

Palladium-Catalyzed Dimerization of Vinyl Ethers to Acetals

Changle Chen and Richard F. Jordan*

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

Received May 25, 2010; E-mail: rfjordan@uchicago.edu

Abstract: (α -Diimine) PdCl^+ species catalytically dimerize alkyl and silyl vinyl ethers to β,γ -unsaturated $\text{CH}_2=\text{CHCH}_2\text{CH}(\text{OR})_2$ acetals, and they cyclize divinyl ethers to analogous cyclic acetals. A plausible mechanism comprises in situ generation of an active PdOR alkoxide species, double vinyl ether insertion to generate $\text{Pd}\{\text{CH}_2\text{-CH}(\text{OR})\text{CH}_2\text{CH}(\text{OR})_2\}$ species, and β -OR elimination to generate the acetal product. In the presence of vinyl ethers, (α -diimine) PdCl^+ species can be used to initiate ethylene polymerization.

(α -Diimine) PdR^+ alkyl complexes¹ react with vinyl ethers by two pathways.^{2,3} First, (α -diimine) PdR^+ can initiate the cationic polymerization of vinyl ethers with concomitant formation of Pd^0 . This reaction proceeds via (α -diimine) $\text{PdR}(\text{CH}_2=\text{CHOR}^+)$ π -complexes in which the C=C bond is polarized with carbocation character at the substituted carbon (C_{int}). Electrophilic attack of C_{int} on the monomer initiates polymerization. Cationic polymerization is the dominant process for alkyl vinyl ethers. Alternatively, (α -diimine) $\text{PdR}(\text{CH}_2=\text{CHOR}^+)$ adducts can undergo insertion to form O-chelated (α -diimine) $\text{Pd}(\text{CH}_2\text{CHROR}^+)$ species, which can react further by β -OR' elimination to generate (α -diimine) $\text{Pd}(\text{OR}')(\text{CH}_2=\text{CHR})^+$ (not observed) and subsequent allylic C-H activation to yield (α -diimine) $\text{Pd}(\text{allyl})^+$ species and R'OH. For aryl-silyl vinyl ethers, insertion out-competes cationic polymerization, enabling copolymerization of these substrates with olefins and multiple vinyl ether insertion reactions.⁴ For aryl vinyl ethers, both insertion and β -OAr elimination are fast, and the latter reaction precludes copolymerization or multiple insertion processes. Here we report that (α -diimine) PdCl^+ chloride complexes catalyze a third reaction, the dimerization of vinyl ethers to β,γ -unsaturated acetals.

The reaction of (α -diimine) PdCl_2 with $\text{Na}[\text{B}(3,5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_3)_4]$ in CH_2Cl_2 yields the dinuclear dicationic species $\{[(\alpha\text{-diimine})\text{Pd}(\mu\text{-Cl})_2][\text{B}(3,5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_3)_4]_2$ (**1a**, α -diimine = 1,2-(2,6-*i*-Pr₂-C₆H₃)N=CAnCAn=N(2,6-*i*-Pr₂-C₆H₃); An = acenaphthyl). **1a** catalytically dimerizes alkyl and silyl vinyl ethers $\text{CH}_2=\text{CHOR}$ (**2a-g**; R = Et (**a**), *n*Bu (**b**), *t*Bu (**c**), SiMe₃ (**d**), SiMe₂Ph (**e**), SiMePh₂ (**f**), SiPh₃ (**g**)) to $\text{CH}_2=\text{CHCH}_2\text{CH}(\text{OR})_2$ acetals (**3a-g**, eq 1, Table 1). No Pd^0 formation is observed in these reactions, except for the case of **2c**. After complete consumption of the vinyl ether (**2a,g**), catalysis resumes if more substrate is added. A small amount (<5%) of cationic polymerization of **2a,b,d-g** is observed, and this competing process becomes more significant as the concentration of H₂O in the solvent is increased. However, for **2a,b,d-g**, the addition of 2,6-di-*tert*-butylpyridine (DTBP, 3 equiv vs Pd) prevents cationic polymerization but does not affect the dimerization reaction. This result suggests that the cationic polymerization is proton-initiated. In contrast, for **2c**, cationic polymerization and Pd^0 formation are observed even with 20 equiv of DTBP. This result is indicative of initiation by a cationic Pd species and reflects the high susceptibility of **2c** to cationic polymerization.⁵

