

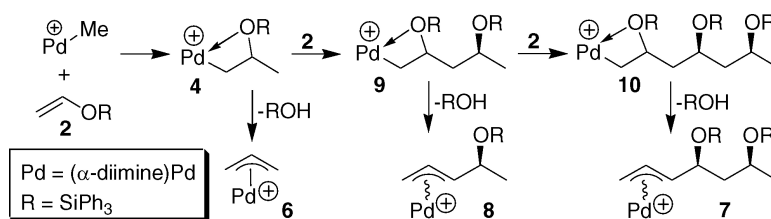
Communication

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Multiple Insertion of a Silyl Vinyl Ether by (α -Diimine)PdMe⁺ Species

Changle Chen, Shuji Luo, and Richard F. Jordan*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois, 60637

Received July 21, 2008; E-mail: rfjordan@uchicago.edu

The polymerization of functionalized CH₂=CHX vinyl monomers by metal-catalyzed insertion mechanisms may enable catalyst-based control of polymer microstructure and the synthesis of new materials that are unavailable by radical or ionic polymerization.¹ This approach will require systems that undergo multiple insertions of CH₂=CHX monomers into metal-alkyl bonds. Rh, Ru, Ni, and Pd species catalyze the tail-to-tail dimerization of methyl acrylate (MA) by 1,2-MA insertion into a metal hydride bond to yield L_nMCH₂CH₂CO₂CH₃ species followed by 2,1-MA insertion and β -H elimination to release a dimer and regenerate the metal hydride.² Here we report that (α -diimine)PdMe⁺ species (α -diimine = (2,6-*i*-Pr₂-C₆H₃)N=CMeCMe=N(2,6-*i*-Pr₂-C₆H₃)) undergo up to three sequential insertions of a silyl vinyl ether, ultimately forming Pd allyl products.

We reported that [(α -diimine)PdMe][B(C₆F₅)₄] (**1**-B(C₆F₅)₄) copolymerizes α -olefins and CH₂=CHOSiPh₃ (**2**) to form OSiPh₃-substituted polyolefins, which can be desilylated to form hydroxy polyolefins.³ Mechanistic studies showed that **1**-B(C₆F₅)₄ reacts with stoichiometric quantities of alkyl, aryl, and silyl vinyl ethers (VEs) by sequential (i) VE coordination to form the (α -diimine)Pd-(Me)(VE)⁺ π -complex (**3**), (ii) 1,2 insertion to give O-chelated (α -diimine)PdCH₂CH(OR)Me⁺ (**4**), (iii) reversible chain walking by β -H elimination/reinsertion to form O-chelated (α -diimine)PdCMe₂OR⁺ (**5**), and (iv) irreversible β -OR elimination of **4** to form (α -diimine)Pd(OR)(propene)⁺ (not observed), which (v) undergoes allylic C-H activation to yield (α -diimine)Pd(η^3 -allyl)⁺ (**6**) and ROH. **1**-Catalyzed copolymerization of olefins and **2** is possible because (α -diimine)PdCH₂CH(OSiPh₃)R⁺ species are trapped by olefin and undergo subsequent insertion faster than they undergo β -OSiPh₃ elimination leading to inactive Pd-allyl species, and because **2** is not electron-rich enough to be cationically polymerized by **1**. These results suggested that (α -diimine)PdMe⁺ species might undergo *multiple* insertions of **2** when **2** is present in excess.

