# Palladium-catalyzed carbonylation of benzyl chlorides to phenylacetic acids — a new two-phase process [1]

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## Abstract

Palladium-catalyzed carbonylation of substituted benzyl chlorides in a two-phase system at atmospheric carbon monoxide pressure generates the corresponding phenylacetic acids in 80–94% yield. The palladium catalyst is dissolved in the aqueous phase by using water-soluble phosphine ligands. The turnover numbers (TON) are higher than 1500 and turnover frequencies (TOF) of 135 $h^{-1}$ are reached. The length of the induction period observed is in inverse order to the phosphine–palladium ratio. The reaction rate is strongly dependent on the temperature and the initial substrate concentration. Continuous addition of substrates is increasing the life time of the catalyst. The proposed active species is generated via chloride- and hydroxy-bridged palladium dimers.

Keywords: Carbonylation; Water-soluble phosphine; Water-soluble palladium catalyst; Benzylic chlorides; Phenylacetic acids

## 1. Introduction

Phenylacetic acid and substituted derivatives are valuable intermediates in the manufacturing of pharmaceuticals, cosmetics, and fragrances. The current industrial production of phenylacetic acids starts with the corresponding benzyl chloride which is converted by a chloride/cyanide exchange to benzyl cyanide. Subsequent hydrolysis with sulfuric acid yields the phenylacetic acids (Eq. (1)). This two-step process has considerable drawbacks such as formation of a stoichiometric amount of salt, e.g., sodium chloride (exchange reaction) and ammonium sulfate (hydrolysis). Additionally, the introduction of a carbon atom by a cyanide molecule is fairly expensive compared to the much cheaper carbon monoxide (1.40 vs. 0.2 $/kg, respectively).
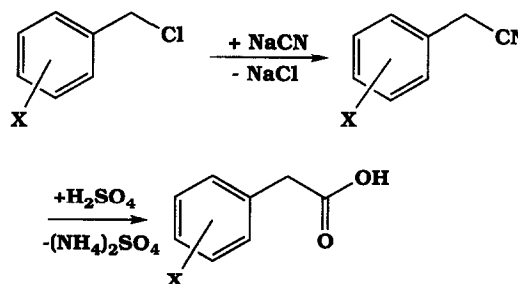
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The transition metal-catalyzed carbonylation of benzyl halides to yield phenylacetic acids was extensively studied in the past [1,16]. Two-phase systems are applied with the catalyst and the substrate being dissolved in the organic phase and an alkaline aqueous solution as the second phase. The phenylacetic acid formed during the reaction is dissolved in the water-phase as the corresponding sodium salt (Fig. 1). The excess of base is necessary for two reasons: The acid $HX$ ($X =$ Cl, Br, I) formed during the carbonylation reaction has to be neutralized to maintain a high reaction rate. Secondly, the catalyst-product separation is achieved only if the phenylacetic acid is deprotonated and dissolved in the aqueous phase.

The crude product is obtained after phase separation, acidification of the water phase, and extraction of the phenylacetic acid with a non-miscible organic solvent. Additional salt is formed as the alkaline aqueous solution is neutralized by the acid. The amount of salt is directly related to the excess of base which is used in the carbonylation step. The final product is isolated by further purification steps from the organic solution. Despite significant disadvan-

tages such as high catalyst loading (5–10 mol% of $Co_2(CO)_8$), indispensable addition of phase transfer reagents, significant metal loss with the product stream, and limitation to the expensive benzyl bromides as starting materials, this process has been reported to be practiced by Montedison [1,16].

