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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 CH_2═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 CH_2═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 $L_nMCH_2CH_2CO_2CH_3$ 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}Pr$_2$−C$_6$H$_3$)N═CMeCMe═N(2,6-^{i}Pr$_2$−C$_6$H$_3$)) undergo up to three sequential insertions of a silyl vinyl ether, ultimately forming Pd allyl products.

We reported that [(α-diimine)PdMe][B(C$_6$F$_5$)$_4$] (**1**-B(C$_6$F$_5$)$_4$) copolymerizes α-olefins and CH_2═CHOSiPh$_3$ (**2**) to form OSiPh$_3$-substituted polyolefins, which can be desilylated to form hydroxy polyolefins.[3] Mechanistic studies showed that **1**-B(C$_6$F$_5$)$_4$ 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)PdCH$_2$CH(OR)Me$^+$ (**4**), (iii) reversible chain walking by β-H elimination/reinsertion to form O-chelated (α-diimine)PdCMe$_2$OR$^+$ (**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)PdCH$_2$CH(OSiPh$_3$)R$^+$ species are trapped by olefin and undergo subsequent insertion faster than they undergo β-OSiPh$_3$ 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(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$], and 8 equiv of **2** in CH_2Cl_2 at −78 °C (6 h) followed by warming to 23 °C (6 h) and stirring for 6 h yields [(α-diimine)Pd{η^3-CH$_2$CHCHCH(OSiPh$_3$)CH$_2$CH(OSiPh$_3$)-Me}][B(C$_6$F$_5$)$_4$] (**7**-B(C$_6$F$_5$)$_4$) 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(OSiPh$_3$)CH$_2$CH(OSiPh$_3$)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,

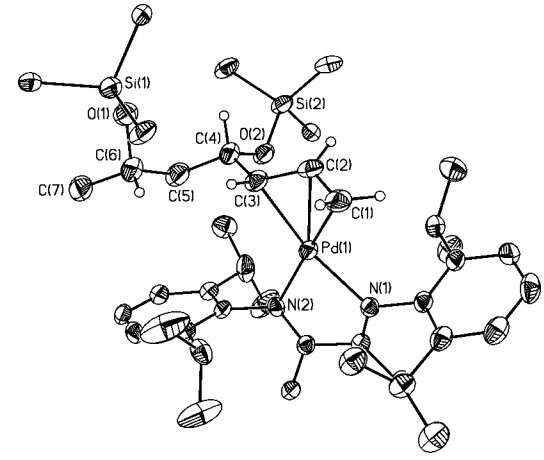
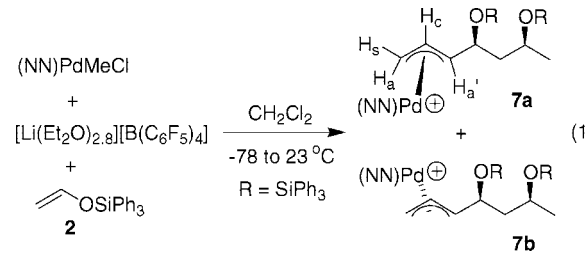


Figure 1. Structure of the cation of *S*,*S*,*S*-**7a**-B(C$_6$F$_5$)$_4$. Only the ipso-carbons of the Si-*Ph* groups are included. The allyl and methine hydrogens of the allyl group are shown; other hydrogens are omitted.

respectively. The −OSiPh$_3$ 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 ^{1}H 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*). ^{1}H, ^{13}C, 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[SbF$_6$], and 8 equiv of **2** under the conditions of eq 1 yields