The reaction of (α -diimine)PdMeCl, 1 equiv of [Li(Et₂O)_{2.8}][B(C₆F₅)₄], and 8 equiv of **2** in CH₂Cl₂ at -78 °C (6 h) followed by warming to 23 °C (6 h) and stirring for 6 h yields [(α -diimine)Pd{ η^3 -CH₂CHCHCH(OSiPh₃)CH₂CH(OSiPh₃)Me}][B(C₆F₅)₄] (**7**-B(C₆F₅)₄) in 83% NMR yield (eq 1). **7** is formed as a 95/5 mixture of isomers (**7a**/**7b**), which is converted to an equilibrium 40/60 mixture after 2 days at room temperature. The kinetically favored isomer **7a** was isolated as red crystals in 35% yield by recrystallization from benzene/hexanes. Under these conditions, **7a** crystallizes as a racemic conglomerate, i.e. as a mixture of individual crystals that are enantiomerically pure but together comprise a racemate.⁴ X-ray diffraction analysis (Figure 1) established that the kinetically favored isomer **7a** is a Pd allyl complex with a -CH(OSiPh₃)CH₂CH(OSiPh₃)Me substituent *syn* to the central allyl hydrogen (H_c). The configuration of **7a** is S,S,S (*ent*-R,R,R), where the descriptors refer to the configurations of the substituted allyl carbon and the side chain methine carbons,

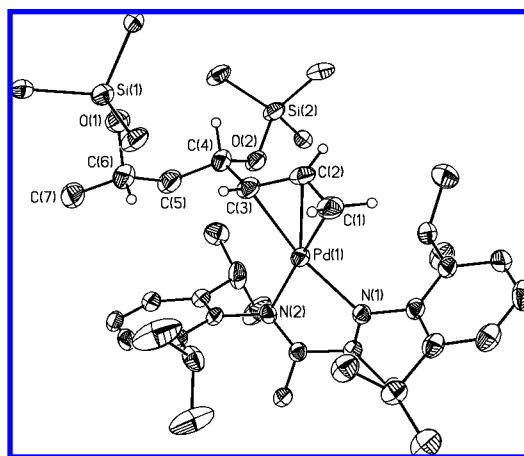
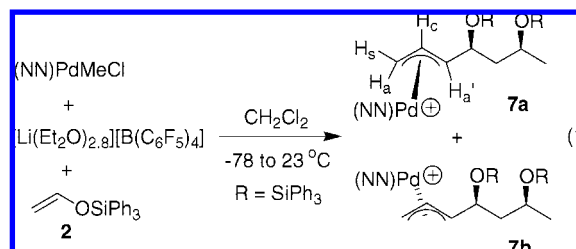


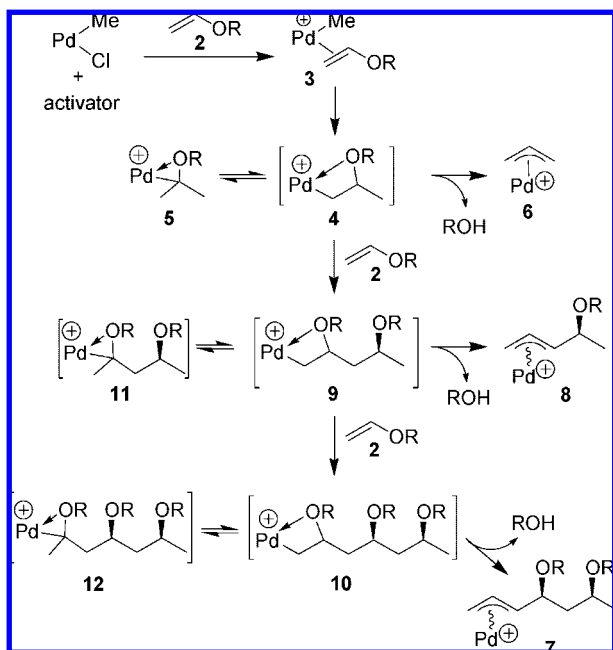
Figure 1. Structure of the cation of S,S,S-**7a**-B(C₆F₅)₄. Only the ipso-carbons of the Si-Ph groups are included. The allyl and methine hydrogens of the allyl group are shown; other hydrogens are omitted.

respectively. The -OSiPh₃ substituents would both point toward Pd in the fully extended conformation of the side chain, as shown in eq 1.

