

# Cyclocarbonylation of 2-allylphenols catalyzed by palladium-montmorillonite

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## Abstract

Pd-clays, prepared using montmorillonite and either dichloro(1,5-cyclooctadiene)palladium (II) or dichlorobis(benzonitrile)palladium (II), are effective catalysts for the carbonylation of 2-allylphenols, affording seven-membered ring lactones as the principal products. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Cyclocarbonylation; 2-Allylphenols; Palladium-montmorillonite

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## 1. Introduction

There is substantial interest in organic reactions using inorganic solids as reaction media [1–3], whether as high-surface-area supports for reagents or as catalysts. In the catalysis field intensive work has been directed to the development of supported metal complexes [4]. The objective of immobilized transition metals on clays is that they can combine the advantages of homogeneous and heterogeneous catalysts.

In the past decade montmorillonite, which has a smectite structure, has been extensively studied for use in organic reactions [5–13]. In our research, montmorillonite has been used to anchor a variety of metals and the activity of the clay was determined for different catalytic systems. Montmorillonite-bipyridinylpalladium (II) acetate is of value for the reductive carbonylation of mono- and dinitroarenes [14]; oxidative carbonylation of aliphatic mono-, di- and triamines [15]; hydroesterification of olefins and vinylsilanes [16,17] and stereospecific synthesis of  $\beta$ ,  $\gamma$ -unsaturated acids by the carbonylation of allylic alcohols [18]. Rhodium montmorillonite was an effective catalyst for the hydroformylation of vinylsilanes and allyl acetates [19,20]. Ruthenium montmorillonite clays are effective catalysts for the reduction of unsaturated esters, epoxides, sulfones and phosphonates [21].

The objective of the present study was to synthesize and examine the properties of new clay-intercalated palladium catalysts and assess their activity for the cyclocarbonylation of 2-allyl-

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lylphenols. The latter process, using homogeneous palladium catalysts, is effective for the preparation of 5- and 7-membered ring lactones [22].

## 2. Results and discussion

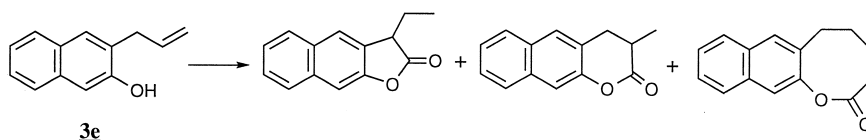
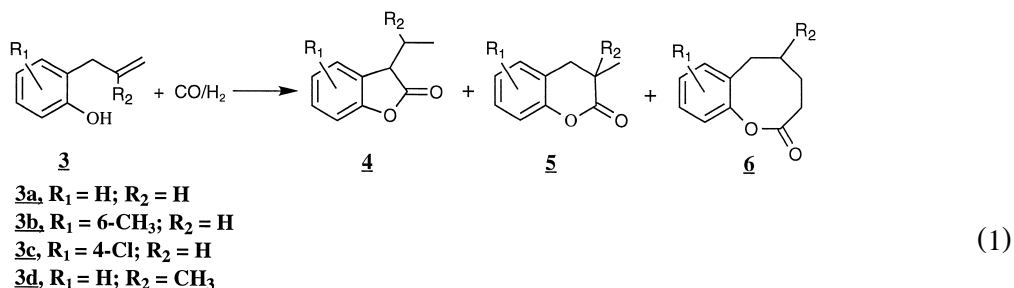
### 2.1. Intercalation of $[Pd(COD)Cl_2]$ and $[Pd(PhCN)_2Cl_2]$ between the interlayers of montmorillonite

$[Pd(COD)Cl_2]$  and  $[Pd(PhCN)_2Cl_2]$  were reacted with  $Na^+$ -exchanged montmorillonite in dichloromethane at room temperature overnight to form palladium-intercalated montmorillonite materials (Pd-clay **1** and Pd-clay **2**). The driving force for the reaction may be the elimination of NaCl as previously noted in the literature [19,23] (Scheme 1).

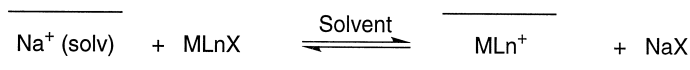
Elemental analysis of Pd-clay **1** indicated the presence of 0.03 mmol of palladium/g of the clay and Pd-clay **2** contained 0.08 mmol palladium/g clay. X-ray powder diffraction showed a basal region expansion ( $d_{001}$ ) of 12.56 Å for Pd-clay **1** and 12.58 Å for Pd-clay **2** in comparison with 9.6 Å in the dehydrated sodium montmorillonite.

### 2.2. Cyclocarbonylation of 2-allylphenols

The first reaction examined was the carbonylation of 2-allylphenol **3a** (Eq. (1)).



