

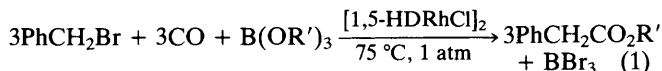
## Mono- and Bi-metallic Catalysed Formate-Halide Carbonylation Reactions

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Benzylic, aryl, and alkyl halides react with formate esters and carbon monoxide, in the presence of the dimer of chloro(hexa-1,5-diene)rhodium(i), [1,5-HDRhCl]<sub>2</sub>, to give carboxylic esters; bimetallic catalysis (*i.e.*, Pd(PPh<sub>3</sub>)<sub>4</sub>/[1,5-HDRhCl]<sub>2</sub>) is particularly beneficial when an aromatic halide is used as the substrate.

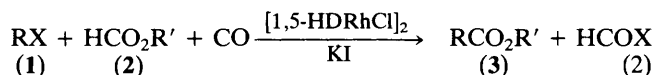
Recently we initiated an investigation of metal complex catalysed alkoxy transfer reactions. Borate esters react with benzylic bromides and carbon monoxide, in the presence of the dimer of chloro(1,5-hexadiene)rhodium(i), [1,5-HDRhCl]<sub>2</sub>, to give primary, secondary, and tertiary esters (equation 1).<sup>1</sup> The reaction can be successfully applied to



aromatic and aliphatic bromides using a bimetallic catalysis system consisting of the rhodium(i) catalyst and tetrakis(triphenylphosphine)palladium(0).<sup>2</sup> Chlorides can be employed as substrates when potassium iodide is present.<sup>3</sup> Good yields of esters were also attained by the mono- or bi-metallic catalysed carbonylation reaction of aluminium alkoxides with benzyl, vinyl, and aryl bromides.<sup>4</sup> Alkoxides of other metals such as titanium and zirconium can also function as formal alkoxy transfer agents.<sup>5</sup>

Although the process is quite general for metal alkoxides, the question arises as to whether one can effect alkoxy transfer with carbon instead of metal systems. It seemed conceivable that a formate ester would be a good source of the alkoxy function. Indeed, as the results of this communication show, esters can be isolated in reasonable yields by treatment of formates with various bromides and chlorides using mono- or bi-metallic catalysis, as required.

The carbonylation reaction of 2-bromomethylnaphthalene (1), R = 2-C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>, X = Br, with n-butyl formate (2), R' = n-C<sub>4</sub>H<sub>9</sub>, as reagent and solvent, at room temperature and 1 atmosphere pressure, gave (3), R = 2-C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>, R' = n-C<sub>4</sub>H<sub>9</sub> in 21% yield. This transformation, which is catalysed



by [1,5-HDRhCl]<sub>2</sub> and iodide, becomes useful if the reaction is simply effected at 50 °C [95% yield of (3)]. In the absence of potassium iodide, the yield of ester was reduced by a factor of two. Other benzylic chlorides and bromides afforded esters in good to excellent yields using methyl, n-butyl, or t-butyl formate. One noteworthy result is the formation of rearranged esters as by-products when 1-bromophenylethane was treated with either methyl or n-butyl formate in the presence of the rhodium(i) catalyst. See Table 1.

Alkyl bromides such as 1-bromohexane and 1-bromooctane are also convertible into esters with formate esters, but higher temperatures (150 °C) and some pressure (80–110 p.s.i.) are beneficial in terms of product yields. The carbonylation reaction is ineffective for aromatic bromides using either the rhodium(i) complex or tetrakis(triphenylphosphine)palladium(0) as the catalyst. However, as clearly demonstrated for *m*-bromotoluene, the use of *both* metal complexes as catalysts results in the isolation of esters in high yields.

The ratio of substrate to rhodium catalyst to potassium iodide used in these reactions was 10–50:1.0:0.5–0.6.

Table 1. Esters obtained from reaction of halides with formates, CO, KI, and [1,5-HDRhCl]<sub>2</sub>.