The use of water-soluble catalysts [2] for carbonylation of organic halides was scarcely studied in the past [3–7]. In Refs. [3] and [4], ruthenium-EDTA (EDTA = ethylenediaminetetraacetate) and cobalt-TPPTS (TPPTS = triphenylphosphine trisulfonate trisodium salt, 1) are described, respectively. The application of palladium with TPPMS (TPPMS = triphenylphosphine monosulfonate monosodium salt) is described in Ref. [5]. In the case of EDTA and TPPMS modified metal complexes, the product/catalyst separation is insufficient. Loss of metal with the product stream and low product quality due to metal impurities result. The cobalt-TPPTS complex performs only at 20 bar CO pressure and has to be used at concentrations $> 8$ mol% in the double carbonylation of phenylethyl bromide to benzylpyruvic acid. Recently, Monteil and Kalck
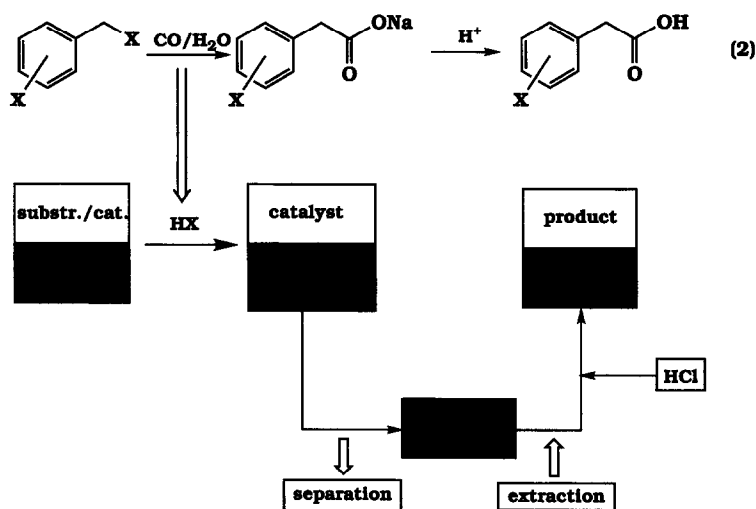


Fig. 1. Two-phase carbonylation of benzyl halides with organic-soluble metal catalysts. Substrate and catalyst are dissolved in the organic phase and an aqueous alkaline solution serves as the second phase (left). During carbonylation acid $HX$ is formed, the substrate converted to the product, which is dissolved in the alkaline aqueous phase (middle). The latter is separated and extracted with an organic solvent. Acid is added to transfer the product as its free acid form into the organic phase (right).

reported the carbonylation of bromobenzene with palladium-TPPTS complexes [6].

The present report describes a new carbonylation process for substituted benzyl chlorides based on a water-soluble palladium catalyst which circumvents most of the aforementioned disadvantages of the current carbonylation process [7].

## 2. Results

### 2.1. Description of the process

The reaction is performed in a two-phase system (see Fig. 2, Eq. (3)). The catalyst consisting of a palladium salt and a water-soluble phosphine is dissolved in an alkaline aqueous solution. The organic phase, typically toluene or xylene, contains the substrate. During the reaction the phenylacetic acid molecule is formed with concomitant consumption of carbon monoxide and HCl production. The caustic solution neutralizes the acid formed (formation of NaCl) and the phenylacetic acid is dissolved in the aqueous phase as the corresponding sodium salt. In contrast to the conventional process (catalyst dissolved in the organic phase), the carbonylation can be performed in an acidic media approaching pH 2 without affecting the
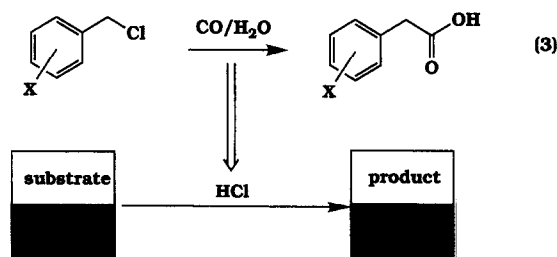


Fig. 2. Two-phase carbonylation of benzyl chlorides with water-soluble catalysts. The substrate is dissolved in the organic phase whereas the catalyst remains in the alkaline aqueous solution (left). The HCl formed during the reaction neutralizes and acidifies the aqueous solution and the product is dissolved in the organic phase (right).

efficient product/catalyst separation. At this pH more than 99% of the phenylacetic acid sodium salt is protonated ($pK_a \approx 4$) and dissolved in the organic phase. After phase separation, the product is isolated from the organic solution. Recrystallization yields the product in $> 99\%$ purity.

### 2.2. Catalytic results

Table 1 summarizes the results obtained for various benzyl chlorides (batchwise process). In all cases a catalyst formed in situ from $PdCl_2$ or $Pd(OAc)_2$ and TPPTS was used. The nature of the palladium source ($PdCl_2$ vs. $Pd(OAc)_2$) did not influence the catalytic results obtained (not shown in the table).