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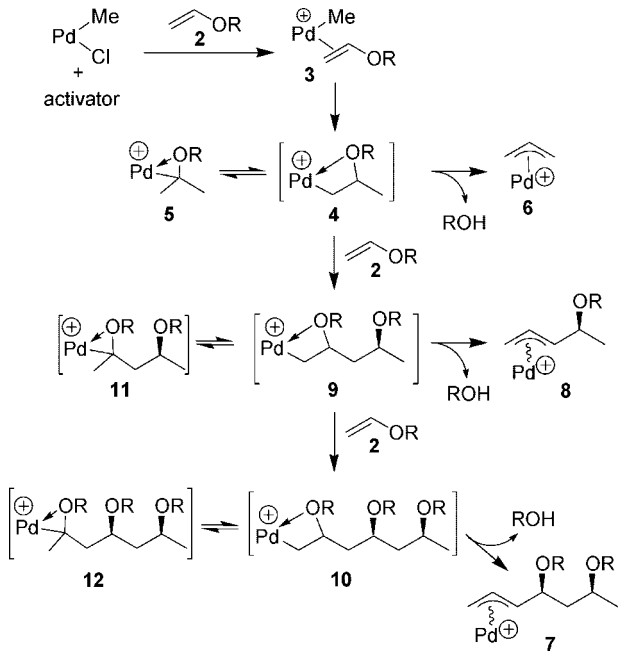
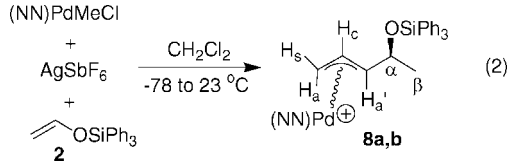
Scheme 1. Pd = (α-diimine)Pd; R = $SiPh_3$



[(α-diimine)Pd{η^3-$CH_2CHCHCH(OSiPh_3)Me$}][SbF_6] (**8**-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**-SbF_6 was identified by NMR, ESI-MS, and elemental analysis. In the ^{1}H 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 −$CH(OSiPh_3)Me$ 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**-SbF_6 contains a major signal for (α-diimine)Pd{η^3-$CH_2CHCHCH(OSiPh_3)Me$}$^+$ (calcd m/z = 853.4, found 853.3). The reaction of **8**-SbF_6 with Et_3SiH gave *trans*-$CH_3CH{=}CHCH(OSiPh_3)CH_3$.[6]

8-$B(C_6F_5)_4$ is formed as a minor product in eq 1 (17% NMR), and **7**-SbF_6 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 $CH_2{=}CHOSiPh_3$ π-complex **3**. **3** undergoes 1,2 insertion to give **4**, reversible chain walking to give **5**, and β-$OSiPh_3$ elimination from **4** to give **6** and Ph_3SiOH. In the presence of excess **2**, **4** undergoes a second insertion of **2** to form **9**, which can undergo β-$OSiPh_3$ 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 (α-diimine)PdMeCl, 1 equiv of [$Li(Et_2O)_{2.8}$][$B(C_6F_5)_4$], 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). ^{1}H NMR monitoring of the reaction of the isolated complex [(α-diimine)Pd(Me)(Et_2O)][$B(C_6F_5)_4$] with 8 equiv of **2** in CD_2Cl_2 at −20 °C reveals the formation of **3** (30%), **5** (18%), and unreacted [(α-diimine)Pd(Me)(Et_2O)][$B(C_6F_5)_4$] (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 Pd$CMe(OSiPh_3)CH_2$− 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 Et_2O 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 (α-diimine)Pd(H)-{$CH_2{=}C(OSiPh_3)(CH_2CHOSiPh_3)_nMe$}$^+$ (n = 1,2) intermediates that link **9** with **11** and **10** with **12**.[9]

This work shows that (α-diimine)$PdMe^+$ species can undergo multiple insertions of silyl vinyl ethers. For the case of $CH_2{=}CHOSiPh_3$, up to three sequential insertions are observed. Steric crowding may inhibit further chain growth.

Acknowledgment. This work was supported by the U.S. Department of Energy (DE-FG-02-00ER15036).

Supporting Information Available: Experimental procedures and characterization data for **7** and **8** and X-ray data for *S*,*S*,*S*-**7**-$B(C_6F_5)_4$ and *R*,*R*,*R*-**7**-$B(C_6F_5)_4$.This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Cationic polymerization of **2** was not observed in the experiments described here. **2** is polymerized by [Ph_3C][$B(C_6F_5)_4$], [$H(Et_2O)_2$][$B(C_6F_5)_4$], or [$Li(Et_2O)_{2.8}$][$B(C_6F_5)_4$] in the presence of H_2O.
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