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Hydroesterification of Olefins Catalyzed by $Pd(OAc)_2$ Immobilized on Montmorillonite

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Palladium acetate immobilized on montmorillonite is an efficient catalyst for the hydroesterification of olefins with carbon monoxide and methanol, in the presence of triphenylphosphine and an acid promoter, affording branched chain esters. The reaction is regiospecific for aryl olefins as well as for vinyl benzoate and regioselective for aliphatic olefins.

Introduction

The transition metal complex catalyzed hydroesterification of olefins with CO and an alcohol is of great interest for the synthesis of industrially valuable carboxylic esters such as linear fatty acid esters and 2-arylpropionic acid esters (eq 1).[1−3] Both linear and branched esters can be formed in these reactions.

$$\underset{\mathbf{1}}{RCH{=}CH_2} + CO + R'OH \rightarrow \underset{\mathbf{2}}{RCH(CH_3)COOR'} + \underset{\mathbf{3}}{RCH_2CH_2COOR'} \quad (1)$$

In most cases, homogeneous catalysts are used and the regiochemistry strongly depends on the catalytic system employed.[4,5]

In order to increase the selectivity and to make the catalyst recovery more facile, swelling-type smectite clays such as montmorillonite have recently attracted interest as supports for "heterogenized" homogeneous catalytic reactions[6−12] since clays can be functionalized by replacement of surface hydroxyl groups with organic ligands to which a metal can coordinate[6,7] or via ion exchange with a positively charged metal complex.[8−10] Transition-metal complexes immobilized on montmorillonite show enhanced reactivity and better selectivity in hydrogenation, hydroformylation, and carbonylation reactions.[6−12] The enhanced selectivities are due to their lamellar swelling structure, large surface area, availability of both Bronsted and Lewis surface acidic sites, and redox properties.[6,11] Recently, Crocker and Herold[13] described the use of ion-exchanged palladium derivatives in montmorillonite for the hydroesterification reactions. However, little has been described in the literature using palladium-phosphinated clays. We now report the efficient hydroesterification of olefins in good yields and selectivities using palladium acetate immobilized on montmorillonite as the catalyst.

Results and Discussion

Montmorillonite has a layer lattice structure in which two-dimensional silicate sheets approximately 9.6 Å thick are separated by interlayer cations,[9] which can be swollen in the 001 direction by adsorbed solvents.[8] The X-ray diffraction patterns of palladium acetate immobilized on montmorillonite (Pd-clay) showed basal plane expansion to 15.0 Å from 9.6 Å of dehydrated sodium montmorillonite. The basal spacing (001) of 15.0 Å corresponds to interlamellar spacing of 5.4 Å. Elemental analysis revealed a Pd content of 1.14 wt %, which corresponds to 0.11 mequiv/g of catalyst. These results indicate the existence of a metal complex in the interlamellar region. The palladium content is half and the basal spacing is the same compared with bipyridinepalladium acetate on montmorillonite.[6a−c]

The effects of various reaction conditions on the hydroesterification of styrene in the presence of the Pd-clay catalyst are summarized in Table 1 (eq 2). The conversion of styrene and the yield of products were calculated by GLC using biphenyl as the internal standard.

$$\underset{\mathbf{1},\ R = Ph}{PhCH{=}CH_2} + CO + MeOH \xrightarrow[\substack{C_6H_6,\ 24\ h\\ 600\ psi\ CO}]{Pd\text{-}clay,\ HCl} \underset{\mathbf{2},\ R = Ph}{PhCH(CH_3)COOMe} + \underset{\mathbf{4}}{PhCH(CH_3)OMe} \quad (2)$$

When benzene was used as the solvent, the linear ester **3** was not formed and 1-methoxy-1-phenylethane (**4**) was obtained as a byproduct. The presence of an acid promoter is essential for significant catalytic activity, although montmorillonite has both Bronsted and Lewis acidic sites corresponding to a Hammett acidity function (H_o) value of +1.5 to −3.0.[12] Note that the Bronsted acidity is reduced by treatment with $SOCl_2$ and that without an acid promoter, the reaction proceeded very

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(1) Stille, J. K. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 4, Chapter 4.5, pp 913−950.

