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Rhodium-catalyzed reductive carbonylation of iodobenzene

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Rhodium-phosphine complexes are efficient catalysts for the reductive carbonylation of iodobenzene to benzaldehyde.

Aromatic aldehydes belong to one of the most useful classes of products as far as the formyl group can be easily involved in C–C, C–N and C–S coupling reactions and other transformations. Generally, they are synthesized by the Gattermann–Koch, Reimer–Tiemann, Vielsmeier–Haag, and Duff reactions. However, these methods suffer from drawbacks like low yield, poor selectivity and generating waste and by-products.[1,2] Alternatively, the catalytic formylation (reductive carbonylation) of aryl halides with synthesis gas in the presence of palladium-phosphine complexes was reported in 1974 by Schoenberg and Heck (Scheme 1).[3] However, high pressure (8–10 MPa) and temperature (125–150 °C) as well as high catalyst loading are obvious limitations of this method. Lately, palladium/di-1-adamantyl-*n*-butylphosphine,[4,5] palladium/di-*tert*-butylphosphinite,[6] and $Pd(acac)_2$/dppm[7] systems have been proposed. Despite high yields of aldehydes were reached, serious disadvantages of these catalysts are low turnover frequency (10–25 h^{-1}) and sophisticated ligands used in catalyst formulations.

$$ArX + CO + H_2 \xrightarrow[base]{Cat.} ArCHO$$

X = I, Br

Scheme 1

Rhodium complexes are well-known homogeneous catalysts for olefin hydrogenation, hydroformylation and carbonylation of methanol. Surprisingly, rhodium seems to be unexplored as a catalyst for the reductive carbonylation of aryl halides. This encouraged us to test rhodium salts and complexes in the reductive carbonylation of iodobenzene as a model substrate.

The target reaction is accompanied by reductive dehalogenation leading to the formation of biphenyl, trace amounts of benzene and some unidentified heavier products. Rhodium(III) chloride in the absence of stabilizing phosphine ligands gave only a poor yield of aldehyde but greater amounts of benzene and biphenyl. Good results were obtained with $HRh(CO)(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$.† These catalysts surpass the standard palladium complex $PdCl_2(PPh_3)_2$ in terms of selectivity to benzaldehyde (Table 1).

† Catalytic runs were carried out in a pressurized 50 ml glass-lined steel reactor equipped with a magnetic stirrer and arrangements for automatic temperature control. The reactor was charged with reagents and a catalyst, flushed with CO/H_2 (1:1) and filled with synthesis gas up to a desired pressure. Then, the stirrer was switched on and the reactor was heated to a desired temperature. After reaction complete the reactor was cooled to ambient temperature and depressurized, the reaction mixture was extracted with diethyl ether and analyzed by GC with nonane as an internal standard. The product composition was confirmed by ^1H NMR analysis.

Table 1 Effect of catalyst on the reductive carbonylation of iodobenzene. Reaction conditions: 4.5 mmol of PhI, 22 μmol of catalyst, 1.5 equiv. of NEt_3 and 5 ml of toluene. P = 1 MPa (CO/H_2, 1:1), 4 h.

Catalyst	T/°C	Conversion (%)	Yield (%)		
			PhCHO	Benzene	Biphenyl
$PdCl_2(PPh_3)_2$	100	67.0	48.0	0.1	3.5
$RhCl_3 \cdot 4H_2O$	100	18.0	2.3	10.6	2.4
$HRh(CO)(PPh_3)_3$	100	65.9	58.7	7.0	–
$RhCl(CO)(PPh_3)_2$	100	67.0	56.9	7.0	–
$RhCl(CO)(PPh_3)_2$	90	43.9	37.2	0.1	–
$RhCl(CO)(PPh_3)_2$	110	100	85.4	11.9	–
$RhCl(CO)(PPh_3)_2$	120	100	85.3	11.8	2.8

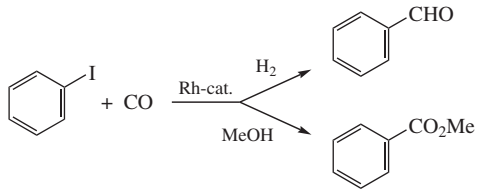
To find out the best reaction conditions, the effects of temperature, synthesis gas pressure, bases and solvents on the reaction have been studied. Decreasing temperature to 90 °C in the presence of $RhCl(CO)(PPh_3)_2$ led to a sharp decrease in both iodobenzene conversion and benzaldehyde yield. On the contrary, 100% conversion and a high yield of benzaldehyde (85%) were achieved at 110–120 °C (Table 1).

