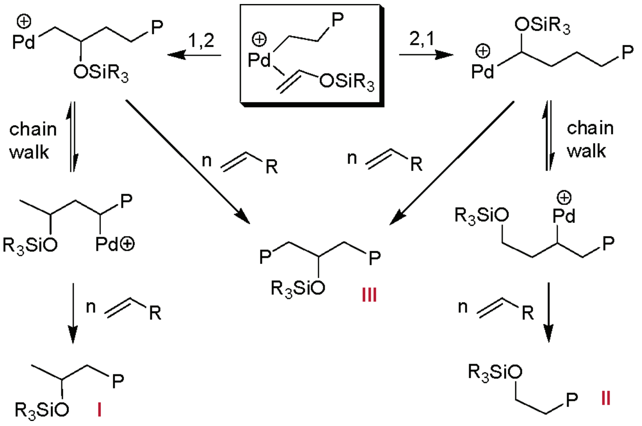
The following lines of evidence establish that the poly(hexene-*co*-$CH_2{=}CHOSiPh_3$) is a copolymer and does not contain $-[CH_2CHOSiPh_3]_n-$ homopolymer. (i) As noted above, **1c** is not polymerized by (α-diimine)$PdMe^+$ under these conditions. (ii) If $-[CH_2CHOSiPh_3]_n-$ had formed, it would be removed by the workup procedure, since it is soluble in acetone but not hexane. (iii) NMR spectra of the copolymer do not contain the characteristic broad resonances of $-[CH_2CHOSiPh_3]_n-$. (iv) HMBC NMR data establish that the $-OSiPh_3$ units of the copolymer are covalently linked to the polyhexene chain.

The 1-hexene/**1c** copolymer was desilylated by reaction with HCl ($CHCl_3$, 2 d; 94% conversion of $OSiPh_3$ groups to OH groups). The NMR spectra of the desilylated copolymer were unchanged after elution through SiO_2 with hexanes, which would remove any $-[CH_2CHOH]_n-$ (if present). This result confirms that the hexene/**1c** copolymer does not contain $-[CH_2CHOSiPh_3]_n-$.

The reaction of 1-hexene/**1b** mixtures with (α-diimine)$PdMe^+$ generates mixtures of $-[CH_2CHOSiMe_3]_n-$ homopolymer and 1-hexene/$CH_2{=}CHOSiMe_3$ copolymers containing up to 11 mol % comonomer. The consumption of hexene is significantly decreased compared to control hexene homopolymerizations under identical conditions due to the Pd^0 formation associated with the cationic polymerization of **1b**. The $-[CH_2CHOSiMe_3]_n-$ can be removed from the hexene/**1b** copolymer by eluting the polymer/copolymer mixture through SiO_2 with hexanes. The major comonomer units are $CH_3CH(OSiMe_3)CH_2-$ (**I**, 60%) and $-CH_2CH(OSiMe_3)CH_2-$ (**III**, 30%).

The reaction of 1-hexene/**1c** mixtures with $[H(Et_2O)_2][B(C_6F_5)_4]$ under the conditions of Scheme 2 results in cationic polymerization of **1c** with no hexene incorporation. The reaction of 1-hexene/**1c** mixtures with AIBN in C_6D_5Cl at 60 °C for 20 h, in the presence or absence of Li salts, does not produce copolymer. In contrast, (α-diimine)$PdMe^+$ copolymerizes 1-hexene/**1c** under these conditions. These results argue against cationic and radical mechanisms in Scheme 2.

Scheme 3[a]



[a] P = growing chain.

We propose that the copolymerization in Scheme 2 proceeds by a normal insertion/chain-walking mechanism.[2] As shown in Scheme 3, comonomer units **I** and **II** are generated by 1,2 or 2,1 insertion followed by chain-walking and hexene insertion, and **III** is generated by 1,2 or 2,1 insertion followed directly by hexene insertion. Although only 1,2 insertion was observed in the stoichiometric reactions of **1a**−**d** with (α-diimine)$PdMe^+$, steric crowding between the migrating polymeryl (*P*) group and the $OSiPh_3$ group in (α-diimine)$Pd(CH_2{=}CHOSiPh_3)P^+$ species may inhibit this process, so that 2,1 insertion becomes competitive in **1c** copolymerization. The “in-chain” placement **III** may be disfavored for **1c** because the (α-diimine)$PdCH_2CH(OSiPh_3)P^+$ and (α-diimine)$PdCH(OSiPh_3)CH_2P^+$ species generated by insertion of **1c** are too crowded to readily insert olefins.

In summary, silyl vinyl ethers are readily incorporated in hexene insertion polymerization catalyzed by (α-diimine)$PdMe^+$ and the mode of incorporation is influenced by the structure of the $OSiR_3$ group. The copolymers can be desilylated to produce hexene/$CH_2{=}CHOH$ copolymers. Monomer **1c** has also been copolymerized with other olefins ranging from ethylene to 1-octadecene. We anticipate that silyl vinyl ethers will be suitable comonomers for other olefin polymerization catalysts, and our studies in this direction will be reported in due course.

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Supporting Information Available: Experimental procedures and characterization data for all compounds and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) **1c** is polymerized by $[Ph_3C][B(C_6F_5)_4]$ and $[H(Et_2O)_2][B(C_6F_5)_4]$ and by (α-diimine)$PdMeCl/[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ when excess Li^+ salt is used.
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