Table 1
Carbonylation of various benzyl chlorides (batchwise procedure) [a]

| Substrate [b] | Catalyst | Conversion (%) | Selectivity [c] (%) | Yield (%) | TON [d] | TOF [e] |
|---|---|---|---|---|---|---|
| BC [f] | Pd(OAc)$_2$/1 | 96 | 92 | 88 | 176 | 8.8 |
| 2-FBC | PdCl$_2$/1 | 98 | 96 | 94 | 189 | 11.8 |
| 4-FBC | Pd(OAc)$_2$/1 | 100 | 82 | 82 | 164 | 13.1 |
| 2-CBC | PdCl$_2$/1 | 98 | 82 | 80 | 159 | 11.3 |
| 4-CBC | PdCl$_2$/1 | 97 | 86 | 83 | 165 | 20.6 |
| 2-MBC | Pd(OAc)$_2$/1 | 99 | 84 | 83 | 166 | 16.6 |

[a] Substrate: Pd: TPPTS = 40: 0.2: 2.0 mmol, 60 mmol NaOH, 30 ml water, 30 ml $o$-xylene, $P_{CO}$ = 1 bar, $T$ = 70°C.
[b] BC = benzyl chloride, 2-FBC = 2-fluorobenzyl chloride, 4-FBC = 4-fluorobenzyl chloride, 2-CBC = 2-chlorobenzyl chloride, 4-CBC = 4-chlorobenzyl chloride, 2-MBC = 2-methylbenzyl chloride.
[c] Byproducts: substituted benzyl alcohols ($ArCH_2OH$, Ar = $XC_6H_4$, $X$ = H, F, Cl, $CH_3$), dibenzyl ethers ($ArCH_2OCH_2Ar$), benzyl phenylacetic acid esters ($ArCH_2C(O)OCH_2Ar$), and toluenes ($ArCH_3$).
[d] mmol(product)/mmol(catalyst).
[e] mmol(product)/[mmol(catalyst) h].
[f] $P_{CO}$ = 20 bar.

Conversions are generally > 96% with high selectivities to the acid. By-products formed are benzyl alcohols (by hydrolysis), dibenzyl ethers (Williams' ether synthesis) and benzyl phenylacetic acid esters. Minor amounts of the substrate are hydrogenolyzed (water–gas shift reaction) to form substituted toluenes. The reaction performed better at higher CO pressure for benzyl chloride only. For all other substrates rates and selectivities dropped at higher CO pressure.

For a more general approach, various transition metals were studied in the carbonylation of 4-fluorobenzyl chloride (4-FBC). The results are summarized in Table 2. As mentioned earlier, cobalt carbonyl has to be applied in > 5 mol% quantities to achieve a significant conversion (entries 1, 2). By increasing the CO pressure, conversion becomes worse (entries 3–6). Even Pd/C showed a tenfold higher activity in presence of TPPTS (entry 7). Under identical reaction conditions, a comparative experiment with TPP (*tri phenyl phosphine*) yielded phenylacetic acid in < 5%. The dependence of the catalytic results on the properties of the phosphine (water-soluble vs. organic-soluble) suggests that palladium is leaching from the support. An active palladium complex might be

formed whose activity is higher in water (Pd/TPPTS) than in the organic medium (Pd/TPP). The activation of a heterogeneous catalyst by phosphines was observed previously by El Ali et al. [8].

$Pd^0$ sources like $Pd(PPh_3)_4$ afford the same results as $Pd^{II}$ species (entry 8). The induction period observed in previous runs (see below) was not shortened. Palladium colloids prepared according to Bönnemann et al. [9] showed no activity at all, with or without addition of TPPTS (entries 9, 10). $PdCl_2$ without added TPPTS is inactive as well (entry 11). Thus, the presence of phosphines is necessary to perform the reaction. Other transition metals like nickel or rhodium are inactive under the applied reaction conditions.

## 2.3. Palladium / BINAS catalyst

The sulfonated diphosphine NAPHOS [10], abbreviated as BINAS (**2**, $Ar = m\text{-}C_6H_4\text{-}SO_3Na$), has shown superior activity in the two-phase hydroformylation of propene [11] and reduction of aromatic nitro compounds [12]. In the present reaction, the catalyst formed from $Pd(OAc)_2$ and BINAS showed a carbonylation