Treatment of **3a** (1.0 mmol) in dichloromethane with a 1/5 mixture of carbon monoxide and hydrogen, 0.1 g Pd-clay **1** (0.003 mmol palladium) and 1,4-bis(diphenylphosphino)butane (0.012 mmol dppb) at 120°C and 600 psi for 48 h (Table 1, entry 1) resulted in 28% conversion to lactones with 27% isomerization to 2-propenylphenol, with a moderate regioselectivity for the five-membered ring heterocycle (62/34/4 ratio of **4/5/6**). A similar conversion and isomerization resulted using



Scheme 1. Intercalation of metal complexes into clays.

Table 1  
Cyclocarbonylation of 2-allylphenol (**3a**) by clay-Pd **1**/dppb/CO/H<sub>2</sub><sup>a</sup>

Entry	Solvent	L/Pd <sup>b</sup>	T (°C)	P <sub>CO</sub> (psi)	P <sub>H<sub>2</sub></sub> (psi)	% C <sub>prod</sub>	% Isom	Product distribution %		
								<b>4</b>	<b>5</b>	<b>6</b>
1	CH <sub>2</sub> Cl <sub>2</sub>	4	120	100	500	28	27	62	34	4
2	toluene	4	120	100	500	23	24	3	18	79
3	toluene	4	120	300	300	90	9	1	9	90
4	toluene	4	120	600	0	37	3	–	10	90
5	toluene	4	130	300	300	86	14	8	11	81
6	toluene	4	160	300	300	14	18	14	21	65
7	toluene	2	120	300	300	68	25	10	18	72
8	toluene	2	120	200	200	41	27	7	23	70
9	toluene	2	120	500	100	33	9	2	20	78

<sup>a</sup>Reaction conditions: 0.1 g clay (0.003 mmol Pd), 1 mmol substrate, 5 ml solvent, *t* = 48 h. The percent conversion, isomerization and ratio of **4/5/6** was determined by GC and <sup>1</sup>H NMR spectroscopy; <sup>b</sup>L = dppb.

toluene in place of dichloromethane (entry 2) although the seven-membered ring heterocycle was the major product in this case (3/18/79 ratio of **4/5/6**).

Nearly complete reaction occurred using a 1/1 ratio of CO/H<sub>2</sub> in toluene as the solvent (entry 3). In this case the seven-membered ring lactone could be formed in high regioselectivity.

It was previously reported [22] that the reaction of 2-allylphenol, in either dichloromethane or toluene, in the absence of hydrogen and catalyzed by Pd(PCy<sub>3</sub>)<sub>2</sub>(H)(H<sub>2</sub>O)<sup>+</sup>BF<sub>4</sub><sup>-</sup> or Pd(OAc)<sub>2</sub> and dppb, gave only traces of lactones. The use of Pd-clay **1**, in the absence of hydrogen, gives 37% conversion to lactones with high regioselectivity for the seven-membered ring product (entry 4). While in the homogeneous system the regioselectivity for the seven-membered ring heterocycle increases with increasing temperature, the regioselectivity for **6** decreases, as does the conversion, when Pd-clay **1** is used as the catalyst (compare entries 3, 5 and 6). Although the clay cannot be recycled in these cases, the results obtained indicate a different behavior of the clay in the cyclocarbonylation of allylphenol in comparison with the homogeneous system.

If the quantity of diphosphine is reduced from 0.012 mmol to 0.006 mmol the catalytic activity is lower, as is the regioselectivity for **6** (entry 7) but the clay catalyst can be reused in this case. When the pressure is reduced from 600 psi to 400 psi, 41% conversion to products results with 70% regioselectivity for the seven membered ring product (entry 8). There is only 33% conversion at 600 psi pressure using a CO/H<sub>2</sub> ratio of 5/1 (entry 9).

Pd-clay **2**, prepared using the same procedure as Pd-clay **1**, contains benzonitrile ligands instead of cyclooctadiene ligands. When **2** was employed for the cyclocarbonylation of 2-allylphenol at 600 psi pressure (CO/H<sub>2</sub> = 1/1) and 120°C for 48 h in the presence of different L/Pd ratios (L/Pd ratios used were 1, 2 and 4) there was complete conversion to products with no isomerization. The use of different L/Pd ratios does not affect the rather poor regioselectivity in this case (57/22/21 ratio of **4/5/6**, R<sub>1</sub> = H, R<sub>2</sub> = H).

Other allylphenols were used for the cyclocarbonylation reaction at 300 psi CO and 300 psi H<sub>2</sub> and 120°C using a L/Pd-clay **1** ratio of 2 and 4, and the results are presented in Table 2.

