

## Simple preparation of bimetallic palladium-copper catalysts for selective liquid phase semihydrogenation of functionalized acetylenes and propargylic alcohols

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Silica supported palladium-copper catalysts were obtained in a fast and simple preparation method by reduction of bimetallic organometallic compounds on the support surface in the liquid phase at room temperature. The supported bimetallic particles were analysed by TEM and EDAX. Directly after preparation the silica supported palladium-copper catalysts could be used in the semihydrogenation of triple bonds. The catalysts are selective in the hydrogenation of acetylenes and propargylic alcohols giving high yields of either olefins or saturated hydrocarbons, depending on reaction time. In addition, the catalytic system shows reasonable selectivity towards *cis*-olefins in the hydrogenation of disubstituted acetylenes.

### 1. INTRODUCTION

Catalytic liquid phase semihydrogenation of acetylenes is an important industrial and laboratory reaction, especially in fine chemical synthesis [1]. The use of supported metal catalysts for this selective hydrogenation readily facilitates the separation of organic products from the catalyst. However, liquid phase reactions with supported catalysts tend towards mass transport limitation [2] and, therefore, the support particles should be between 1 and 10  $\mu\text{m}$  in size; this avoids transport limitations and separation problems. With support particles of this size high temperature reduction in a flow of  $\text{H}_2$  gas is very difficult and to avoid this step it is possible to prepare supported metal particles by decomposing organometallic compounds under mild conditions [3-5].

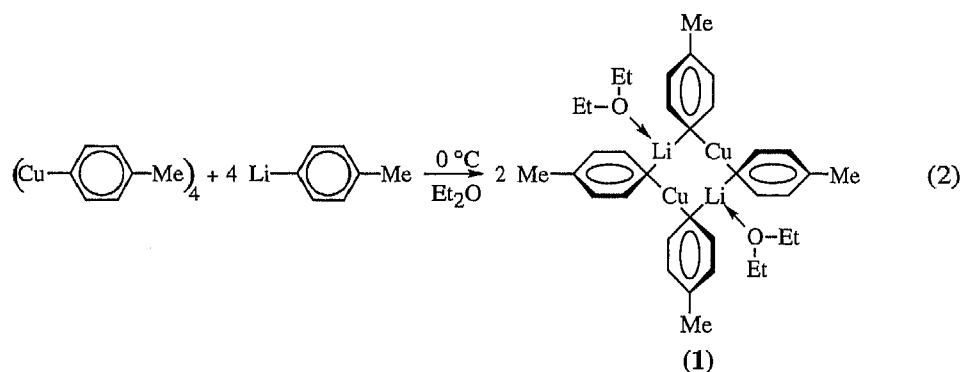
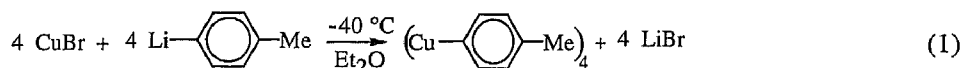
As part of a major research topic concerning characterization and mode of operation of novel (bi-)metallic catalysts for liquid phase catalysis, we have now developed a fast and simple preparation method for supported bimetallic catalysts, even of less noble metals. This method involves reduction of bimetallic

organometallic compounds on the support surface in the liquid phase at room temperature. This method has been used to prepare silica supported palladium-copper catalysts (Pd/Cu/SiO<sub>2</sub>) which were tested in the liquid phase semihydrogenation of functionalized acetylenes and propargylic alcohols.