Table 2
Carbonylation of benzyl chlorides with various catalysts [a]

| No. | Catalyst | Substr. [b] | Cat. (mol%) | $M$/P ratio | $P_{CO}$ (bar) | Yield (%) | TON [c] |
|-----|----------|-------------|-------------|-------------|----------------|-----------|---------|
| 1 | $Co_2(CO)_8$/1 | 4-FBC | 5.0 | 1:5 | 1 | 10 | 1.9 |
| 2 | $Co_2(CO)_8$/1 | 4-FBC | 10.0 | 1:2.5 | 1 | 52 | 5.2 |
| 3 | $Co_2(CO)_8$/1 | 4-FBC | 2.0 | 1:2.5 | 20 | 19 | 9.5 |
| 4 | $Co_2(CO)_8$/1 | 4-FBC | 2.0 | 1:5 | 70 | 12 | 6.0 |
| 5 | $Co_2(CO)_8$/1 | BC | 5.0 | 1:5 | 150 | 8 | 1.5 |
| 6 | $Co_2(CO)_8$ | BC | 8.0 | 0 | 50 | 21 | 2.6 |
| 7 | 5% Pd/C/1 | 2-FBC | 0.5 | 1:10 | 1 | 43 | 86 |
| 8 | $Pd(PPh_3)_4$/1 | 4-FBC | 0.5 | 1:10 | 1 | 79 | 158 |
| 9 | Pd-colloid [d]/1 | 4-FBC | 0.5 | 1:10 | 1 | 0 | 0 |
| 10 | Pd-colloid [d] | 4-FBC | 0.5 | 0 | 1 | 0 | 0 |
| 11 | $PdCl_2$ [e] | 4-FBC | 0.5 | 0 | 1 | 0 | 0 |
| 12 | $NiCl_2$/1 | BC | 0.5 | 1:10 | 20 | 0 | 0 |
| 13 | $RhCl_3$/1 | 2-FBC | 0.5 | 1:10 | 1 | 0 | 0 |
| 14 | $RhCl_3$/1 | 2-FBC | 0.5 | 1:10 | 50 | 0 | 0 |

[a] Reaction conditions: 40 mmol substrate, 60 mmol NaOH, 50 ml *o*-xylene, 20 ml water, $T = 80°C$, catalyst concentration in mol% based on substrate.
[b], [c] Explanations see Table 1.
[d] Pd-Colloids prepared according to Ref. [9].
[e] Addition of methyl trioctylammonium chloride (MTOAC) as colloid stabilizer.

Table 3
Pd/BINAS catalyst in the carbonylation of benzyl chloride[a]

| No. | pH [b] | Conversion (%) | Selectivity (%) | Yield (%) | TON [c] | pH [d] |
|---|---|---|---|---|---|---|
| 1 | 12.0 | 99 | 98 | 97 | 97 | 1.0 |
| 2 | 7.0 | 85 | 74 | 63 | 63 | 4.1 |
| 3 | 7.0 | 10 | 4 [e] | < 1 | 0 | 3.5 |
| 4 [f] | 5.8 | 98 | 98 | 96 | 48 | 0.9 |
| 5 | 7.0 | 78 | 94 | 73 | 36 | 1.0 |
| 6 [g] | 5.8 | 40 | 88 | 35 | 140 | 0.8 |
| 7 | 7.0 | 28 | 69 | 19 | 76 | 0.3 |

[a] Reaction conditions: 20 mmol benzyl chloride, 0.2 mmol Pd(OAc)$_2$, 0.8 mmol BINAS, 30 mmol NaOH, 30 ml toluene, 30 ml water, $T = 70°C$, $P_{CO} = 20$ atm.
[b] Initial.
[c] Definition see Table 1.
[d] Final.
[e] Almost exclusive formation of benzyl alcohol.
[f] Fresh catalyst added. Totally employed: 0.4 mmol Pd(OAc)$_2$, 1.6 mmol BINAS.
[g] Reaction conditions: 80 mmol benzyl chloride, 0.2 mmol Pd(OAc)$_2$, 0.8 mmol BINAS, 30 mmol NaOH, 30 ml toluene, 30 ml water, $T = 70°C$, $P_{CO} = 20$ atm.

activity even at acidic conditions (Table 3). After complete conversion of the substrate the catalyst is still active at pH $\approx$ 1. In contrast to the Pd/TPPTS catalyst, no precipitation of palladium is observed at the end of the reaction. Addition of base at the beginning of the next batch run to adjust the pH at 7 is sufficient to
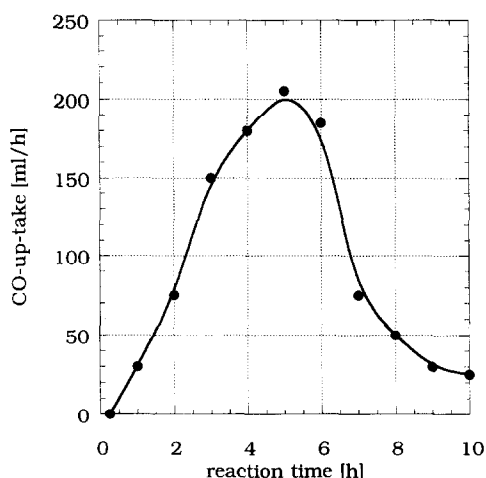
make a second run with the same catalyst solution. Conversion and selectivity are slightly lower. After the third recovery, the catalyst is deactivated effecting almost no conversion. By addition of a fresh equivalent of catalyst solution, high conversion and selectivity are restored (entry 4). However, the catalyst tends to deactivate faster after the first recovery. At high substrate concentrations (entry 6), a freshly prepared Pd/BINAS catalyst shows lower total activity and conversion worsens after the first recycle (entry 7).