(2) Tkatchenko, I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, pp 101−223.

(3) Alper, H.; Hamel, N. *J. Am. Chem. Soc.* **1990**, *112*, 2803.

(4) Mullen, A. In *New Synthesis with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: Berlin, 1980; pp 243−308.

(5) Alper, H.; Woell. J. B.; Despeyroux, B.; Smith, D. J. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1270.

(6) (a) Choudary, B. M.; Vasantha G.; Sharma, M; Bharathi, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 465. (b) Choudary, B. M.; Bharathi, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1505. (c) Kumar, K. R.; Choudary, B. M.; Jamil, Z.;Thyagarajan, G. *J. Chem. Soc., Chem. Commun.* **1986**, 130. (d) Choudary, B. M.; Kumar, K. R.; Jamil, Z.; Thyagarajan, G. *J. Chem. Soc., Chem. Commun.* **1985**, 931. (e) Choudary, B. M.; Rani, S. S.; Narender, N. *Catal. Lett.* **1993**, *19*, 299.

(7) Valli, V. L. K.; Alper, H. *J. Am Chem. Soc.* **1993**, *115*, 3778.

(8) Farzaneh E.; Pinnavaia, T. J. *Inorg. Chem.* **1983**, *22*, 2216.

(9) Pinnavaia, T. J.; Raythatha, R.; Lee, J. G.-S.; Halloran, L. J.; Hoffman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 6891.

(10) Chin, C. S.; Lee, B.; Yoo, I.; Kwon, T. *J. Chem. Soc., Dalton Trans.* **1993**, 581.

(11) Cornelis, A.; Laszlo, P. *Synlett* **1994**, 155.

(12) Laszlo, P., Ed. In *Preparative Chemistry using Supported Reagents*; Academic Press; San Diego, CA, 1987, pp 437−458.

(13) Crocker, M.; Herold, R. H. M. *J. Mol. Catal.* **1991**, *70*, 209.

0022-3263/95/1960-0250$09.00/0

Table 1. Pd-Clay Catalyzed Hydroesterification of Styrene with CO and Methanol[a]

entry	temp (°C)	PPh_3/Pd	c-HCl (mL)	conversn[b] (%)	yield[b] (%) **2**, R = Ph	yield[b] (%) **4**
1[c]	100	10	0.5	54	34	16
2[c]	100	10		nr[d]		
3	125	5	0.3	100	88 (77)	8
4	125	5		3	3	
5	125		0.3	16		16
6[e]	125	5	0.3	100	64 (60)	9
7[f]	125	5	*p*-TSA	33	33	
8	166	5	0.3	34	12	20

[a] Reaction conditions: Pd-clay 30 mg (Pd 0.003 mequiv); **1**, R = Ph, 1.5 mmol; MeOH 15 mmol; benzene 10 mL; CO 600 psi; 24 h. [b] Calculated by GLC analysis using biphenyl as an internal standard. Isolated yield in parentheses. [c] Reaction time 66 h. [d] No reaction. [e] O_2 100 psi was added. [f] *p*-Toluenesulfonic acid was used instead of HCl (*p*-TSA/Pd = 5).

Table 2. Effect of Various Reaction Conditions on the Hydroesterification of Styrene in the Presence of the Pd-Clay Catalyst[a]

entry	MeOH **1**, R = Ph	PPh_3/Pd	c-HCl (mL)	conversn[b] (%)	yield[c] (%) **2**, R = Ph	yield[c] (%) **4**
1	10	5	0.3	100	88 (77)	8
2	8	5	0.3	100	85 (66)	6
3	6	5	0.3	100	90 (78)	4
4	5	5	0.3	100	81	4
5	4	5	0.3	97	72	3
6	2	5	0.3	80	48	1
7	6	5	0.1	100	91	4
8	6	5	0.05	100	94 (80)	3
9	6	5	0.05	57	50	2
10	6	5	0.02	69	64	1
11[d]	6	5	*p*-TSA	33	33	0
12	6	8	0.05	100	92 (78)	3
13	6	2	0.05	56	50	2

[a] Reaction conditions: Pd-clay 30 mg (Pd 0.003 mequiv); **1**, R = Ph, 1.5 mmol; benzene 10 mL; CO 600 psi; 24 h, 125 °C. [b] Calculated by GLC analysis using biphenyl as an internal standard. [c]Isolated yield in parentheses. [d]*p*-Toluenesulfonic acid was used instead of HCl (p-TSA/Pd = 5).

