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Novel Palladium(II) Complex Containing a Chelating Anionic N−O Ligand: Efficient Carbonylation Catalyst

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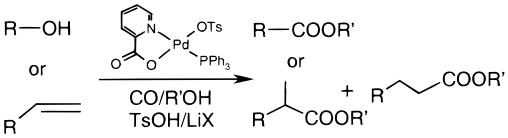
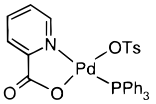
ABSTRACT



A novel palladium(II) complex containing chelating anionic pyridine-2-carboxylato and labile tosylato ligands is a highly efficient catalyst for the carbonylation of organic alcohols and olefins to carboxylic acids/esters. Carbonylation of primary, secondary, and tertiary alcohols as well as linear and functionalized terminal olefins was studied. In all cases remarkable activity and selectivity were observed. The catalyst is stable under reaction conditions even in the absence of excess phosphine ligands.

Catalytic carbonylation of organic substrates is a very promising and clean route for the synthesis of carbonyl compounds[1] such as carboxylic acids, esters, ketones, amides, and amino acids. In general, group VIII metal complexes have been used and a specific class of reaction requires unique catalytic properties and operating conditions. Even though many carbonylation catalysts have emerged in the past few decades,[2] the search for new catalysts and processes continues because of the economical and environmental demands. Our interest has been in the development of novel palladium-based catalytic systems for liquid-phase carbonylation reactions to form carboxylic acid/ester products.[3] Here, we report the novel palladium complex **1**[4] containing the chelating anionic N−O ligand (pyridine-2-carboxylato) and labile TsO (tosylato) ligand as an efficient catalyst for carbonylation of a variety of alcohols and olefins, providing high selectivity to carboxylic acid/ester. Complex **1** was prepared[5] by reacting $Pd(OAc)_2$ with 1 equiv of pyridine-2-carboxylic acid and 1−2 equiv of TsOH and PPh_3. An IR spectrum of the complex showed carbonyl stretching vibrations at 1668 cm^{-1} ($\nu_{C=O}$) and 1330 cm^{-1} ($\nu_{O=C-O}$) and a Pd−N stretching vibration at 568 cm^{-1}.



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^{1}H NMR and elemental analysis[6] of complex **1** was consistent with the given formulation. A ^{31}P NMR spectrum

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(4) Chaudhari, R. V.; Jayasree, S.; Seayad, A. Indian Patent Appl. 3697 DEL 98, March 1999; U.S. Appl. No. 09/291,929, 31-03-1999.

(5) Equimolar amounts of $Pd(OAc)_2$ and pyridine-2-carboxylic acid and 1 or 2 equiv of TsOH and PPh_3 in chloroform were vigorously stirred or shaken at room temperature for a few minutes. After all the components were dissolved and the solution turned yellow, the product was isolated as an yellow oil by addtion of *n*-hexane or diethyl ether. The oily product was washed several times with diethyl ether and hexane and was kept under vacuum, forming an yellow fluffy solid.

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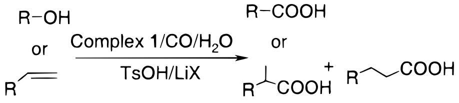
showed a strong signal at δ 34.58 ppm along with a weak signal at δ 36.19 ppm, which may be the trans (N trans to PPh_3) and cis (N cis to PPh_3) isomers, respectively.[7] At room temperature, complex **1** was highly soluble in most of the polar solvents, moderately soluble in less polar solvents, and hygroscopic. Crystals suitable for X-ray crystallography were not obtained by common techniques, and an oil of the complex was found to separate out in all the cases.

The carbonylation of alkyl and aryl alcohols as well as olefins has been carried out to investigate the activity and chemo- as well as regioselectivity of the catalyst toward the formation of carboxylic acids (Scheme 1). Complex **1** showed improved activity compared to that of the conventional catalysts in all the cases. A unique advantage of complex **1** as a catalyst is that it is stable without using excess ligands in addition to giving a high TOF[8] and selectivity at milder conditions. In addition, only small amount of catalyst (0.2 mol %) and short reaction times were required in most cases. Table 1 presents the typical results of carbonylation[9] of various alcohols and olefins. All the reactions except the hydrocarbomethoxylation of styrene (entry 7, Table 1) were carried out in methyl ethyl ketone as a solvent using TsOH and LiX as promoters, where X is Cl⁻ or I⁻.