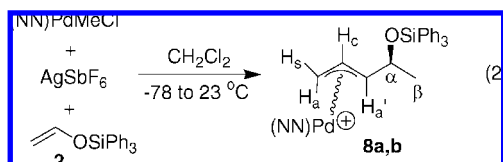


As **7a** and **7b** interconvert under mild conditions and are the only isomers of **7** detected in eq 1, it is likely that they differ in the stereochemistry of the Pd-allyl unit. In the ¹H and COSY NMR spectra of **7a**, the allyl H_c resonance (see eq 1) appears as a triplet of doublets at δ 5.05 ($J = 12, 7$ Hz), which is coupled to a doublet of doublets at δ 2.82 (H_a', $J_{H_a'-H_c} = 12$ Hz, characteristic of *anti* coupling), a doublet at 2.71 (H_s, $J = 7$ Hz, *syn* coupling), and a doublet at 2.59 (H_a, $J = 12$ Hz, *anti* coupling). For **7b**, the H_c resonance appears as a triplet of doublets at δ 5.34 ($J = 12, 7$ Hz), which is coupled to a doublet of doublets at δ 4.20 (H_a', $J_{H_a'-H_c} = 12$ Hz), a doublet at 2.79 (H_s, $J = 7$ Hz), and a doublet at 2.58 (H_a, $J = 12$ Hz). These results show that the allyl side chain is *syn* to H_c in both isomers. Therefore, **7a/b** must differ in the allyl enantioface that the Pd unit is coordinated to; i.e. the configuration of **7b** is R,S,S (*ent*-S,R,R). ¹H, ¹³C, and DEPT NMR, 2-D NMR, ESI-MS, and elemental analysis results are fully consistent with the proposed structures of **7a,b**. **7a,b** probably interconvert via a σ -allyl intermediate.⁵

Similarly, the reaction of (α -diimine)PdMeCl, 1 equiv of Ag[SbF₆], and 8 equiv of **2** under the conditions of eq 1 yields

Scheme 1. Pd = (α -diimine)Pd; R = SiPh₃

$[(\alpha\text{-diimine})\text{Pd}\{\eta^3\text{-CH}_2\text{CHCHCH}(\text{OSiPh}_3)\text{Me}\}][\text{SbF}_6] (\mathbf{8}\text{-SbF}_6)$ in 90–100% NMR yield (eq 2). Compound **8** was isolated in 81% yield as a 90/10 mixture of isomers (**8a/8b**), which converts to a 70/30 equilibrium mixture in 7 days at room temperature.



Compound **8-SbF₆** was identified by NMR, ESI-MS, and elemental analysis. In the ¹H and COSY NMR spectra of the major isomer **8a**, the side chain H_α resonance appears at δ 3.03 (q of d, $J = 6, 3$ Hz), and is coupled to the allyl H_{a'} resonance at δ 3.71 (dd, $J = 12, 3$ Hz) and a doublet at δ 0.70 ($J = 6$ Hz, H_β). The allyl H_c resonance appears as a triplet of doublets at δ 5.70 ($J = 12, 7$ Hz), which is coupled to H_{a'} ($J = 12$ Hz), a doublet at δ 3.15 (H_a, $J = 12$ Hz), and a doublet at δ 3.09 (H_s, $J = 7$ Hz). The NMR data for **8b** are similar. These results show that the $-\text{CH}(\text{OSiPh}_3)\text{Me}$ group is *syn* to H_c in both isomers and imply that, as for **7a,b**, **8a,b** differ in the allyl enantioface that the Pd unit is coordinated to. The specific configurations of **8a,b** have not yet been determined. The ESI-MS spectrum of **8-SbF₆** contains a major signal for $(\alpha\text{-diimine})\text{Pd}\{\eta^3\text{-CH}_2\text{CHCHCH}(\text{OSiPh}_3)\text{Me}\}^+$ (calcd $m/z = 853.4$, found 853.3). The reaction of **8-SbF₆** with Et₃SiH gave *trans*-CH₃CH=CHCH(OSiPh₃)CH₃.⁶

