Carbonylation of aryl and alkyl halides catalyzed by a binuclear rhodium hydroxide complex

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Abstract

The binuclear rhodium complex $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2] \cdot 2C_6H_6$ is an effective catalyst for the carbonylation of aryl iodides to acids. This Rh-catalyzed carbonylation is applicable to the synthesis of diacids. Iodoalkanes also undergo carbonylation, but in low yields.

Keywords: Rhodium complex; Iodobenzenes; Acids; Carbonylation; Diacids

1. Introduction

The transition metal-catalyzed carbonylation of aryl halides is an efficient and simple method for the synthesis of various carbonyl compounds, including carboxylic acids and esters. Iron, cobalt, nickel, and palladium complexes are commonly used for the carbonylation of aryl iodides and bromides [1–4]. Of particular note is the efficient biphasic palladium-catalyzed carbonylation of aromatic halides, including chloroarenes, under mild conditions [5–7]. In this reaction system, a divalent palladium complex, $[L_2PdCl_2]$ (L = tertiary phosphine) reacts with aqueous alkali (KOH) and aryl halides to form a binuclear palladium complex with two bridging hydroxo ligands, $[L_2Ar_2Pd_2(\mu\text{-}OH)_2]$, as a key catalytic intermediate.

One of us recently developed a new and effective preparative method for the synthesis of $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2] \cdot 2C_6H_6$ (1) [8,9], a binuclear rhodium complex with two bridging hydroxo ligands, by reacting Wilkinson's catalyst with potassium hydroxide in 75–80% yields [10]. It was anticipated that 1 would be of value as a catalyst for the carbonylation of aryl halides. We herein report the highly efficient carbonylation of aryl halides (2), catalyzed by 1, to give the corresponding acids (3) in good yields.
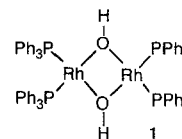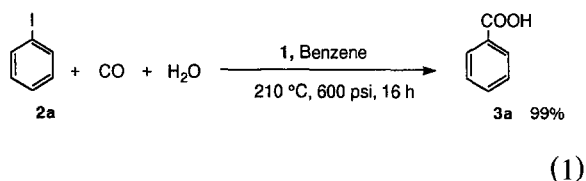

2. Results and discussion

Treatment of iodobenzene (2a) and water, in the presence of a catalytic amount (0.5 mol%)

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of $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2] \cdot 2C_6H_6$ (1) in dry benzene at 210°C and 600 psi of carbon monoxide, for 16 h, affords benzoic acid (3a) in 99% isolated yield (Eq. (1)).

$$(1)$$

The use of a lower reaction temperature (180°C, 120°C) gave benzoic acid (3a) in reduced yields (69, 0%, respectively). Using THF as the solvent afforded 3a in low yield (17%), while toluene can be used instead of benzene as the reaction solvent (93%). Biphasic methods, using aqueous alkali (KOH) in the presence of palladium, gave excellent results for the carbonylation of aryl halides [5–7]. However, using the rhodium catalyst (1) and aqueous alkali (KOH) in place of water afforded 3a in poor yields (2% of KOH at 180°C, 19% yield; 5% of KOH at 180°C, 5%; 10% of KOH at 180°C, 0%, respectively). Tetrabutylammonium iodide (0.2 mmol) as an additive is also not effective, [yield was 17% at 180°C], while addition of triethylamine (10 mmol) gave 5% of 3a. Bromobenzene is not carbonylated using 1 as the catalyst.

A variety of iodobenzenes (2a–2o) were subjected to carbonylation in the presence of $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2] \cdot 2C_6H_6$ (1) affording the corresponding benzoic acids (3a–3o). The results are presented in Table 1. Generally, iodobenzenes having moderate electron donating groups (*m*-methyl, *p*-methyl), electron withdrawing groups (*m*-chloro, *p*-chloro, *m*-bromo, *p*-bromo), and 1-iodonaphthalene (2m) showed high reactivities to give the corresponding acids 3 in good yields (3f, 83%; 3g, 99%; 3i, 89%; 3j, 65%; 3k, 85%; 3l, 95%; 3m, 63%, respectively). However, iodoanisoles (2c, 2d) which have strong electron donating groups gave poor results (3c, 26%; 3d, 5%). This reactivity for substituted iodobenzenes (2) is similar to that found in the reductive carbonylation of ni-

trobenzenes using 1 [11]. The reason for this substituent effect is not clear. In the case of ortho-substituted iodobenzenes (*o*-methyl, *o*-chloro), yields of the corresponding benzoic acids were low-moderate (3e, 4%; 3h, 50%) in part because of the effective bulk of ortho-substituents. Furthermore, it was interesting to observe that the carbonylation of 2-iodoanisole (2b) afforded salicylic acid (54%) in place of 3b. However, the reaction of 2-iodophenol with carbon monoxide and water under the same reaction conditions gave salicylic acid in only 5% yield.

The present Rh-catalyzed carbonylation is particularly valuable for the synthesis of diacids, which are important intermediates for the manufacture of high-performance plastics, polyesters and polyamides. The carbonylation of 1,4-diiodobenzene (2n) and 4,4′-diiodobiphenyl (2o) afforded the corresponding diacids in good yields (3n, 86%; 3o, 100%).

The synthesis of esters using 1 is also possible. Methyl benzoate (4a) was obtained by the use of methanol (30 mmol) in place of water.