Scheme 1



Carbonylations of primary, secondary, and tertiary alcohols are demonstrated. Methanol on carbonylation gave acetic acid (50%) and methyl acetate (20%) along with dimethyl ether (28%) and methyl iodide (2%) with a TOF of 41 h^{-1}. Similarly, carbonylation of benzyl alcohol yielded phenylacetic acid (29%) and benzyl phenylacetate (41%) together with dibenzyl ether (25%) and benzyl iodide (5%) (TOF = 25 h^{-1}). In both the cases, LiI was used as a promoter and the reaction rates were much higher than the earlier reported catalyst systems based on palladium (TOF = 5−7 h^{-1} at 140 °C for methanol;[10] TOF = 2−3 h^{-1} at 90 °C for benzyl alcohol[11]).

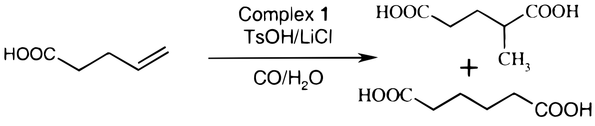
Among the secondary and tertiary alcohols, the important reactions investigated were the carbonylation of 1-(4-isobutylphenyl)ethanol (IBPE) to 2-(4-isobutylphenyl)propionic acid (Ibuprofen)[12] and carbonylation of *tert*-butyl alcohol to pivalic acid. Using complex **1** as the catalyst precursor, high TOFs (up to 804 h^{-1}) (entry 4, Table 1) and up to 99% regioselectivity for Ibuprofen were achieved for the carbonylation of IBPE at moderate reaction conditions (115 °C/5.4 MPa). Here LiCl was used as the halide promoter. The catalytic activity was found to increase with promoters (TsOH/LiCl) and IBPE concentrations as well as with CO partial pressure. The Ibuprofen selectivity remained in the range of 85−99% under these conditions even at lower CO partial pressures such as 1.36 MPa. These results are a significant improvement over the conventional catalyst system $PdCl_2(PPh_3)_2$/HCl (TOF = 50−70 h^{-1} at 130 °C)[12a] which gave high selectivity (>95%) only at high CO pressures of >15 MPa. However, the TOFs were comparable to those of the catalyst system $PdCl_2(PPh_3)_2$/TsOH/LiCl (TOF = 850 h^{-1} at 115 °C) reported in our previous work.[3a]

Under similar conditions, carbonylation of *tert*-butyl alcohol gave pivalic acid (60%) and isovaleric acid (32%) with a TOF of 30 h^{-1} (entry 2, Table 1). Even though the hydrocarbalkoxylation of *tert*-butyl alcohol to isovaleric acid esters was reported earlier,[13] to the best of our knowledge this is the first report in which pivalic acid is demonstrated to be synthesized by transition metal catalyzed carbonylation.[14]

Remarkable improvement in catalytic activity [1-hexene (TOF = 613 h^{-1}), 1-dodecene (TOF = 400 h^{-1}), styrene (TOF = 2600 h^{-1}), and 4-isobutylstyrene (TOF = 1313 h^{-1}) (Table 1)] and regioselectivity were also observed for carbonylation of aliphatic and aryl-substituted terminal olefins[9] using complex **1** as the catalyst precursor. Aryl-substituted terminal olefins yielded the corresponding 2-arylpropionic acids almost regiospecifically. In the case of 1-hexene and 1-dodecene, both branched and linear carboxylic acids were obtained with *i*/*n* ratio of 3.26 and 2.41, respectively.

The carbonylation of a functionalized olefin, 4-pentenoic acid (Scheme 2), using complex **1** gave 2-methylglutaric acid and adipic acid with high rates (TOF = 674 h^{-1}) and isolated[15] yields of 60% and 25%, respectively (entry 10,

Scheme 2



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(6) **Data for 1**: IR (KBr) 1668 vs ($\nu_{C=O}$), 1604 s ($\nu_{C=C}$), 1330 s ($\nu_{O=C-O}$), 568 s cm^{-1} (ν_{Pd-N}). ^{31}P (121. 1 MHz, $CDCl_3$) δ 34.58 s (N trans to PPh_3), δ 36.19 w (N cis to PPh_3). ^{1}H (300 MHz, $CDCl_3$) δ 2.3 s (3H, tolyl CH_3), δ 7−7.9 m (Ph and pyridil).^{13}C (75.5 MHz, $CDCl_3$) δ 21 s (tolyl CH_3), δ 142 s (O═C−O). Anal. Calcd for $C_{31}H_{26}NO_5PPdS\cdot H_2O$: C, 54.75; H, 4.15; N, 2.06; S, 4.71. Found: C, 55.18; H, 4.23; N, 1.91; S, 4.38. The presence of water was detected by ^{1}H NMR and IR spectroscopy.