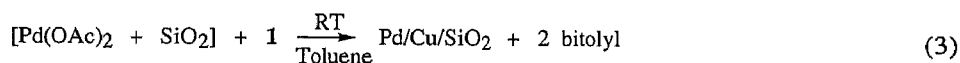
## 2. RESULTS AND DISCUSSION

### 2.1. Catalyst preparation

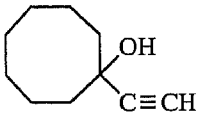
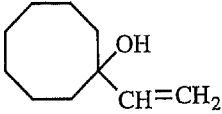
The organometallic copper precursor is synthesized in two steps. First *p*-tolylcopper, Cu<sub>4</sub>(*p*-tolyl)<sub>4</sub>, is prepared from *p*-tolyllithium and copper(I) bromide in diethyl ether. Reaction between *p*-tolylcopper and a second equivalent of *p*-tolyllithium affords the cuprate [6-8]. (See equations 1-2.)



Addition of a toluene solution of the cuprate, Cu<sub>2</sub>Li<sub>2</sub>(*p*-tolyl)<sub>4</sub>·2Et<sub>2</sub>O (1), to a solution of palladium(II) acetate in toluene leads to the *in situ* formation of a thermally unstable organocopper complex in which the lithium atom of 1 has been replaced by the more electronegative precious metal. Subsequent reductive elimination of the organic tolyl group from the unstable bimetallic complex in the presence of silica affords supported bimetallic particles, which without further treatment are an active catalytic system. (Equation 3)



**Table I.**  
Liquid phase semihydrogenation of monosubstituted acetylenes (5 mmol)  
catalysed by Pd(4 w%)/Cu(2 w%)/SiO<sub>2</sub> (circa 35 mg) in ethanol.

Substrate	$t_{\max}^a$ (min)	Semihydrogenated product	Yield <sup>b,c</sup> (%)
Ph-C≡CH	5	Ph-CH=CH <sub>2</sub>	95
$\begin{array}{c} \text{OH} \\   \\ \text{Me}-\text{C}-\text{C}\equiv\text{CH} \\   \\ \text{Me} \end{array}$	11	$\begin{array}{c} \text{OH} \\   \\ \text{Me}-\text{C}-\text{CH}=\text{CH}_2 \\   \\ \text{Me} \end{array}$	98
$\begin{array}{c} \text{OH} \\   \\ \text{Et}-\text{C}-\text{C}\equiv\text{CH} \\   \\ \text{Me} \end{array}$	2	$\begin{array}{c} \text{OH} \\   \\ \text{Et}-\text{C}-\text{CH}=\text{CH}_2 \\   \\ \text{Me} \end{array}$	97
$\begin{array}{c} \text{O} \quad \text{Me} \\    \quad   \\ \text{Me}-\text{C}-\text{O}-\text{C}-\text{C}\equiv\text{CH} \\ \quad \quad   \\ \quad \quad \text{Et} \end{array}$	3	$\begin{array}{c} \text{O} \quad \text{Me} \\    \quad   \\ \text{Me}-\text{C}-\text{O}-\text{C}-\text{CH}=\text{CH}_2 \\ \quad \quad   \\ \quad \quad \text{Et} \end{array}$	95
	2		94

<sup>a</sup>Time for maximum percentage of semihydrogenated compound. <sup>b</sup>Yield at 100% alkyne conversion determined by G.C. peak area analysis. <sup>c</sup>In all cases the by-product was the fully saturated compound.

## 2.2. Catalytic hydrogenations

To test the selectivity of the bimetallic system, monosubstituted acetylenes (Table I) and disubstituted acetylenes (Table II) were hydrogenated with the use of the silica supported palladium-copper catalysts. The yields of the olefins at 100% conversion of the acetylene are given. However, in all cases with longer hydrogenation times it was possible to end up with the fully saturated product.

Table II.

Liquid phase semihydrogenation of disubstituted acetylenes (5 mmol) catalysed by Pd(4 w%)/Cu(2 w%)/SiO<sub>2</sub> (circa 35 mg) in ethanol.