Table 3. Solvent Effect on the Hydroesterification of Styrene with CO and Methanol in the Presence of the Pd-Clay Catalyst[a]

entry	solvent	conversn[b] (%)	yield[b] (%) **2 + 3**	yield[b] (%) **4**	**2**, R = Ph:**3**, R = Ph[b]
1	benzene	100	88 (77)	8	100:0
2	toluene	100	84	8	100:0
3	CH_2Cl_2	98	75 (68)	12	98:2
4[c]	acetone	96	66	3	99:1
5	CH_3OH	65	29	30	62:38
6	THF	100	63 (60)	36	100:0

[a] Reaction conditions: Pd-clay 30 mg (Pd 0.003 mequiv); PPh_3 0.015 mmol; **1**, R = Ph, 1.5 mmol; MeOH 15 mmol; c-HCl 0.05 mL; solvent 10 mL; CO 600 psi; 24 h; 125 °C. [b] Calculated by GLC analysis using biphenyl as an internal standard. Isolated yield in parentheses. [c] An unidentified product was also formed.

Table 4. Pd-Clay Catalyzed Hydroesterification of Various Olefins with CO and Methanol[a]

entry	substrate	time (h)	conversn (%)	yield[b] (%)	2:3
1	*p*-methylstyrene	24	100	88 (76)	100:0
2	2-methylstyrene	24	100	95 (83)	100:0
3	*p*-isobutylstyrene	24	88	77 (70)	100:0
4	vinyl benzoate	24	64	51 (36)	100:0
5		48	95	71 (64)	100:0
6	1-octene	24	29	29 (19)	66:34
7	1-decene	24	25	25 (17)	72:28
8		66	61	59 (48)	66:34

[a] Reaction conditions: Pd-clay 30 mg (Pd 0.003 mequiv); PPh_3 0.015 mmol; **1**, R = Ph, 1.5 mmol; MeOH 9 mmol; c-HCl 0.05 mL; benzene 10 mL; CO 600 psi; 24 h; 125 °C. [b] Calculated by NMR. Isolated yield in parentheses.

slowly (entries 2 and 4). It seems that only Bronsted acidic sites are important in this reaction. As an acid promoter, HCl was more active than *p*-toluenesulfonic acid (*p*-TSA; entries 3 and 7). When *p*-TSA was used, **2**, R = Ph, was formed as the only product. Only **4** was formed in the absence of PPh_3 (entry 5). When oxygen was used (entry 6), the conversion of **1**, R = Ph, was 100%, but unidentified byproducts were produced in the reaction. Bidentate phosphine ligands such as dppp or dppb were inactive in the present system. Both the conversion and the yield increased as the temperature was raised from 100 °C to 125 °C. However, when the temperature was further increased to 166 °C, the conversion and the yield decreased. It is evident that catalytic species decompose to inactive palladium metal without PPh_3 or at high temperature.

In order to determine the optimum reaction conditions, the effect of mole ratio of methanol to styrene, mole ratio of PPh_3 to Pd, and the amount of HCl was examined, and the results are presented in Table 2. As the mole ratio of methanol to styrene was raised, the amount of **4** also increased. As the amount of HCl increased, more **4** was obtained in the reaction. When the mole ratio of methanol to **1** was less than 4, or the amount of c-HCl was below 0.0 mL, the conversion was not complete. The best result was obtained [94% yield of **3**, R = Ph (isolated yield of 80%)] when styrene was reacted with CO and methanol at 125 °C and 600 psi of carbon monoxide (entry 8). The ratio of Pd/PPh_3/**1**, R = Ph/MeOH, was 1/5/500/3000.