(7) Jin, H.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton. Trans.* **1995**, 2159.

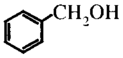
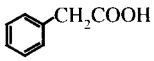
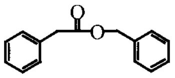
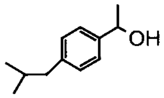
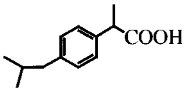
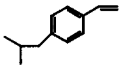
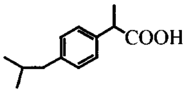
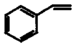
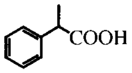
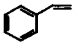
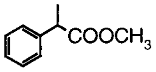
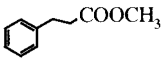
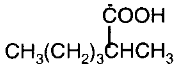
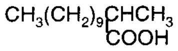
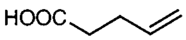
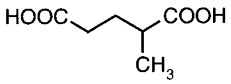
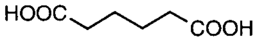
(8) TOF = turnover frequency = number of moles of carbonylation product formed per mole of catalyst per hour.

(9) In a typical experiment,[15] the substrate (28.08 mmol) and the required amount of complex **1**, promoters, water, and solvent were charged to a stirred pressure reactor and the reaction was carried out at 5.4 MPa of CO partial pressure at 115 °C under 1000 rpm for a specified time. After the reaction, the reactor was cooled to room temperature and the products were analyzed by gas chromatography ((FFAP capillary column 25 m × 0.2 mm, FID) and further confirmed by GC-MS, IR, MS, and ^{1}H NMR. Hydrocarbomethoxylation of styrene (14.5 mmol) was carried out using the same method but at 75 °C and 3.4 MPa of CO pressure in methanol as solvent.

(10) Yang, J.; Haynes, A.; Maitlis, P. M. *Chem. Commun.* **1999**, 179.

(11) Lin, Y. S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 723.

Table 1. Carbonylation of Alcohols and Olefins Using Palladium Complex **1**[a] as Catalyst

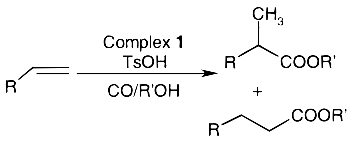
entry	substrate	halide promoter	conversion[b], %	time, h	product (selectivity, %)[b, c]		TOF[g], h^{-1}
1[d].	CH_3OH	LiI	88	8	CH_3COOH CH_3COOCH_3	(50) (20)	41
2[e].	$(CH_3)_3COH$	LiCl	65	10	$(CH_3)_3CCOOH$ $(CH_3)_2CHCH_2COOH$	(60) (32)	30
3.		LiI	90	12	 	(29) (41)	25
4.		LiCl	99	0.6		(99)[f]	804
5.		LiCl	95	0.35		(99)[f]	1313
6.		LiCl	97	0.183		(99)[f]	2600
7[g].		-	97	1.60	 	(55) (45)	150
8[h].	$CH_3(CH_2)_3CH{=}CH_2$	LiCl	85	0.67	 $CH_3(CH_2)_3\overset{COOH}{C}HCH_3$ $CH_3(CH_2)_5COOH$	(75) (23)	613
9[h].	$CH_3(CH_2)_9CH{=}CH_2$	LiCl	83	1	 $CH_3(CH_2)_9\underset{COOH}{C}HCH_3$ $CH_3(CH_2)_{11}COOH$	(70) (29)	400
10.		LiCl	95	0.6	 	(60)[i] (25)[i]	674

[a] Complex **1** = 0.2 mol %. TsOH = 39 mol %, LiX = 39 mol %, H_2O = 238 mol %. [b] Calculated by GC analysis. [c] for carbonylation products. [d] MeOH = 31.25 mmol. [e] H_2O = 35 mol %, tertiary butyl chloride (6-8%) was also detected. [f] corresponding linear carboxylic acid isomer (1%) was also detected. [g] TsOH = 4 mol %. [h] 1-2% of corresponding 2-ethyl carboxylic acid was also detected. [i] isolated yield (the percentage yield in the isolated acid mixture calculated from ^1H NMR analysis)

Table 1). These results are highly promising for the synthesis of dicarboxylic acids.