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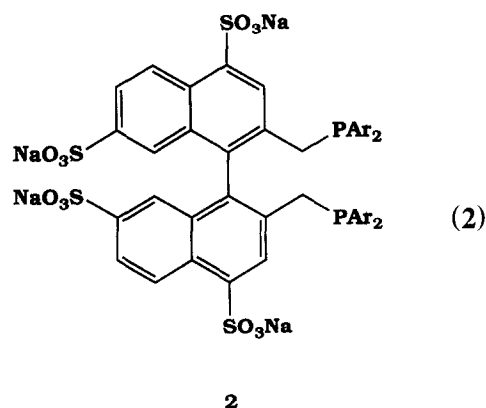
### 2.4. Reaction parameters

In all experiments, an induction period ($t_{ind}$) is observed. In the present report $t_{ind}$ is defined as the time passing until 1 mol% of CO relative to the substrate is consumed. After $t_{ind}$, the catalyst soon reaches its highest activity. A typical CO uptake curve with time is shown in Fig. 3. During the induction period, a small amount of carbon monoxide is consumed and the reaction mixture slowly turns dark. Precipitation of palladium black (powder or particles) is not observed.

Fig. 3. Typical CO-uptake rate curve. Reaction conditions: 0.2 mmol PdCl$_2$, 1.0 mmol TPPTS, 60 mmol NaOH (32 wt%), 20 ml H$_2$O, 40 mmol 4-FBC, 50 ml o-xylene, $P_{CO} = 1$ bar, $T = 70°C$.

### 2.5. Phosphine / Pd ratio

At constant temperature (70°C), the initial activity as determined by the CO-uptake in the

first 2 h is negative order with respect to the TPPTS/Pd ratio (Fig. 4). The initial reaction rate decreases with increasing phosphine/Pd ratios. However, the total activity is lower for small phosphine/Pd ratios as the catalyst deactivates previous to complete conversion. As a compromise between length of induction period and total conversion, the optimized phosphine/Pd ratio is 5:1. Ratios of 10:1 or 20:1 do not further improve the overall performance of the catalyst.

## 2.6. Temperature

The length of the induction period is strongly dependent on the temperature. For a standard run, $t_{ind}$ is reduced from about 6 h at 70°C to about 10 to 15 min at 90°C. However, at higher temperatures the catalyst deactivates considerably faster. Use of a temperature profile during the reaction, e.g., to start with 80–90°C and to reduce the temperature to about 70°C after $t_{ind}$, is advantageous for expanding the life time of the catalyst and for improving the catalytic results.

## 2.7. Initial substrate concentration ($C_0$)

In Fig. 5, the CO up-take curve as a function of time is depicted in dependence of the initial
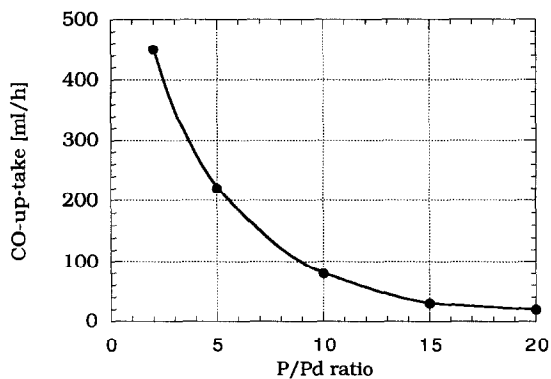


