

## 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

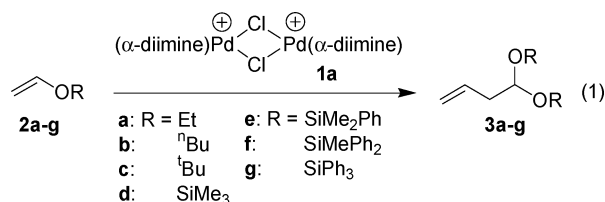
**Abstract:** ( $\alpha$ -Diimine)PdCl<sup>+</sup> species catalytically dimerize alkyl and silyl vinyl ethers to  $\beta,\gamma$ -unsaturated CH<sub>2</sub>=CHCH<sub>2</sub>CH(OR)<sub>2</sub> acetals, and they cyclize divinyl ethers to analogous cyclic acetals. A plausible mechanism comprises in situ generation of an active PdOR alkoxide species, double vinyl ether insertion to generate Pd{CH<sub>2</sub>-CH(OR)CH<sub>2</sub>CH(OR)<sub>2</sub>} species, and  $\beta$ -OR elimination to generate the acetal product. In the presence of vinyl ethers, ( $\alpha$ -diimine)PdCl<sup>+</sup> species can be used to initiate ethylene polymerization.

( $\alpha$ -Diimine)PdR<sup>+</sup> alkyl complexes<sup>1</sup> react with vinyl ethers by two pathways.<sup>2,3</sup> First, ( $\alpha$ -diimine)PdR<sup>+</sup> can initiate the cationic polymerization of vinyl ethers with concomitant formation of Pd<sup>0</sup>. This reaction proceeds via ( $\alpha$ -diimine)PdR(CH<sub>2</sub>=CHOR')<sup>+</sup>  $\pi$ -complexes in which the C=C bond is polarized with carbocation character at the substituted carbon (C<sub>int</sub>). Electrophilic attack of C<sub>int</sub> on the monomer initiates polymerization. Cationic polymerization is the dominant process for alkyl vinyl ethers. Alternatively, ( $\alpha$ -diimine)PdR-(CH<sub>2</sub>=CHOR')<sup>+</sup> adducts can undergo insertion to form O-chelated ( $\alpha$ -diimine)Pd(CH<sub>2</sub>CH(OR')CH<sub>2</sub>CH(OR'))<sup>+</sup> species, which can react further by  $\beta$ -OR' elimination to generate ( $\alpha$ -diimine)Pd(OR')(CH<sub>2</sub>=CHR)<sup>+</sup> (not observed) and subsequent allylic C-H activation to yield ( $\alpha$ -diimine)Pd(allyl)<sup>+</sup> 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.<sup>4</sup> For aryl vinyl ethers, both insertion and  $\beta$ -OAr elimination are fast, and the latter reaction precludes copolymerization or multiple insertion processes. Here we report that ( $\alpha$ -diimine)PdCl<sup>+</sup> chloride complexes catalyze a third reaction, the dimerization of vinyl ethers to  $\beta,\gamma$ -unsaturated acetals.

The reaction of ( $\alpha$ -diimine)PdCl<sub>2</sub> with Na[B(3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>] in CH<sub>2</sub>Cl<sub>2</sub> yields the dinuclear dicationic species [( $\alpha$ -diimine)Pd( $\mu$ -Cl)]<sub>2</sub>[B(3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>]<sub>2</sub> (**1a**,  $\alpha$ -diimine = 1,2-(2,6-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)N=CAnCAn=N(2,6-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>); An = acenaphthyl). **1a** catalytically dimerizes alkyl and silyl vinyl ethers CH<sub>2</sub>=CHOR (**2a–g**; R = Et (**a**), *n*-Bu (**b**), *t*-Bu (**c**), SiMe<sub>3</sub> (**d**), SiMe<sub>2</sub>Ph (**e**), SiMePh<sub>2</sub> (**f**), SiPh<sub>3</sub> (**g**)) to CH<sub>2</sub>=CHCH<sub>2</sub>CH(OR)<sub>2</sub> acetals (**3a–g**, eq 1, Table 1). No Pd<sup>0</sup> 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 H<sub>2</sub>O 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<sup>0</sup> 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.<sup>5</sup>

The dinuclear monocationic species [( $\alpha$ -diimine)Pd-Cl]<sub>2</sub>( $\mu$ -Cl)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**1b**), which is generated in situ by the reaction of ( $\alpha$ -diimine)PdCl<sub>2</sub> with [Li(OEt)<sub>2</sub>]<sub>2</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in CD<sub>2</sub>Cl<sub>2</sub>, 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-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)N=CMeCMe=N(2,6-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}PdCl<sub>2</sub> and (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub> also catalytically dimerize **2a** when activated by [Li(OEt)<sub>2</sub>]<sub>2</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].