Hydrocarbalkoxylation of olefins to carboxylic acid esters in the absence of halide promoters is of much current interest (Scheme 3). These reactions are efficiently carried out using cationic palladium complexes, which are the most active

Scheme 3



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(12) (a) Elango, V.; Davenport, K. G.; Murphy, M. A.; Mott, G. N.; Zey, E. G.; Smith, B. L.; Moss, G. L. Eur. Pat. Appl. 400 892, 1990. (b) Jang, E. J.; Lee, K. H.; Lee, J. S.; Kim, Y. G. *J. Mol. Catal. A: Chem.* **1999**, *138*, 25. (c) Seayad, A.; Kelkar, A. A.; Chaudhari, R. V. *Stud. Surf. Sci. Catal.* **1998**, *113*, 883.

(13) Zhou, H.; Lu, S.; Li, H.; Chen, J.; Fu, H.; Wang, H. *J. Mol. Catal. A: Chem.* **1997**, *116*, 329.

catalysts reported for such reactions.[16] Here, the hydrocarbomethoxylation of styrene was carried out using **1** in the presence of TsOH in methanol yielding methyl 2-phenylpropionate and methyl 3-phenylpropionate with a TOF of 150 h^{-1} ($i/n = 0.82$) (entry 7, Table 1), which is significantly higher compared to that of cationic complexes such as $[Pd(MeCN)_2(PPh_3)_2](BF_4)_2$ and $[Pd(PhCN)_2(PPh_3)_2](BF_4)_2$ reported in the literature (TOF in the range of 10−15 h^{-1} at 80 °C)[16a] and is comparable to that of the catalyst system $Pd(OAc)_2/4PPh_3/TsOH$ (TOF = 200 h^{-1} at 75 °C) as previously reported by us.[16b,c]

The reusability of complex **1** as a catalyst was checked by carrying out the recycle by adding fresh styrene to the final reaction mixture (of entries 6 and 7) after attaining complete conversion, and no significant loss in catalytic activity and selectivity was observed. All these observations indicate that complex **1** is highly active toward carbonylation and the labile sites provide easy coordination of substrates, thereby providing high reaction rates. It can act as an alternative for classical neutral palladium complexes such as $PdCl_2(PPh_3)_2$ as well as cationic complexes such as $Pd(PPh_3)_2(OTs)_2$ or $[Pd(PhCN)_2(PPh_3)_2][BF_4]_2$. Any of the two catalytic cycles involving Pd^0/Pd^{II} or Pd^{II}/Pd^{IV} seems to be possible for the carbonylation of alcohols and olefins in the presence of LiX promoter, in which case the reaction proceeds through the corresponding halo derivatives as intermediates.[3] In the case of hydrocarbomethoxylation of styrene, the active catalytic species might be a palladium hydrido complex that activates the olefin by insertion to the Pd−H bond as described in our previous reports.[16c,17] Although more studies are required to further investigate the catalytic properties and reaction mechanism, it is noteworthy that this novel palladium complex is a versatile catalyst for the carbonylation of a variety of substrates.

In conclusion, we have shown that a novel palladium complex consisting of chelating anionic pyridine-2-carboxylato and labile tosylato ligands is a highly active catalyst for carbonylation of a variety of organic alcohols and olefins. The catalyst is stable under the reaction conditions even in the absence of excess phosphine ligands and also provides high turnovers and selectivity. The kind of new complex described here also has additional advantageous properties such as easy accessibility and possible derivatization to form catalysts of desired steric, electronic, and physical properties. One such potential derivative is its water-soluble analogue, studies on which are currently in progress at our laboratory.

Acknowledgment. S.J. and A.S. thank the CSIR (Council of Scientific and Industrial Research), India, for a research fellowship.

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(14) Conventional method for the synthesis of pivalic acid is by Koch carbonylation using concentrated H_2SO_4 and BF_3 as catalysts. (a) Koch, H.; *Brennstoff-Chem.* **1955**, *36*, 321. (b) Brilman, D. W. F.; van Swaaij, W. P. M.; Versteeg, G. F. *Chem. Eng. Sci.* **1999**, *54*, 4801.

(15) The detailed procedure is given in ref 3c.

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