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ChemInform Abstract: Palladium-Catalyzed Dimerization of Vinyl Ethers to Acetals.

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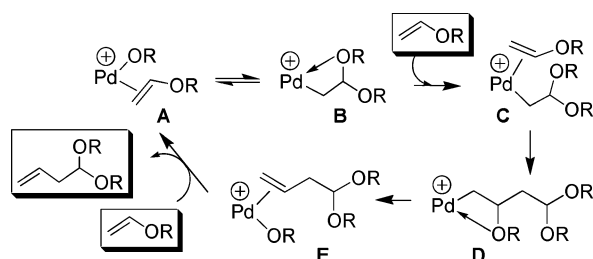


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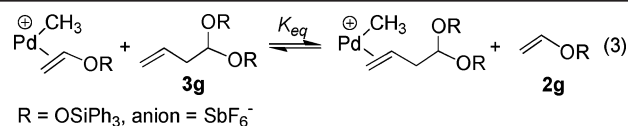
Scheme 1^a^a Pd = (α-diimine)Pd.

interchange,¹² and isomerization reactions.¹³ Such insertions can have lower barriers than analogous insertions into Pd–R bonds due to the destabilization of the Pd–OR complex by repulsion between the filled metal d and oxygen p orbitals and the fact that the Pd–OR bond need not be fully cleaved during the insertion since O-chelated products are formed.^{10b} DFT calculations show that the insertion barrier of the model complex (HN=CHCH=NH)Pd(OMe)(CH₂=CH₂)⁺ (9.7 kcal/mol) is much lower than that for (HN=CHCH=NH)Pd(Me)(CH₂=CH₂)⁺ (17 kcal/mol). The failure of phenyl vinyl ether to be dimerized by **1a,b** may be due to fast β-Oph elimination of **B** to reform **A**.^{2,3} For comparison, (tmeda)Pd(OPh)⁺ does not react with **2a** or **3a** under these conditions. The proposed insertion of **C** is analogous to the multiple insertion of **2g** into (α-diimine)PdMe⁺, which, following allylic C–H activation, yields Pd allyl products.⁴ No Pd allyl species have been detected in **1a,b**-catalyzed vinyl ether dimerizations. Allylic C–H activation of **E** may be inhibited by the geminal bis-alkoxide unit, so that ligand exchange/product release dominates.

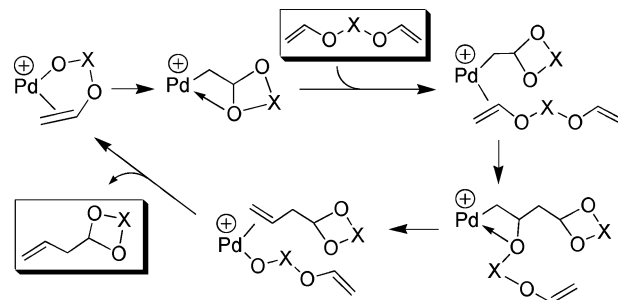
The addition of olefins to **1a**-catalyzed vinyl ether dimerization reactions was studied to probe the proposed intermediates in Scheme 1. The addition of 1-hexene (60 equiv) to the **1a**-catalyzed dimerization of **2f** (40 equiv) resulted in termination of catalysis after 4 h, with 50% conversion of **2f** to **3f** and complete conversion of **1a** to a mixture of (α-diimine)Pd(η³-C₆H₁₁)⁺ allyl species. This result can be explained by reaction of **A** or **E** with hexene to form (α-diimine)Pd(OR)(hexene)⁺ and allylic C–H activation.¹⁴ The reaction of **1a** with **2f** (12 equiv) under 150 psi of ethylene pressure (CH₂Cl₂, 1 h, 23 °C) yields branched polyethylene (113 br/10³ C, *M_n* = 5100, *M_w/M_n* = 1.97).¹⁵ This result can be explained by trapping of **A–E** by ethylene and further ethylene insertion.¹ No polymer was generated in the absence of **2f**.

A similar dimerization of vinyl ethers to acetals by Hg(OAc)₂/BF₃·Et₂O has been reported.¹⁶ This system produces a significant amount of trimer, tetramer, and polymer side products and also dimerizes substituted vinyl ethers such as EtCH=CHOEt and CH₂=CMeOEt. These results are most consistent with a cationic oligomerization mechanism. In contrast, **1a**/DTBP does not produce detectable oligomer or polymer byproducts in eq 1,⁶ and it does not react with MeCH=CHOEt or CH₂=CHOPh, even at elevated temperatures. Furthermore, as noted above, DTBP does not influence the Pd-catalyzed dimerization reaction. These results argue that the **1a,b**-catalyzed dimerization process is mechanistically distinct from the Hg system and does not proceed by a cationic mechanism.

As shown in Table 1, turnover frequencies in eq 1 decay with time. Product inhibition due to binding of the product to the active Pd species may contribute to this decay. For example, the reaction of **1a** with 13 equiv of **2g** produces 1.2 and 5.2 equiv of **3g** after 4 and 26 h, respectively. In contrast, in the presence of 20 equiv of **3g** under the same conditions, only 0.1 and 1.9 equiv of **2g** are consumed after 4 and 26 h, respectively. To model the competitive binding of **2g** and **3g** to the active Pd species, the reaction of **2g/3g** with (α-diimine)-PdMe⁺ was studied. The equilibrium constant (*K_{eq}*) for eq 3 was determined to be 0.12(1) at –20 °C. Assuming Δ*S* = 0, *K_{eq}* = 0.16 at 23 °C.



The cyclization of divinyl ethers likely proceeds by an analogous mechanism (Scheme 2).

Scheme 2^a^a Pd = (α-diimine)Pd.

This work shows that (α-diimine)PdCl⁺ species catalytically dimerize vinyl ethers to CH₂=CHCH₂CH(OR)₂ acetals and cyclize divinyl ethers to analogous cyclic acetals. In situ-generated (α-diimine)-Pd(OR)⁺ alkoxide complexes may be the active species in these reactions. An interesting application of this reaction is olefin polymerization by (α-diimine)PdCl⁺/vinyl ether mixtures.

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Supporting Information Available: Experimental procedures and characterization of compounds (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) A small amount (<10%) of cationic polymerization but no Pd⁰ was observed for **2h–k**, even in the presence of 10 equiv of DTBP.
- (7) Except for the Pd⁰ formation that accompanies the cationic polymerization of **2c**, no consumption of **1a,b** or new Pd species was detected in these reactions. Neither (α-diimine)PdCl₂ nor Na[B(3,5-C₆H₃(CF₃)₂)₄] alone reacts with vinyl ethers under these conditions. [Li(OEt)₂]₂[B(C₆F₅)₄] catalyzes the cationic polymerization of alkyl vinyl ethers.
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- (14) The reaction of **1a** with 1-hexene (60 equiv) in the absence of **2f** results in isomerization of 1-hexene to a mixture of internal hexenes, with no observable change (NMR) of **1a**.
- (15) Under these conditions, incorporation of **2f** into the polyethylene was not detected. In a similar experiment at 20 psi of ethylene pressure, 0.2 mol % of **2f** was incorporated as –CH₂CH(OSiMePh₂)Me and –CH₂CH₂(OSiMePh₂) units. Similar results were obtained in the copolymerization of ethylene and **2f** by (α-diimine)PdMe⁺ catalysts.²
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