Fig. 4. CO-uptake rate [ml/h] within 2 h of reaction in dependence of the P/Pd ratio. 0.2 mmol PdCl$_2$, variable amounts of TPPTS, 60 mmol NaOH (32 wt%), 20 ml H$_2$O, 40 mmol 4-FBC, 50 ml o-xylene, $P_{CO}$ = 1 bar, T = 70°C.
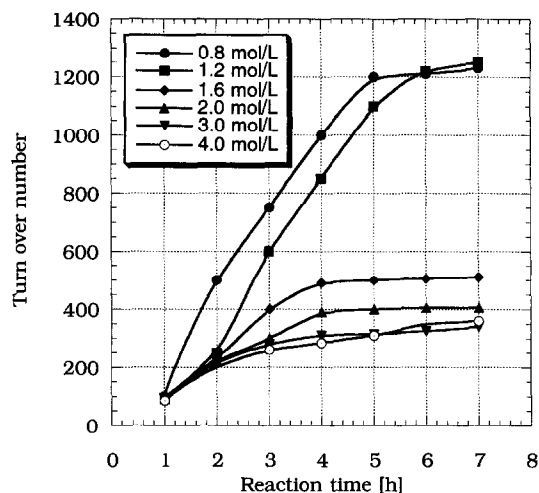


Fig. 5. Total TON of the PdCl$_2$/TPPTS catalyst in dependence of the initial substrate (4-FBC) concentration. 0.2 mmol PdCl$_2$, 1.0 mmol TPPTS, 20 ml H$_2$O, 50 ml o-xylene, mmol NaOH (32 wt%) = 1.5 times of 4-FBC, $P_{CO}$ = 1 bar, T = 70°C.

substrate concentration. After 2 h of reaction, considerable differences are observed. At low substrate concentrations ($C_0$), especially for $C_0$ = 0.8 mol/l, the turnover number (TON) is significantly higher. For the experiments shown in Fig. 5, the quantity of the palladium catalyst in the aqueous phase is kept constant at 0.2 mmol. After 2 h of reaction ($t$ = 2 h), the pH is adjusted to 7.0 and NaOH (60 mmol) and substrate (40 mmol) are added to determine the maximum achievable TON. Base and substrate are added every time after 80% of the substrate is converted (based on CO-uptake). The original volume of o-xylene remains unchanged. The initial substrate concentration has a significant impact on the overall performance of the catalyst. Starting with the lowest $C_0$, the highest TON are reached and vice versa.

## 2.8. Continuous operation

From the previous batch experiments, one can conclude that continuous addition of base and substrate is beneficial to the catalyst's performance. To determine the maximum achievable TON, 1.5 eq. of base and 1 eq. of substrate were added after 80% conversion of the initial

substrate (based on CO-uptake). A maximum TON of 1560 was reached under optimized conditions. In using a temperature profile as described previously, the average turnover frequency (TOF, $[h^{-1}]$) was improved to 135.

## 3. Discussion

### 3.1. Induction period $(t_{ind})$

Based on the generally accepted mechanism for palladium-catalyzed carbonylation reactions, the catalytic cycle starts with a coordinatively unsaturated $Pd^0$ species. In this respect, Grushin and Alper showed that under carbonylation conditions in alkaline solutions and in the presence of a phosphine, a $Pd^{II}$ precursor is reduced to $Pd^0$ by $OH^-$. The phosphine ligand is oxidized at the same time and a highly reactive unsaturated $Pd^0$ species is generated (Eq. (4)) [13]. Carbon monoxide or hydrogen (generated by water–gas shift reaction) can be excluded as the reducing agents. Even after hours of sparging CO through a vigorously stirred boiling benzene solution of $PdCl_2(PPh_3)_2$ and water, no precipitation of palladium was observed [13].



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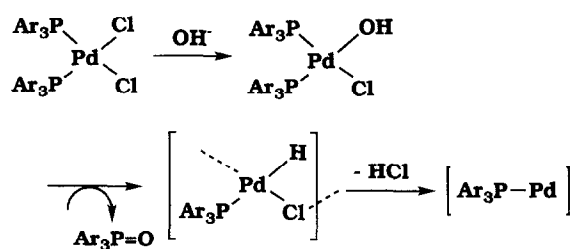
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In the present case, some TPPTS is oxidized during $t_{ind}$ to the corresponding oxide, which

was monitored by $^{31}P$-NMR spectroscopy. However, with TPPTS as a ligand, the precipitation of palladium black is strongly dependent on the pH of the solution. Sparging CO through an aqueous solution of $PdCl_2$/TPPTS precipitation of palladium black is much slower at basic (pH > 11) and acidic (pH < 3) conditions as in the range of 3 < pH < 11. Thus, depending on the pH, carbon monoxide and/or hydroxide may effect the reduction.