Aromatic solvents such as toluene and *o*-xylene seem to be the most suitable media, like previously mentioned for palladium-catalyzed formylation.[4–7] Other solvents such as heptane, 1,4-dioxane, methyl ethyl ketone, DMF and acetonitrile gave a poor yield of benzaldehyde. Virtually no reaction occurred in a tetrabutylammonium bromide (TBAB) melt. In a methanol solution, methyl benzoate was the main product (Table 2). Obviously,

Table 2 Effect of solvent and base on the reductive carbonylation of iodobenzene. Reaction conditions: 4.5 mmol of PhI, 22 μmol of $RhCl(CO)(PPh_3)_2$, 1.5 equiv. of base and 5 ml of solvent. T = 110 °C, P = 1 MPa (CO/H_2, 1:1), 2 h.

Solvent	Base	Conversion (%)	Yield (%)	
			PhCHO	Benzene
Toluene	NEt_3	76.9	69.5	7.3
o-Xylene	NEt_3	78.9	68.8	8.5
Heptane	NEt_3	26.3	17.1	5.8
1,4-Dioxane	NEt_3	29.6	18.2	9.5
MeC(=O)Et	NEt_3	37.4	29.6	5.5
DMF	NEt_3	34.0	23.3	6.7
MeCN	NEt_3	19.8	14.5	3.9
TBAB	NEt_3	4.4	1.5	1.4
MeOH	NEt_3	100.0	21.8	5.5[a]
Toluene	NBu_3	30.8	24.4	4.6
Toluene	NPr^i_2Et	63.7	54.4	7.9
Toluene	K_2CO_3	8.8	4.5	1.0
Toluene	Cs_2CO_3	7.6	5.5	0.5

[a] Methyl benzoate (65%) was found in the reaction mixture.



Scheme 2

the methoxycarbonylation of iodobenzene is a competing reaction in the presence of a nucleophile such as methanol (Scheme 2).

The sensitivity of the reaction to the nature of the base should be noted. Replacing NEt_3 with NBu_3 resulted in an almost threefold reduction in the benzaldehyde yield. Somewhat higher but still low yield was achieved with Hünig's base. Inorganic bases such as potassium and cesium carbonates provided poor iodobenzene conversion and benzaldehyde yield (Table 2).

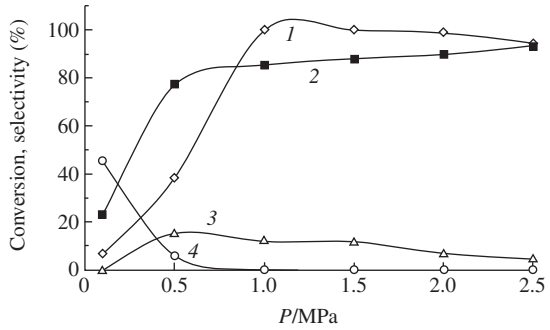


Figure 1 Effect of pressure (CO/H_2, 1:1) on (*1*) iodobenzene conversion and selectivity to (*2*) benzaldehyde, (*3*) benzene and (*4*) and biphenyl. Reaction conditions: 4.5 mmol of PhI, 22 μmol of $RhCl(CO)(PPh_3)_2$, 1.5 equiv. of NEt_3 and 5 ml of toluene, 110 °C, 4 h.

The synthesis gas pressure has a great effect on the course of the reaction. Iodobenzene conversion reaches 100% at a total pressure of about 1 MPa and slightly decreases at higher pressures. Both selectivity and the yield of benzaldehyde increase with pressure while selectivity to benzene decreases. Biphenyl is the main product at atmospheric pressure but it fully disappears at a pressure of 1 MPa or higher (Figure 1).

In conclusion, the obtained results demonstrate that rhodium(I) triphenylphosphine complexes are good catalysts for the reductive carbonylation of iodobenzene. Studies on scope and limitation of the reaction are in progress.

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