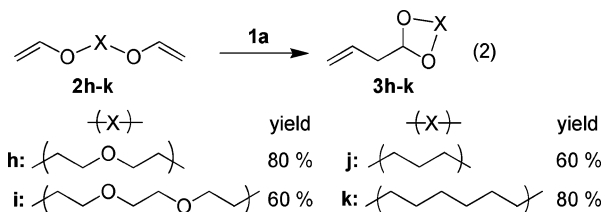
**Table 1.** Dimerization of Vinyl Ethers by [( $\alpha$ -Diimine)Pd( $\mu$ -Cl)]<sub>2</sub>[B(3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>]<sub>2</sub> (**1a**)<sup>a</sup>

CH <sub>2</sub> =CHOR	mol % cat	time (h)	yield (%)	TON <sup>b</sup>	TOF (h <sup>-1</sup> ) <sup>c</sup>
CH <sub>2</sub> =CHOEt ( <b>2a</b> )	0.5	0.25	70	140	560
	0.5	1	84	168	168
	0.5	48	98	196	4
CH <sub>2</sub> =CHO <sup>n</sup> Bu ( <b>2b</b> )	0.5	0.25	69	140	560
CH <sub>2</sub> =CHO <sup>n</sup> Bu ( <b>2c</b> ) <sup>d</sup>	2	0.25	35	17	70
CH <sub>2</sub> =CHOSiMe <sub>3</sub> ( <b>2d</b> )	2.5	0.25	10	4	16
CH <sub>2</sub> =CHOSiMe <sub>2</sub> Ph ( <b>2e</b> )	5	10	50	10	1
CH <sub>2</sub> =CHOSiMePh <sub>2</sub> ( <b>2f</b> )	3	4	59	20	5
CH <sub>2</sub> =CHOSiPh <sub>3</sub> ( <b>2g</b> )	5	10	10	2	0.2
	5	60	47	9	0.15
	5	300	85	15	0.05

<sup>a</sup> 23 °C, CH<sub>2</sub>Cl<sub>2</sub>, with 3 equiv of DTBP (vs Pd), [Pd] = 4 mM.

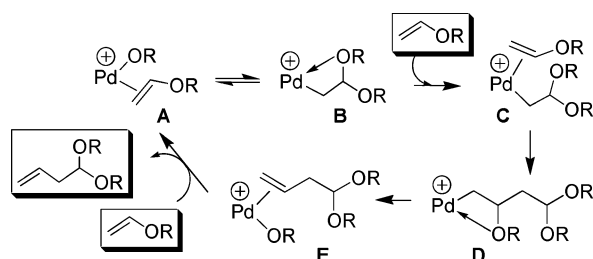
<sup>b</sup> Turnover number. <sup>c</sup> Average turnover frequency for the reaction period. <sup>d</sup> Ca. 35% of **2c** was dimerized, and 65% of **2c** was cationically polymerized.

**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.<sup>6</sup> The TOF for the generation of **3h–k** is ca. 1 h<sup>-1</sup> (room temperature, CH<sub>2</sub>Cl<sub>2</sub>, 5 h). NMR yields are shown in eq 2.



The catalytically active Pd species responsible for vinyl ether dimerization has not yet been identified.<sup>7</sup> However, a plausible mechanism involving in situ generation of an active Pd-OR species (**A**) and double vinyl ether insertion,  $\beta$ -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.<sup>8–10</sup> In particular, the insertion of vinyl ethers into Pd–OR bonds was proposed to be a key step in transfer vinylation,<sup>11</sup> vinyl

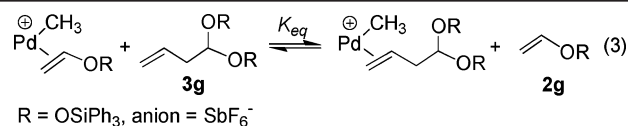
Scheme 1<sup>a</sup><sup>a</sup> Pd = (α-diimine)Pd.

interchange,<sup>12</sup> and isomerization reactions.<sup>13</sup> 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.<sup>10b</sup> DFT calculations show that the insertion barrier of the model complex (HN=CHCH=NH)Pd(OMe)(CH<sub>2</sub>=CH<sub>2</sub>)<sup>+</sup> (9.7 kcal/mol) is much lower than that for (HN=CHCH=NH)Pd(Me)(CH<sub>2</sub>=CH<sub>2</sub>)<sup>+</sup> (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**.<sup>2,3</sup> For comparison, (tmeda)Pd(OPh)<sup>+</sup> 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<sup>+</sup>, which, following allylic C–H activation, yields Pd allyl products.<sup>4</sup> 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.