8-B(C₆F₅)₄ is formed as a minor product in eq 1 (17% NMR), and **7-SbF₆** is a minor product of eq 2 (0–10% NMR).⁷

These results are consistent with the mechanism in Scheme 1. In situ formation of **1** and coordination of **2** generate the CH₂=CHOSiPh₃ π -complex **3**. **3** undergoes 1,2 insertion to give **4**, reversible chain walking to give **5**, and β -OSiPh₃ elimination from **4** to give **6** and Ph₃SiOH. In the presence of excess **2**, **4** undergoes a second insertion of **2** to form **9**, which can undergo

β -OSiPh₃ elimination and allylic C–H activation to form **8**, or a third insertion of **2** to form **10**, ultimately leading to **7**.

In agreement with Scheme 1, when lower concentrations of **2** are used, the yields of the multiple insertion products are reduced. For example, the reaction of $(\alpha\text{-diimine})\text{PdMeCl}$, 1 equiv of $[\text{Li}(\text{Et}_2\text{O})_{2.8}][\text{B}(\text{C}_6\text{F}_5)_4]$, and 2 equiv of **2** under the conditions of eq 1 yields a mixture of **6** (33%), **8a/8b** (58%, 60/40 ratio), and **7a/7b** (9%, 83/17 ratio). ¹H NMR monitoring of the reaction of the isolated complex $[(\alpha\text{-diimine})\text{Pd}(\text{Me})(\text{Et}_2\text{O})][\text{B}(\text{C}_6\text{F}_5)_4]$ with **8** equiv of **2** in CD₂Cl₂ at -20 °C reveals the formation of **3** (30%), **5** (18%), and unreacted $[(\alpha\text{-diimine})\text{Pd}(\text{Me})(\text{Et}_2\text{O})][\text{B}(\text{C}_6\text{F}_5)_4]$ (52%) after 2 h and subsequent conversion to a mixture of **8a/8b** (55%, 74/26 ratio), **7a/7b** (41%, 47/53 ratio) and an unidentified Pd-allyl species (4%) after 20 h. The proposed intermediates **9** and **10** were not detected, but transient signals at δ 0.34 and 0.10 were observed at intermediate times, which may be due to the PdMe(OSiPh₃)CH₂– groups of **11** and **12**, the expected chain walk isomers of **9** and **10**. Further studies are required to understand the factors (counterion, presence of Et₂O or Cl[–], etc.) that control the product distribution in Scheme 1 and to optimize conditions to favor chain growth.⁸

The stereochemistry of **7a** implies that the three insertions leading to **10** occur with the same face selectivity (i.e. isotactic). This result may reflect the stereoselectivity of the insertion steps or may result from a chain end epimerization process involving olefin face exchange (alkene flipping) of the $(\alpha\text{-diimine})\text{Pd}(\text{H})\text{-}\{\text{CH}_2=\text{C}(\text{OSiPh}_3)(\text{CH}_2\text{CHOSiPh}_3)_n\text{Me}\}^+$ ($n = 1, 2$) intermediates that link **9** with **11** and **10** with **12**.⁹

This work shows that $(\alpha\text{-diimine})\text{PdMe}^+$ species can undergo multiple insertions of silyl vinyl ethers. For the case of CH₂=CHOSiPh₃, up to three sequential insertions are observed. Steric crowding may inhibit further chain growth.

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Supporting Information Available: Experimental procedures and characterization data for **7** and **8** and X-ray data for *S,S,S,S*-**7-B(C₆F₅)₄** and *R,R,R,R*-**7-B(C₆F₅)₄**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The NMR spectra of **7** and **8** vary slightly with counterion and temperature.
- Cationic polymerization of **2** was not observed in the experiments described here. **2** is polymerized by $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{H}(\text{Et}_2\text{O})_2][\text{B}(\text{C}_6\text{F}_5)_4]$, or $[\text{Li}(\text{Et}_2\text{O})_{2.8}][\text{B}(\text{C}_6\text{F}_5)_4]$ in the presence of H₂O.
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