When 2-allyl-6-methylphenol (**3b**) is used as the reactant, and the L/Pd ratio is 4 (entry 1, Table 2) there was good regioselectivity for the seven-membered ring product **6**, R<sub>1</sub> = 6-Me, R<sub>2</sub> = H. Only 15% conversion to products occurred when the L/Pd ratio was reduced to 2 (entry 2, Table 2). The regioselectivity for the seven-membered ring product was 66–69% when 2-allyl-4-chlorophenol (**3c**) was employed as the reactant (entries 3 and 4, Table 2). Only isomerization products are observed

Table 2

Cyclocarbonylation of allylphenols using clay-Pd **1**/dppb/CO/H<sub>2</sub><sup>a</sup>

Entry	Substrate	L/Pd <sup>b</sup>	% C <sub>prod</sub>	% Isom	Product distribution %		
					<b>4</b>	<b>5</b>	<b>6</b>
1	<b>3b</b>	4	100	–	6	11	83
2	<b>3b</b>	2	15	3	–	32	68
3	<b>3c</b>	4	94	3	18	13	69
4	<b>3c</b>	2	45	23	5	29	66
5	<b>3d</b>	4	–	29	–	–	–
6	<b>3d</b>	2	–	44	–	–	–
7	<b>3e</b>	4	72	27	–	18	82
8	<b>3e</b>	2	48	26	3	15	82

<sup>a</sup>Reaction conditions: 0.1 g clay (0.003 mmol Pd), 1 mmol substrate, 5 ml toluene,  $t = 48$  h,  $P_{CO} = 300$ ,  $P_{H_2} = 300$ ,  $T = 120^\circ\text{C}$ . The percent conversion, isomerization and ratio of **4**/**5**/**6** was determined by GC and <sup>1</sup>H NMR spectroscopy; <sup>b</sup>L = dppb.

when **3d** was the reactant (entries 5 and 6, Table 2). 1-Allyl-2-naphthol undergoes 72% conversion to products with 27% isomerization (entry 7, Table 2). Reducing the quantity of dppb lowers the activity but the regioselectivity for the seven membered ring is maintained (entry 8, Table 2).

### 3. Conclusion

In conclusion, the reaction of [Pd(COD)Cl<sub>2</sub>] and [Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>] with Na<sup>+</sup>-exchanged montmorillonite afforded new organometallic palladium complexes intercalated into montmorillonite. Both Pd-clays are active for the cyclocarbonylation of 2-allylphenol; nevertheless they show different regioselectivity for the reaction, with Pd-clay **1** affording the seven-membered ring as the major product and Pd-clay **2** showing poor regioselectivity. The regioselectivity obtained with Pd-clay **1** is similar to the homogeneous system although the clay shows different temperature effects. The regioselectivity obtained in the cyclocarbonylation reaction using Pd-clay **2** is appreciably different from the homogeneous system and is also unaffected by the use of increasing quantities of diphosphine.

### 4. Experimental

Toluene was dried and distilled from sodium under nitrogen prior to use. Dichloromethane was freshly distilled under nitrogen from P<sub>2</sub>O<sub>5</sub>. <sup>1</sup>H NMR spectra were recorded on a Varian Gemini 200 and a Varian 3400 Chromatograph was used for GC analyses. X-ray basal spacing of Pd-clays were determined with a Philips PW 3710 based analytical diffractometer. Most chemicals were used as obtained from commercial sources. 2-Allylphenol (**3a**), 6-methyl-2-allylphenol (**3b**) and 4-chloro-2-allylphenol (**3c**) are commercially available, while **3d** and **3e** were prepared according to literature procedures [24,25].

#### 4.1. Preparation of clays

##### 4.1.1. Pd-clay **1**

A mixture of [Pd(COD)Cl<sub>2</sub>] (14.28 mg, 0.05 mmol), Na<sup>+</sup>-montmorillonite (1 g, from Crook Country WY, was purchased from Clay Minerals Society, Columbia, MO; further purified by

sedimentation prior to use) in dry dichloromethane (25 ml) under nitrogen was subjected to vigorous stirring overnight at room temperature. The resulting pale gray solid material (Pd-clay **1**) was filtered, washed thoroughly with dry dichloromethane, and dried using nitrogen.

#### 4.1.2. Pd-clay **2**

A mixture of  $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$  (38.3 mg, 0.1 mmol),  $\text{Na}^+$ -montmorillonite (1 g) in dry dichloromethane (25 ml) under nitrogen was subjected to vigorous stirring overnight at room temperature. The resulting pale orange solid material (Pd-clay **2**) was filtered, washed thoroughly with dry dichloromethane, and dried using nitrogen.

### 4.2. General procedure for the carbonylation of 2-allylphenols

A mixture of 1.0 mmol of substrate, 0.1 g of Pd-clay (Pd-clay **1** contains 0.003 mmol palladium and Pd-clay **2** contains 0.008 mmol Pd), the phosphorus compound and dry solvent (5 ml) was placed in a 50 ml autoclave. The autoclave was flushed thoroughly with carbon monoxide and pressurized to the desired level with carbon monoxide and hydrogen. The reactor was then placed in a preheated oil bath. After the reaction, the autoclave was cooled to room temperature and the solution filtered through celite. Conversions and regioselectivities were determined by GC and  $^1\text{H}$  NMR.

#### 4.2.1. Lactones

The following lactones are known compounds and have spectral data in accord with literature results: **4a**, **4b**, **4c**, **4d**, **4e**, **5b**, **5c**, **5d**, **5e** [26], **5a** [27,28], **6a** [29] and **6b**, **6c**, **6d**, **6e** [23].

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