The dinuclear monocationic species $\{[(\alpha\text{-diimine})\text{Pd}(\text{Cl})_2(\mu\text{-Cl})][\text{B}(\text{C}_6\text{F}_5)_4]_2$ (**1b**), which is generated in situ by the reaction of (α -diimine) PdCl_2 with $[\text{Li}(\text{OEt}_2)_{2,8}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 , behaves similarly to **1a** in the dimerization of **2f,g**. However, in this case, no cationic

polymerization is observed in dry solvent, even in the absence of DTBP. Phenyl vinyl ether does not react with **1a** or **1b**, even at elevated temperature. $\{(2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)\text{N}=\text{CMeCMe}=\text{N}(2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)\}\text{PdCl}_2$ and $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ also catalytically dimerize **2a** when activated by $[\text{Li}(\text{OEt}_2)_{2,8}][\text{B}(\text{C}_6\text{F}_5)_4]$.

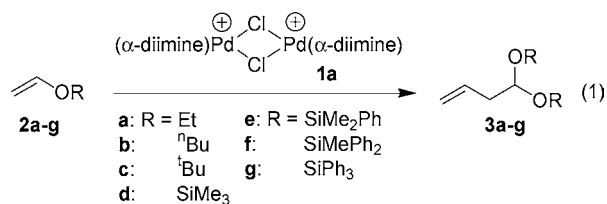
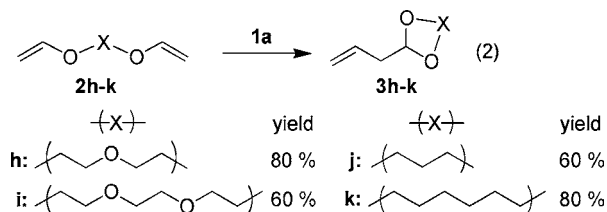


Table 1. Dimerization of Vinyl Ethers by $\{[(\alpha\text{-Diimine})\text{Pd}(\mu\text{-Cl})_2][\text{B}(3,5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_3)_4]_2$ (**1a**)^a

$\text{CH}_2=\text{CHOR}$	mol % cat	time (h)	yield (%)	TON ^b	TOF (h ⁻¹) ^c
$\text{CH}_2=\text{CHOEt}$ (2a)	0.5	0.25	70	140	560
	0.5	1	84	168	168
	0.5	48	98	196	4
$\text{CH}_2=\text{CHO}^n\text{Bu}$ (2b)	0.5	0.25	69	140	560
$\text{CH}_2=\text{CHO}^t\text{Bu}$ (2c) ^d	2	0.25	35	17	70
$\text{CH}_2=\text{CHOSiMe}_3$ (2d)	2.5	0.25	10	4	16
$\text{CH}_2=\text{CHOSiMe}_2\text{Ph}$ (2e)	5	10	50	10	1
$\text{CH}_2=\text{CHOSiMePh}_2$ (2f)	3	4	59	20	5
$\text{CH}_2=\text{CHOSiPh}_3$ (2g)	5	10	10	2	0.2
	5	60	47	9	0.15
	5	300	85	15	0.05

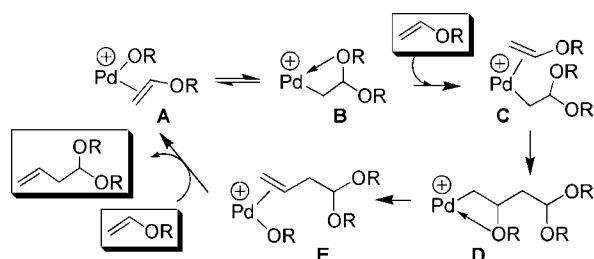
^a 23 °C, CH_2Cl_2 , with 3 equiv of DTBP (vs Pd), $[\text{Pd}] = 4$ mM. ^b Turnover number. ^c Average turnover frequency for the reaction period. ^d Ca. 35% of **2c** was dimerized, and 65% of **2c** was cationically polymerized.

1a also catalytically cyclizes divinyl ethers **2h-k** to cyclic acetals **3h-k** (eq 2). No intermolecular dimerization or oligomerization products were observed in these reactions.⁶ The TOF for the generation of **3h-k** is ca. 1 h⁻¹ (room temperature, CH_2Cl_2 , 5 h). NMR yields are shown in eq 2.