Solvents significantly influence the course of the reaction (Table 3). Nonpolar solvents such as benzene and toluene afforded **2**, R = Ph, in superior yields to polar solvents. In the case of dichloromethane, methanol, and THF, **4** was formed in 12−36% yield. Since **4** can be formed in the absence of palladium, this result suggests that the catalyst is less effective in polar than in nonpolar solvents. The degree of swelling of the clay and leaching of the metal complex can be controlled by the polarity of the solvent and is larger in polar solvents. Palladium acetate itself is easily decomposed in polar solvents such as methanol.

Various terminal olefins were employed as substrates in the hydroesterification reaction (Table 4). When substituted styrenes were used, the conversion and the yield were high and the branched ester was formed regiospecifically (entries 1−3). Regiospecific formation of the branched aryl ester is believed to be due to the π-benzylic interaction of the phenyl group with palladium.[14] These arylpropionic acid esters are industrially important as antiinflammatory agents.[3] Only the branched chain ester was formed in the case of vinyl benzoate (entries 4 and 5). In these cases, transesterification occurred and methyl benzoate was synthesized in 19−24% selectivity. When single olefins were used as substrates, both linear and branched esters were formed with the branched isomer as the major product (66−72% selectivity). In the case of alkenes and vinyl benzoate, hydromethoxylation did not take place.

Early studies in homogeneous Pd-catalyzed hydroesterification of aryl olefins showed that branched esters

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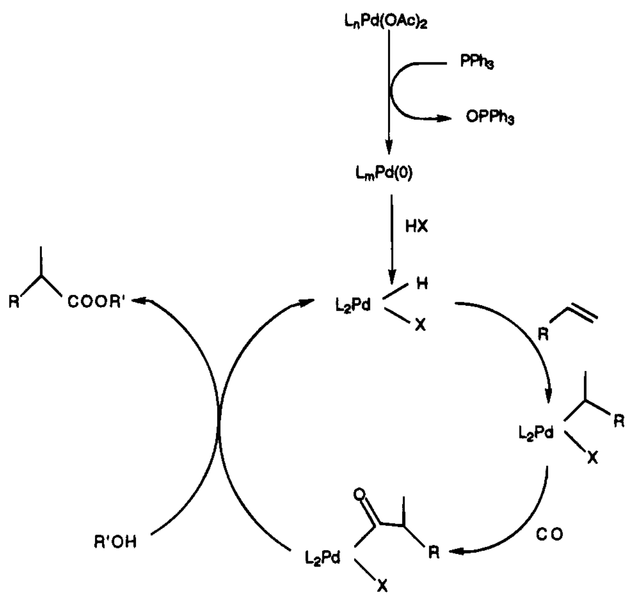
[14] Sugi, Y.; Bando, K.-I. *Chem. Lett.* **1976**, 727.

Scheme 1



are formed regiospecifically in the absence of a phosphine ligand or in the presence of a monodentate phosphine ligand.[14-16] Thus, the branched ester was obtained in 90% yield from the reaction of *p*-methylstyrene with CO, MeOH, and $PdCl_2/CuCl_2/HCl/O_2$ as the catalyst system.[16] An ether byproduct was formed in 8% yield as well. In the case of monoolefins, the regioselectivity is largely controlled by the catalyst system used. For example, Knifton showed that reaction of 1-heptene with CO, MeOH, and $PdCl_2(PPh_3)_2$ as the catalyst gave 42% selectivity to the branched ester and that addition of $SnCl_2$ decreased the selectivity to 13%.[17] On the other hand, Despeyroux and Alper obtained the branched ester as the only product using the $PdCl_2/CuCl_2/HCl/O_2$ catalyst system in the hydroesterification of 1-decene.[16] When $Pd(OAc)_2$ was used as the catalyst in the hydroesterification of styrene and 1-decene, almost the same results as the Pd-clay catalyst were obtained except that a black precipitate was formed after the $Pd(OAc)_2$-catalyzed reaction.