Substrate	$t_{\max}^a$ (min)	Semihydrogenated product	Yield <sup>b,c</sup> (%)
Ph-C≡C-Ph	6	Ph-CH=CH-Ph	<i>cis</i> 85 <i>trans</i> 4
$\begin{array}{c} \text{H} \qquad \qquad \text{H} \\   \qquad \qquad   \\ \text{HO}-\text{C}-\text{C}\equiv\text{C}-\text{C}-\text{OH} \\   \qquad \qquad   \\ \text{H} \qquad \qquad \text{H} \end{array}$	20	$\begin{array}{c} \text{H} \qquad \qquad \text{H} \\   \qquad \qquad   \\ \text{HO}-\text{C}-\text{CH}=\text{CH}-\text{C}-\text{OH} \\   \qquad \qquad   \\ \text{H} \qquad \qquad \text{H} \end{array}$	<i>cis</i> 99 <i>trans</i> - <sup>d</sup>
$\begin{array}{c} \text{OH} \\   \\ \text{H}-\text{C}-\text{C}\equiv\text{C}-\text{Ph} \\   \\ \text{Me} \end{array}$	3	$\begin{array}{c} \text{OH} \\   \\ \text{H}-\text{C}-\text{CH}=\text{CH}-\text{Ph} \\   \\ \text{Me} \end{array}$	<i>cis</i> 80 <i>trans</i> 3
$\begin{array}{c} \text{OH} \\   \\ \text{H}-\text{C}-\text{C}\equiv\text{C}-\text{Ph} \\   \\ \text{Ph} \end{array}$	5	$\begin{array}{c} \text{OH} \\   \\ \text{H}-\text{C}-\text{CH}=\text{CH}-\text{Ph} \\   \\ \text{Ph} \end{array}$	<i>cis</i> 88 <i>trans</i> - <sup>d</sup>
$\begin{array}{c} \text{OH} \\   \\ \text{H}-\text{C}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-4\text{-OMe} \\   \\ \text{Ph} \end{array}$	6	$\begin{array}{c} \text{OH} \\   \\ \text{H}-\text{C}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-4\text{-OMe} \\   \\ \text{Ph} \end{array}$	<i>cis</i> 85 <i>trans</i> - <sup>d</sup>

<sup>a</sup>Time for maximum percentage of semihydrogenated compound. <sup>b</sup>Yield at 100% alkyne conversion determined by G.C. peak area analysis. <sup>c</sup>In all cases the by-product was the fully saturated compound. <sup>d</sup>No *trans* isomer was detected.

### 2.3. Catalyst characterization

Transmission Electron Microscopy (TEM) measurements on the catalysts containing palladium and copper in a ratio of either 1:1 or 1:2 showed a good dispersion of the metal particles (2-5 nm) over the support. Energy Dispersive X-ray Analysis (EDAX) on the samples revealed the presence of both metals in each examined particle. By doubling the amount of copper a proportionate increase of copper content in the metal particles was detected as expected.

### 3. EXPERIMENTAL

#### 3.1. General considerations

Reactions were performed in an atmosphere of dinitrogen using Schlenk techniques. Toluene, benzene, diethyl ether and pentane were freshly distilled from sodium benzophenone-ketyl. All other solvents were used as received.

The support material used was silica OX-50 (surface area 50 m<sup>2</sup>/g) which was purchased from Degussa. Before usage the silica was boiled in bi-distilled water and dried *in vacuo* at 200 °C for 3 d to increase the amount of silanol groups.

Pd(OAc)<sub>2</sub> (47.35 % Pd) was purchased from Degussa. The compounds 4-iodotoluene, n-butyllithium (1.6 M in hexane), 3-methyl-1-pentyn-3-ol, 2-butyne-1,4-diol, phenylacetylene, diphenylacetylene, 1-ethynyl-1-cyclohexanol and 2-methyl-3-butyne-2-ol were obtained from Acros. Other propargylic alcohols were prepared according to the literature [9,10] and purified by kugelrohr distillation and crystallization. The substrates were analysed by G.C., G.C.M.S. and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy prior to use. Complex Cu<sub>2</sub>Li<sub>2</sub>(*p*-tolyl)<sub>4</sub>(Et<sub>2</sub>O)<sub>2</sub> was prepared according to literature procedures [3,4] and analysed by <sup>1</sup>H NMR spectroscopy.

