

## Communications

### Polymer-anchored palladium catalyst in carbonylation of organic halides – The first example of triphase catalysis<sup>†</sup>

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Polymer-anchored palladium-catalysed carbonylation of organic halides affords oxo esters in reasonable yields under solid-liquid-solid phase transfer conditions at mild pressure and short durations.

Carbonylation of organic halides is of current interest since it leads to many industrially important organic intermediates. Recently, we have demonstrated the efficacy of phase transfer agents in palladium catalysed oxidation of primary and secondary alcohols<sup>1</sup> and carbonylation of organic halides<sup>2</sup> in effective yields at mild pressures and short durations under biphase, solid-liquid system.

We report in this communication a triphase<sup>3</sup>, solid-liquid-solid catalytic system consisting of polymer-anchored Pd(II)Cl<sub>2</sub> as catalyst, sodium hydrogen carbonates as base and tetrabutylammonium iodide as phase transfer agent (PTA) in ethanol for carbonylation of organic halides to give corresponding ethyl esters. Although a variety of reactions catalysed by polymer-anchored metal complexes are reported<sup>4,5</sup>, this is incidentally the first application of a triphase catalytic system for carbonylation of organic halides.

Polymer-anchored palladium(II) chloride was prepared from diphenyl-phosphinated polystyrene [Fluka AG, copolymer of 98% styrene and 2% diphenylphosphinated divinylbenzene, 200-400 mesh, 3 mmole triphenylphosphine (g resin<sup>-1</sup>)] and PdCl<sub>2</sub> by the known procedure<sup>6</sup>. The P/Pd ratio was 0.895.

Carbonylation of organic halides was carried out by the following general procedure: A solution of benzyl chloride (10 mmole) in ethanol (40 ml) was placed in 500-ml flask of Parr hydrogenator and to this were added tetrabutylammonium iodide (1 mmole), sodium hydrogen carbonate (25 mmole) and polymer-anchored palladium chloride (45 mg contains 10.5 mg of metal). The Parr hydrogenator was filled with CO gas to 16 psi and

Table 1 - Carbonylation of halides with polymer-anchored palladium(II) chloride

(Reaction time = 6 hr; temp. = 70°C; CO pressure = 16 psi)

Entry	Halide	Product	Yield (%)	
			with PTA	without PTA
1	PhI		60	55
2	PhCH <sub>2</sub> Cl		63	28
3	PhCH <sub>2</sub> Br		65	30
4	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl		70	32
5*	n-Bul		56	45

Reaction time = 8 hr; temp. = 80°C; CO pressure = 30 psi

the temperature adjusted to 70°C. After 6 hr, the mixture was filtered and concentrated. The residue was diluted with water and extracted with ether. The ethereal solution was concentrated and upon Kugel-rohr distillation pure ethyl phenylacetate was obtained in 60% yields.

The use of phase transfer agents in carbonylation reactions offers distinct advantages over polymer-anchored catalysis which is clearly evident in the set of reactions conducted with and without PTA, as shown in Table 1. Further, the efficacy of PTA under solid-liquid-solid phase transfer conditions is unambiguously demonstrated (see entries 2-5 in Table 1) which is not conspicuous in carbonylation of benzyl halides under liquid-liquid phase transfer conditions<sup>7</sup>. However the efficacy of PTA is not distinct in carbonylation of iodobenzene. The versatility of this system is exemplified by carbonylation of different substrates. When chlorobenzyl chloride (entry 4) was carbonylated the chlorine attached to aromatic ring was unaffected. The activity of recovered catalyst was tested for the carbonylation of benzyl chloride for two recycles under triphase catalytic conditions and it was found that the yield of carbonylated product decreased by 10% in each recycle.

In conclusion, the present system amply demonstrates, for the first time, the efficacy of triphase catalysis in organometallic chemistry and provides an easy separation of precious palladium catalyst from the reaction medium, an essential requirement for any industrial process.

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