A possible mechanism for the hydroesterification of olefins with CO and alcohol in the presence of PPh_3 and an acid promoter is outlined in Scheme 1. In the presence of an excess of triphenylphosphine, the zerovalent palladium complex can be generated from palladium acetate via an overall two-electron inner-sphere reduction.[18] Triphenylphosphine is oxidized to triphenylphosphine oxide. The formed Pd(0) can be stabilized by a PPh_3 ligand. Therefore, it is believed that the role of PPh_3 is to promote the formation of Pd(0) and to stabilize the Pd(0) intermediate. Since the degree of swelling of the clay support takes place within rather narrow limits, it is likely that bulky ligands such as dppp and dppb are not capable of entering the interlamellar space and, therefore, are ineffective for the reaction. It is conceivable that a hydridopalladium complex is generated by the reaction of Pd(0) with an acid.[19] Insertion of an olefin into a Pd–H bond followed by CO insertion generates a Pd–acyl complex. The reaction of the latter with alcohol gives the product and the hydridopalladium complex is regenerated. The hydridopalladium complex may exist in an ion pair form such as $[H-PdL_3]^+X^-$, which is presumed as an intermediate in the palladium-catalyzed hydrocarbonylation of alkenes with formic acid.[20]

In conclusion, palladium immobilized on montmorillonite is an effective catalyst for the hydroesterification of terminal olefins with CO and alcohol in the presence of PPh_3 and an acid promoter. The catalyst shows similar regiochemistry to homogeneous analogs.

Experimental Section

Preparation of the Catalyst. The Pd-clay catalyst was prepared according to a literature method[6a-c] and characterized by elemental analysis and X-ray diffraction. Montmorillonite K10, purchased from Fluka, was treated with saturated sodium chloride solution followed by 0.1 N HCl to give H-montmorillonite. Chloromontmorillonite was prepared by the reaction of H-montmorillonite with $SOCl_2$ in dry benzene under reflux for 24 h. The reaction of PPh_2Cl with an excess of Li metal under reflux gave orange PPh_2Li, which was then added to dried chloromontmorillonite. The mixture was refluxed for 24 h, filtered, washed with dry THF until the filtrate was free of chloride ion, and then dried at 70 °C for 24 h. The dried functionalized montmorillonite was reacted with a solution of $Pd(OAc)_2$ to give the Pd-clay catalyst.

General Procedure. Solvents and substrates were purchased from Aldrich and were used as received. *p*-Isobutylstyrene was prepared following a literature procedure.[21] Proton and carbon NMR spectra were recorded on a Varian Gemini 200 spectrometer using $CDCl_3$ as the solvent. A 45 mL stainless steel autoclave (Parr Instruments) was used as a batch reactor. In a typical run, 30 mg of Pd-clay (0.003 mmol Pd), 4.3 mg of PPh_3, 1.5 mmol of olefin, 9 mmol of methanol, 10 mL of benzene, and 0.05 mL of c-HCl were charged into the reactor. The gas phase in the reactor was flushed with carbon monoxide three times and pressurized to the desired pressure. The reactor was then placed in an oil bath maintained at constant temperature. After the reaction, the reactor was cooled to room temperature. The reaction mixture was filtered through neutral alumina, and the solvent was removed by rotary evaporation. Quantitative analysis was carried out by a GLC (Varian 3400) equipped with a 1.5% OV-17 and 1.95% OV-210 packed column with biphenyl as an internal standard. Pure ester was isolated by TLC silica gel chromatography and characterized by comparison of ^{1}H-NMR and mass spectral results with data for authentic materials.

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(15) Bittler, K.; Kutepow, N. v.; Neubauer, D.; Reis, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 329.

(16) Despeyroux, B.; Alper, H. *Ann. N. Y. Acad. Sci.* **1984**, *415*, 148.

(17) Knifton, J. F. *J. Org. Chem.* **1976**, *41*, 2885.

(18) (a) Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992**, *11*, 3009. (b) Amatore, C.; Jutand, A.; Khalil, F.; M'Barki, M. A.; Mottier, L. *Organometallics* **1993**, *12*, 3168. (c) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *13*, 1890.

(19) (a) Kushino, Y.; Itoh, K.; Miura, M.; Nomura, M. *J. Mol. Catal.* **1994**, *89*, 151. (b) Maitlis, P. W.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 6, pp 243–263.

(20) Zargarian, D.; Alper, H. *Organometallics* **1993**, *12*, 712.

(21) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.-I.; Nakajima, I.; Minato, A.; Kumada, *M. Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958.