The NMR spectra were recorded on Bruker AC200 (200 MHz) and AC300 (300 MHz) spectrometers at ambient temperature in NMR solvents obtained from ISOTEC Inc.. G.C. analysis were performed on Unicam PU4600 and PU610 apparatus with 30 m J&W Scientific DB-1, DB-17 and AT-SILAR capillary columns and flame ionization detectors. Product yields were determined by peak area analysis; response factors for selected substrates and products were found to be virtually identical. Internal standards were used in the initial stage of this study, but were found to influence the catalyst characteristics. G.C.M.S. was performed on a Unicam Automass apparatus combined with 610 series G.C. apparatus equipped with 30 m J&W Scientific DB-1 and DB-17 columns. TEM-EDAX was performed on a Phillips CM 200 microscope equipped with a field emission gun. TEM-EDAX samples were prepared by application of a few droplets of a suspension of the catalyst in ethanol onto a holey carbon film which was supported by a nickel grid after which the ethanol was allowed to evaporate.

#### 3.2. Preparation of the copper precursor [Cu<sub>2</sub>Li<sub>2</sub>(*p*-tolyl)<sub>4</sub>(Et<sub>2</sub>O)<sub>2</sub>]

**Preparation of [Li(*p*-tolyl)].** To a solution of 8.76 g (40.2 mmol) 4-iodotoluene in *ca.* 30 mL toluene was added 1.05 equivalent of n-butyllithium at 0 °C. The resulting white suspension was stirred for 30 min., after which the slightly yellow solution was decanted. The white residue was washed with pentane (5 x 50 mL) and dried *in vacuo*. Prior to the next preparation step the white solid was dissolved in diethyl ether, centrifuged and decanted. After evaporation of the solvent a white solid was obtained. Yield 3.70 g (94%).

**Preparation of [Cu<sub>4</sub>(*p*-tolyl)<sub>4</sub>].** To a suspension of 2.09 g (14.6 mmol) CuBr in diethyl ether was slowly added a solution of 1.47 g (15.0 mmol) *p*-tolyl lithium in

ca. 15 mL diethyl ether at  $-78\text{ }^{\circ}\text{C}$ . After 1 h the suspension was allowed to warm to  $0\text{ }^{\circ}\text{C}$ , after which the intense yellow precipitate was isolated by decantation, washed with cold ( $0\text{ }^{\circ}\text{C}$ ) diethyl ether ( $4 \times 50\text{ mL}$ ) and dried *in vacuo*. Yield 1.34 g (62%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 300 MHz):  $\delta$  8.02 (d, 8 H,  $^3J_{\text{HH}} = 7.5\text{ Hz}$ , aryl), 6.86 (d, 8 H,  $^3J_{\text{HH}} = 7.5\text{ Hz}$ , aryl), 1.96 (s, 12 H,  $\text{CH}_3$ ).

**Preparation of  $[\text{Cu}_2\text{Li}_2(p\text{-tolyl})_4(\text{Et}_2\text{O})_2]$ .** To a suspension of 0.70 g (5.0 mmol) *p*-tolylcopper in diethyl ether (25 mL) was slowly added a solution of 0.53 g (5.4 mmol) *p*-tolyl lithium in diethyl ether (20 mL) at  $0\text{ }^{\circ}\text{C}$ . The resulting greenish solution was stirred for 1 h during which time a white precipitate of the product formed. The solid was isolated by decantation, washed twice with pentane and recrystallized from diethyl ether. Yield 1.08 g (66%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 300 MHz):  $\delta$  8.37 (d, 8 H,  $^3J_{\text{HH}} = 7.2\text{ Hz}$ , aryl), 7.07 (d, 8 H,  $^3J_{\text{HH}} = 7.2\text{ Hz}$ , aryl), 2.78 (q,  $^3J_{\text{HH}} = 7.2\text{ Hz}$ ,  $\text{OCH}_2\text{CH}_3$ ), 2.12 (s, 12 H,  $\text{CH}_3$ ), 0.74 (t,  $^3J_{\text{HH}} = 7.2\text{ Hz}$ ,  $\text{OCH}_2\text{CH}_3$ ).