### 3.2. Catalytic cycle

The coordinatively unsaturated $Pd^0$ species is believed to undergo oxidative addition by the substrate and forms the chloro bridged dimer 3 (Fig. 6). At basic conditions, an equilibrium of 3 with an hydroxy bridged dimer 4 is probable. In the case of water-insoluble complexes, Alper showed that 3 reacts faster with CO than the hydroxy bridged dimer 4 [13]. After coordination and insertion, carbon monoxide is incorporated and the benzoyl palladium dimer 5 is formed. Under experimental conditions, 5 reacts to the hydroxy dimer 6 which reductively eliminates the phenylacetic acid. The unsaturated $Pd^0$ species [LPd] is re-generated and the catalytic cycle continues.

### 3.3. Deactivation

We assume that deactivation of the catalyst proceeds via formation of inactive palladium agglomerates. Initially, these agglomerates stabilized by TPPTS might be catalytically active. Metal clusters of this kind have been synthesized by Schmid and co-workers [14]. The constantly colorless organic phase during the reaction indicates that the dark colored agglomerates are dissolved by the water-soluble ligand and remain in the aqueous solution. The aggregation proceeds up to a particle size where the dissolution of the agglomerate cannot be maintained by the ligand and palladium black starts to precipitate. These metal particles, in contrast to the

stabilized agglomerates, are not catalytically active.

## 4. Conclusion

One may conclude from these experiments that base, carbon monoxide and substrate are essential to start and maintain the catalytic cycle. If one of these components is not available in sufficiently high concentrations the agglomeration of palladium atoms accelerates thus terminating the catalysis. The high activity of the palladium-TPPTS catalyst relative to $PdCl_2$/TPP is founded in its presence in the water-phase. The $Cl^-$ and $OH^-$ present in the aqueous solution stabilize the active intermediates in the catalytic cycle. The concentrations of $Cl^-$ and $OH^-$ in the organic phase are by far lower. Due to this lack of stabilization, water-insoluble catalysts are less reactive and conversions and yields are inferior compared with their water-soluble counterparts. Recently, the impor-

tance of hydroxy transition metal complexes in general and especially in catalysis has been recognized [15]. Wherever these hydroxy complexes play a role in a catalytic cycle, water-soluble catalysts should show significant improvements, not only because of product/catalyst separation but also for the sometimes higher magnitudes of activity. So far, the reactivity of Pd/BINAS catalysts at acidic conditions in not understood and further investigations are underway to explain this phenomena.

## 5. Experimental

### 5.1. General procedure

Under inert gas atmosphere (Ar), the reagents are charged to a 250 ml-four-neck flask equipped with thermometer, reflux condenser and gas sparger. The gas sparger is connected to a gas burette. The inert gas is removed by evacuating and refilling the system with carbon monoxide.
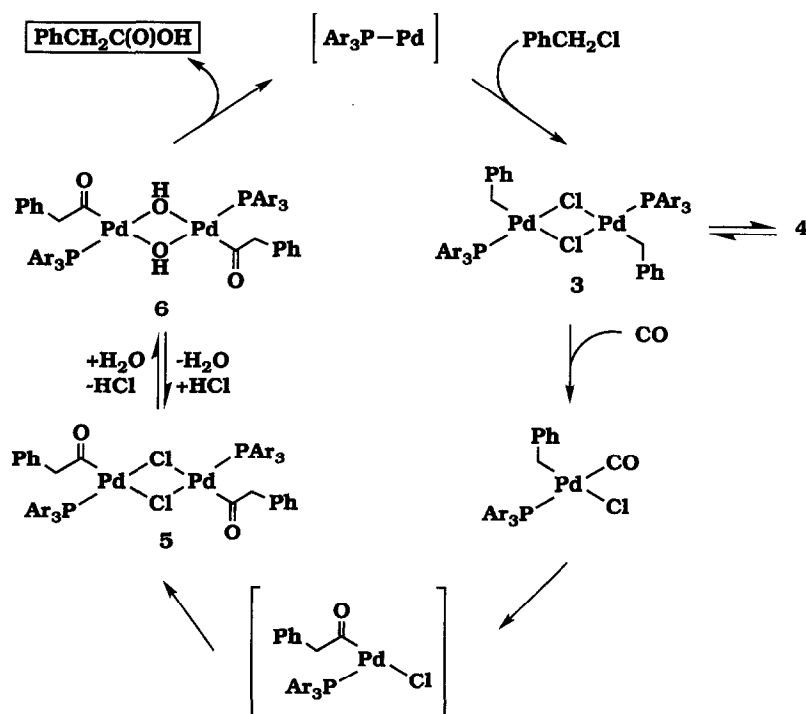


Fig. 6. Postulated mechanism for the formation of phenylacetic acid by carbonylation of benzyl chloride.