The catalytically active Pd species responsible for vinyl ether dimerization has not yet been identified.⁷ However, a plausible mechanism involving in situ generation of an active Pd-OR species (**A**) and double vinyl ether insertion, β -OR elimination, and ligand substitution steps is shown in Scheme 1.

The insertion of olefins into M-OR bonds has been observed in Pt, Rh, and Pd systems and proposed to occur in several catalytic processes.⁸⁻¹⁰ In particular, the insertion of vinyl ethers into Pd-OR bonds was proposed to be a key step in transfer vinylation,¹¹ vinyl

Scheme 1^a

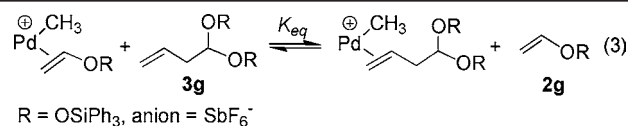
^a Pd = (α -diimine)Pd.

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(η^3 -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**.

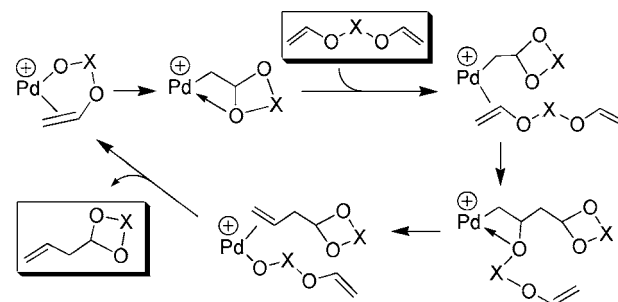
A similar dimerization of vinyl ethers to acetals by Hg(OAc)₂/BF₃·Et₂O has been reported.¹⁶ This system produces a significant amount of trimer, tetramer, and polymer side products and also dimerizes substituted vinyl ethers such as EtCH=CHOEt and CH₂=CMeOEt. These results are most consistent with a 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 $\Delta S = 0$, *K_{eq}* = 0.16 at 23 °C.



R = OSiPh₃, anion = SbF₆[–]

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.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-0911180).

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>.

References

- (1) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.
- (2) Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2006**, *128*, 12072.
- (3) Chen, C.; Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2010**, *132*, 5273.
- (4) Chen, C.; Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2008**, *130*, 12892.
- (5) Hatada, K.; Kitayama, T.; Nishiura, T.; Shibuya, W. *J. Polym. Sci., Part A* **2002**, *40*, 2134.
- (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.
- (8) Bryndza, H. E. *Organometallics* **1985**, *4*, 406.
- (9) Zhao, P. J.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 9642.
- (10) (a) Muzart, J. *Tetrahedron* **2005**, *61*, 5955. (b) Hartwig, J. F. *Nature* **2008**, *455*, 314. (c) Hamed, O.; Thompson, C.; Henry, P. M. *J. Org. Chem.* **1997**, *62*, 7082. (d) Hayashi, T.; Yamasaki, K.; Mimura, M.; Uozumi, Y. *J. Am. Chem. Soc.* **2004**, *126*, 3036. (e) Hay, M. B.; Wolfe, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 16468. (f) Trend, R. M.; Ramtohl, Y. K.; Stoltz, B. M. *J. Am. Chem. Soc.* **2005**, *127*, 17778.
- (11) (a) Bosch, M.; Schlaf, M. *J. Org. Chem.* **2003**, *68*, 5225. (b) Handerson, S.; Schlaf, M. *Org. Lett.* **2002**, *4*, 407.
- (12) (a) Mckee, J. E.; Fitton, P.; Griswold, A. A. *Tetrahedron* **1972**, *28*, 227. (b) Mckee, J. E.; Fitton, P. *Tetrahedron* **1972**, *28*, 233.
- (13) Dumlaio, C. M.; Francis, J. W.; Henry, P. M. *Organometallics* **1991**, *10*, 1400.
- (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
- (16) (a) Hoaglin, R. I.; Kubler, D. G.; Montagna, A. E. *J. Am. Chem. Soc.* **1958**, *80*, 5460. (b) Makin, S. M.; Krupstov, B. K. *Zh. Obshch. Khim.* **1960**, *30*, 3276.

JA104523Y