### 3.3. Preparation of the supported palladium-copper catalysts

Silica supported catalysts with different metal loadings were prepared in several batches: Pd/Cu/SiO<sub>2</sub> (4.0 w% Pd, 2.1 w% Cu; Pd:Cu = 1:1) (I), Pd/Cu/SiO<sub>2</sub> (4.0 w% Pd, 4.2 w% Cu; Pd:Cu = 1:2) (II).

The catalysts were prepared in a reactor vessel of 250 mL. The reactor vessel was equipped with three baffles ( $120^{\circ}$ ) and mechanically stirred with a gas-circulating stirrer (2000 rpm). A red ultrasonically pre-treated solution of palladium(II) acetate in ca. 35 mL toluene was added to an ultrasonically pre-treated suspension of silica in ca. 150 mL toluene using a tube pump (Gilson Minipuls 2, equipped with a PVC tube, type GI 17942 internal diameter 1.52 mm and a Teflon injection tube, outer diameter 1.52 mm). The solution was injected at the height of the stirrer. The formed orange suspension was stirred for 24 h after which a yellow solution of the copper precursor in ca. 50 mL toluene was added by means of the tube pump. This resulted in a dark brown suspension. After stirring for 3 d, dihydrogen was introduced to the resulting black suspension during 3 h to be sure that the reduction process was completed. Stirring was stopped and the colourless solution was decanted from the settled material. The resulting black powder was washed twice with pentane and dried *in vacuo* at room temperature.

Both the activity and selectivity of all catalysts batches were tested in the hydrogenation of 3-methyl-1-pentyn-3-ol before use.

### 3.4 Catalytic hydrogenations

The hydrogenations were performed in a glass reactor vessel applied with a gas-circulating stirrer (2000 rpm) and three vertical glass baffles at atmospheric dihydrogen pressure. The reactor vessel was kept at  $25\text{ }^{\circ}\text{C}$  by circulating thermostated water through the wall of the vessel. In all hydrogenation reactions

the following procedure was executed. The reactor vessel was evacuated and filled with dinitrogen. The catalyst (ca. 35 mg) was added to the reactor followed by addition of 100 mL of ethanol. While stirring the (nitrogen) atmosphere was expelled out of the equipment by subsequent evacuation and flushing with dihydrogen (5x). The suspension was stirred for 1 h under dihydrogen. Next, without stirring, a solution of the substrate (5 mmol) in 1.5 mL ethanol was added with a hypodermic syringe. After the first sample had been taken the hydrogenation reaction was started by switching the stirring device on.

Dihydrogen uptake was monitored using a gas burette system. G.C.(M.S.) samples were taken through a silicon septum with a hypodermic syringe. Substrates and products were analysed with G.C. and confirmed with G.C.M.S.

#### 4. CONCLUSIONS

The method described allows fast and consistent production of silica supported bimetallic palladium-copper catalysts in the liquid phase at room temperature, without the need for high temperature reduction. The catalysts show homogeneous dispersion of the mixed metal particles over the support surface and are ready to use immediately after preparation.

The silica supported palladium-copper catalysts are selective in the hydrogenation of monosubstituted acetylenes giving high yields of either olefins or saturated hydrocarbons, depending on the reaction time. In addition, the catalytic system shows reasonable selectivity towards *cis*-olefins in the hydrogenation of disubstituted acetylenes.

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