The reaction mixture is heated to the desired temperature (70–90°C). The CO uptake is measured with help of the gas burette. The reactions under carbon monoxide pressure are performed in a 200 ml Hastelloy-C autoclave with magnetic stirrer. At the end of the reaction, the pH is measured. If necessary, dilute HCl is added to adjust the pH to 1–2. The organic solution is examined by GC for preliminary results. The organic phase is separated and the aqueous phase extracted twice with a small amount of organic solvent. The organic phases are combined. The solvent is evaporated and the residue re-crystallized from an iso-hexane/o-xylene (1/1 vol./vol.) solvent mixture. The isolated solid material contains the product in > 99% purity. The individual compounds are identified by GC and NMR analysis. The mother liquor contains 10–15 wt% phenylacetic acid. The data on TON, TOF, and yields are based on the isolated products.

## Acknowledgements

## References

[1] M. Beller, B. Cornils, C.-D. Frohning and C.W. Kohlpaintner, J. Mol. Catal. A: Chem. 104 (1995) 17; M. El-Chahawi and U. Prange, Chem. Z. 102 (1978) 1; L. Cassar and M. Foa, US 4128572 (1978); H. des Abbayes and A. Bulop, Tetrahedron Lett. 21 (1980) 4343; H. Alper, K. Hashem and J. Heveling, Organometallics 1 (1982) 775; H. Alper, N. Hamel, D.J.H. Smith and J.B. Woell, Tetrahedron Lett. 26 (1985) 2273; H. Urata, N.-X. Hu, H. Maekawa and T. Fuchikama, Tetrahedron Lett. 32 (1991) 4733; C.S. Chin, H.J. Jung and S.-G. Hong, Bull. Korean Chem. Soc. 13 (1992) 391.

[2] W.A. Herrmann and C.W. Kohlpaintner, Angew. Chem. 105 (1993) 1588; Angew. Chem., Int. Ed. Engl. 32 (1993) 1524.

[3] M.M.T. Khan, S.B. Halligudi and S.H.R. Abdi, J. Mol. Catal. 44 (1988) 179.

[4] E. Monflier, A. Mortreux and F. Petit, Appl. Catal. A 102 (1993) 53; E. Monflier and A. Mortreux, J. Mol. Catal. 88 (1994) 295.

[5] T. Okano, I. Uchida, T. Nakagaki, H. Konishi and J. Kiji, J. Mol. Catal. 54 (1989) 65; T. Okano, T. Hayashi and J. Kiji, Bull. Chem. Soc. Jpn. 67 (1994) 2339.

[6] F. Monteil and P. Kalck, J. Organomet. Chem. 482 (1994) 45.

[7] M. Beller and C.W. Kohlpaintner, DE 4415681 and DE 4415682 (1994).

[8] B. El Ali, G. Vasapollo and H. Alper, J. Org. Chem. 58 (1993) 4739.

[9] H. Bönnemann, W. Brijoux, R. Brinkmann, E. Dinjus, T. Joußen and B. Korall, Angew. Chem. 103 (1991) 1344; Angew. Chem., Int. Ed. Engl. 30 (1991) 1312.

[10] K. Tamao, H. Yamamoto, H. Matsumoto, N. Miyake, T. Hayashi and M. Kumada, Tetrahedron Lett. 16 (1977) 1389.

[11] W.A. Herrmann, C.W. Kohlpaintner, R.B. Manetsberger, H. Bahrmann and H. Kottmann, J. Mol. Catal. A: Chem. 97 (1995) 65.

[12] A.M. Tafesh and M. Beller, Tetrahedron Lett. 36 (1995) 9305.

[13] V.V. Grushin and H. Alper, Organometallics 12 (1993) 1890.

[14] G. Schmid and A. Lehnert, Angew. Chem. 101 (1989) 773; Angew. Chem., Int. Ed. Engl. 28 (1989) 780; G. Schmid, N. Klein, L. Korte, U. Kreibig and D. Schönauer, Polyhedron 7 (1988) 605; S. Peschel and G. Schmid, Angew. Chem. 107 (1995) 1568; Angew. Chem., Int. Ed. Engl. 34 (1995) 1442.

[15] J.W. Gilje and H.W. Roesky, Chem. Rev. 94 (1994) 895.

[16] L. Cassar, Chim. Ind. 67 (1985) 256.