Table 1
Carbonylation of aryl iodides (2a–2o) catalyzed by 1

Acid (3)[a]	Yield (%)[b]	Acid (3)[a]	Yield (%)[b]	Acid (3)[a]	Yield (%)[b]
3a	99	3f	83	3k	85
3b	0[c]	3g	99	3l	95
3c	26	3h	50	3m	63
3d	5	3i	89	3n	86[d]
3e	4	3j	65	3o	100[d]

[a] Acids (3) were identified by comparison of spectral data (IR, NMR (^{1}H, ^{13}C), MS) with authentic materials.
[b] Isolated yields.
[c] Salicylic acid was formed (54%).
[d] Reaction time was 48 h.

Table 2
Carbonylation of alkyl halides (2p–2t) catalyzed by 1

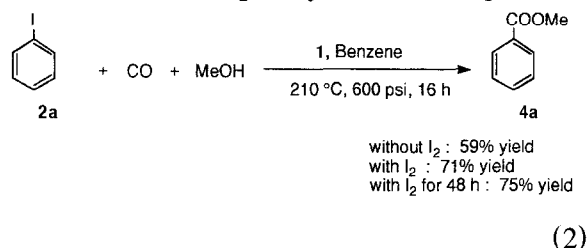| Alkyl halide (2) [a]	Acid (3)	Yield (%) [b]
n-C$_5$H$_{11}$I (2p)	n-C$_5$H$_{11}$COOH (3p)	8
		35 [c]
n-C$_{12}$H$_{25}$I (2q)	n-C$_{12}$H$_{25}$COOH (3q)	3 (82) [d]
		24 (66) [c,d]
PhCH$_2$Br (2r)	PhCH$_2$COOH (3r)	74
PhCH=CHBr (2s)	PhCH=CHCOOH (3s)	24 [c]
PhC≡CBr (2t)	PhC≡CCOOH (3t)	mix.

[a] Acids (3p–3s) were identified by comparison of spectral data (IR, NMR (^{1}H, ^{13}C), MS) with authentic materials.
[b] Isolated yields, with the amount of recovered 2q given in parentheses.
[c] Reaction time was 48 h.
[d] Olefin was not detected.

Addition of iodine (0.2 mmol) is beneficial in this case, increasing the yield of 4a (Eq. (2)).

$$ \text{without I}_2: 59\% \text{ yield} $$
$$ \text{with I}_2: 71\% \text{ yield} $$
$$ \text{with I}_2 \text{ for 48 h}: 75\% \text{ yield} $$

(2)

The carbonylation of alkyl halides (2p–2t) using 1 was next examined in the same manner (Table 2). The reaction of 2p and 2q afforded the corresponding acids in poor yields (3p, 8%; 3q, 3%). However, use of a prolonged reaction time (48 h) slightly improved the product yields (3p, 35%; 3q, 24%). Sometimes the carbonylation of alkyl halides resulted in the formation of corresponding olefins by β-elimination of hydrogen halides [12,13]. However, in this Rh-catalyzed reaction, the olefin was not detected in the carbonylation of 2q. Benzyl bromide (2r) afforded phenylacetic acid (3r, 74%) in reasonable yield. The Rh-catalyzed carbonylation of an alkenyl or alkynyl halide (2s, 2t) gave poor results, either affording the acid in an only low yield (3s, 24%) or complex mixture.

In conclusion, the binuclear complex [(Ph$_3$P)$_4$Rh$_2$(μ-OH)$_2$] · 2C$_6$H$_6$ (1) is an excellent catalyst for the carbonylation of aryl iodides (2) with carbon monoxide and water, af-fording the corresponding acid (2) in good yields. Diacids can be prepared in high yields from diiodides using this catalytic system.

3. Experimental

All solvents were purified by standard methods prior to use. The rhodium complex [(Ph$_3$P)$_4$Rh$_2$(μ-OH)$_2$] · 2C$_6$H$_6$ (1) was prepared according to the literature method [10]. Aryl and alkyl halides (2) were purchased from Aldrich Chemical Co. and were used as received. Proton and Carbon 13 NMR spectra were recorded on a Varian Gemini 200 Spectrometer using CDCl$_3$ or DMSO-d_6 as the solvent. A Bomem MB 100-C15 (FT-IR) was used for recording IR spectra.

3.1. General procedure for the carbonylation of iodobenzenes (2)

A mixture of the substrate (2) (2 mmol), [(Ph$_3$P)$_4$Rh$_2$(μ-OH)$_2$] · 2C$_6$H$_6$ (1) (0.01 mmol, 14 mg) and distilled water (1.0 ml) in dry benzene (12 ml) was placed in a 45 ml autoclave. The autoclave was flushed with carbon monoxide, pressurized to 600 psi and then heated for 16 h at 210°C. The reaction mixture was cooled to room temperature and filtered, 2% aqueous KOH (40 ml) was added and the aqueous layer was washed with ether. The aqueous layer was then acidified with 20% of HCl and extracted with ether (4 × 40 ml). The combined ether solutions were dried over MgSO$_4$, filtered and evaporated. Purification by column-chromatography (benzene-ethyl acetate) gave pure acids (3), which were identified by comparison of spectral data (IR, NMR (^{1}H, ^{13}C), MS) with authentic materials.

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