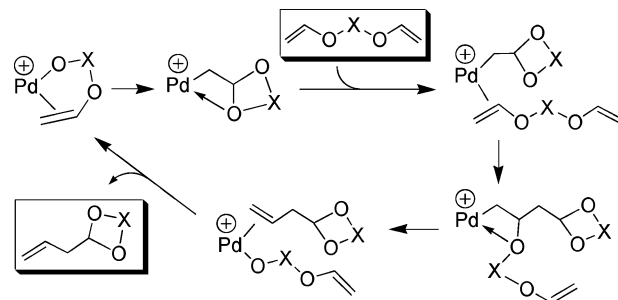
The addition of olefins to **1a**-catalyzed vinyl ether dimerization reactions was studied to probe the proposed intermediates in Scheme 1. The addition of 1-hexene (60 equiv) to the **1a**-catalyzed dimerization of **2f** (40 equiv) resulted in termination of catalysis after 4 h, with 50% conversion of **2f** to **3f** and complete conversion of **1a** to a mixture of (α-diimine)Pd(η<sup>3</sup>-C<sub>6</sub>H<sub>11</sub>)<sup>+</sup> allyl species. This result can be explained by reaction of **A** or **E** with hexene to form (α-diimine)Pd(OR)(hexene)<sup>+</sup> and allylic C–H activation.<sup>14</sup> The reaction of **1a** with **2f** (12 equiv) under 150 psi of ethylene pressure (CH<sub>2</sub>Cl<sub>2</sub>, 1 h, 23 °C) yields branched polyethylene (113 br/10<sup>3</sup> C, *M<sub>n</sub>* = 5100, *M<sub>w</sub>/M<sub>n</sub>* = 1.97).<sup>15</sup> This result can be explained by trapping of **A–E** by ethylene and further ethylene insertion.<sup>1</sup> No polymer was generated in the absence of **2f**.

A similar dimerization of vinyl ethers to acetals by Hg(OAc)<sub>2</sub>/BF<sub>3</sub>·Et<sub>2</sub>O has been reported.<sup>16</sup> This system produces a significant amount of trimer, tetramer, and polymer side products and also dimerizes substituted vinyl ethers such as EtCH=CHOEt and CH<sub>2</sub>=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,<sup>6</sup> and it does not react with MeCH=CHOEt or CH<sub>2</sub>=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<sup>+</sup> was studied. The equilibrium constant (*K<sub>eq</sub>*) for eq 3 was determined to be 0.12(1) at –20 °C. Assuming Δ*S* = 0, *K<sub>eq</sub>* = 0.16 at 23 °C.



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

Scheme 2<sup>a</sup><sup>a</sup> Pd = (α-diimine)Pd.

This work shows that (α-diimine)PdCl<sup>+</sup> species catalytically dimerize vinyl ethers to CH<sub>2</sub>=CHCH<sub>2</sub>CH(OR)<sub>2</sub> acetals and cyclize divinyl ethers to analogous cyclic acetals. In situ-generated (α-diimine)-Pd(OR)<sup>+</sup> alkoxide complexes may be the active species in these reactions. An interesting application of this reaction is olefin polymerization by (α-diimine)PdCl<sup>+</sup>/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 Pd<sup>0</sup> was observed for **2h–k**, even in the presence of 10 equiv of DTBP.
- (7) Except for the Pd<sup>0</sup> 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)PdCl<sub>2</sub> nor Na[B(3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>] alone reacts with vinyl ethers under these conditions. [Li(OEt)<sub>2</sub>]<sub>2</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] 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) McKeon, J. E.; Fitton, P.; Griswold, A. A. *Tetrahedron* **1972**, *28*, 227. (b) McKeon, J. E.; Fitton, P. *Tetrahedron* **1972**, *28*, 233.
- (13) Dumlao, 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 –CH<sub>2</sub>CH(OSiMePh<sub>2</sub>)Me and –CH<sub>2</sub>CH<sub>2</sub>(OSiMePh<sub>2</sub>) units. Similar results were obtained in the copolymerization of ethylene and **2f** by (α-diimine)PdMe<sup>+</sup> catalysts.<sup>2</sup>
- (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