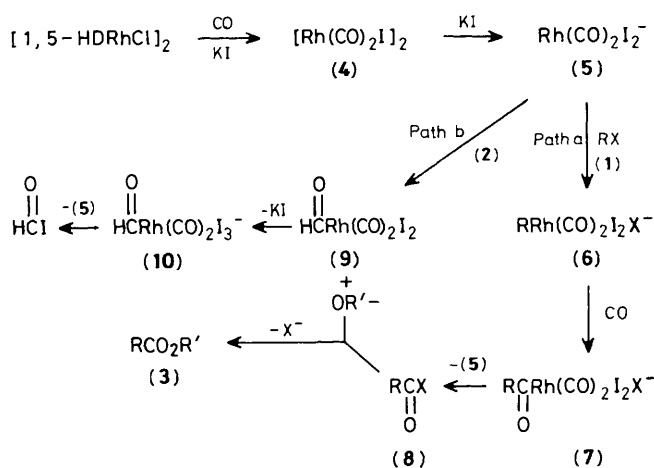
(1)	(2) R'	Reaction temp., °C, (pressure)	(3) %
PhCH <sub>2</sub> Cl	n-C <sub>4</sub> H <sub>9</sub>	75	43
PhCH <sub>2</sub> Br	n-C <sub>4</sub> H <sub>9</sub>	room temp.	60
	Me	room temp.	36
	Me	room temp. (100 p.s.i.)	100
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	n-C <sub>4</sub> H <sub>9</sub> <sup>a</sup>	50	72
	n-C <sub>4</sub> H <sub>9</sub> <sup>b</sup>	50	98
	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	50	49
	Me	room temp. (100 p.s.i.)	56
PhCH(Br)Me	Me	room temp.	40 <sup>c</sup>
	n-C <sub>4</sub> H <sub>9</sub>	50	50 <sup>d</sup>
1-C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> Cl	n-C <sub>4</sub> H <sub>9</sub>	50	85
2-C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> Br	n-C <sub>4</sub> H <sub>9</sub>	room temp.	21
	n-C <sub>4</sub> H <sub>9</sub>	50	94
	n-C <sub>4</sub> H <sub>9</sub>	50 (no KI)	46
	n-C <sub>4</sub> H <sub>9</sub> <sup>a</sup>	50	79
<i>m</i> -BrC <sub>6</sub> H <sub>4</sub> Me	n-C <sub>4</sub> H <sub>9</sub>	150 (100 p.s.i.)	16
	n-C <sub>4</sub> H <sub>9</sub>	150 (80 p.s.i.)	17 <sup>e</sup>
	n-C <sub>4</sub> H <sub>9</sub>	150 (100 p.s.i.)	83 <sup>f</sup>
1-C <sub>10</sub> H <sub>7</sub> Br	n-C <sub>4</sub> H <sub>9</sub>	150 (110 p.s.i.)	81 <sup>f</sup>
2-C <sub>10</sub> H <sub>7</sub> Br	n-C <sub>4</sub> H <sub>9</sub>	150	46
n-C <sub>8</sub> H <sub>17</sub> Br	n-C <sub>4</sub> H <sub>9</sub>	150 (80 p.s.i.)	78
n-C <sub>6</sub> H <sub>13</sub> Br	n-C <sub>4</sub> H <sub>9</sub>	150 (80 p.s.i.)	74

<sup>a</sup> (MeOCH<sub>2</sub>)<sub>2</sub> as solvent. <sup>b</sup> Butanone as solvent. <sup>c</sup> PhCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Me was also formed in 17% yield (all yields are isolated yields), and an unidentified product was isolated as well. <sup>d</sup> PhCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>4</sub>H<sub>9</sub> was obtained in 9% yield. <sup>e</sup> Using Pd(PPh<sub>3</sub>)<sub>4</sub> as the catalyst. <sup>f</sup> Using [1,5-HDRhCl]<sub>2</sub>-Pd(PPh<sub>3</sub>)<sub>4</sub> as catalysts.

Butan-2-one and ethylene glycol dimethyl ether (glyme) are useful solvents, beside the formate itself.

These carbonylation reactions do not proceed in the absence of carbon monoxide, *i.e.*, the formate ester carbonyl group is not the source of the carbonyl function in (3). A metal complex catalyst is also required in order for reaction to occur. The presumed by-product in the formate-halide carbonylation reaction is a formyl halide. Repeated attempts to isolate such a by-product failed.

A possible mechanism for the formate-halide reaction is outlined in Scheme 1. Interaction of the rhodium(i) complex with KI and carbon monoxide would give (4)<sup>3</sup> and then (5). The latter complex can react by two pathways: (a) oxidative addition, (6), carbonylation, (7), and reductive elimination to give the acid halide (8), and regenerate (5); (b) nucleophilic attack at the formate carbonyl carbon to give (9), and subsequently (10) and formyl iodide, and alkoxide ion. The carboxylic ester would then arise by reaction of (8) with OR'<sup>-</sup>. Path a is that proposed, with good evidence, for the iodide promoted carbonylation of methanol to acetic acid.<sup>6</sup> While this scheme may be a plausible one for the potassium iodide promoted reaction, it is important to emphasize that esters are



Scheme 1

also obtained from formates and organic halides in the *absence* of KI (albeit in reduced yields). Such a scheme does not account for the latter process, or for the bimetallic catalysed reactions. A pathway involving oxidative addition of the formate ester to a metal centre is unlikely since the carbonyl group in the product arises from carbon monoxide and not from the formate (and RH should have been formed as well).<sup>7</sup>

The following procedure is representative.† A mixture of (1), R = 2-C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>, X = Br, (0.44 g, 2.00 mmol), [1,5-HDRhCl]<sub>2</sub><sup>8</sup> (0.09 g, 0.20 mmol), and KI (0.02 g, 0.12 mmol) in n-butyl formate (2 ml) was stirred overnight at 50 °C (CO atmosphere). The solution was cooled to room temper-

† Bimetallic reactions were carried out in an identical manner, except that a 1:1 ratio of Pd(PPh<sub>3</sub>)<sub>4</sub>:[1,5-HDRhCl]<sub>2</sub> was used. Reactions under pressure were run in an autoclave.

ature, 1 M NaOH (2 ml) was added, and the reaction mixture was filtered through Celite. The latter was washed with diethyl ether and distilled water and the washings were added to the filtrate. The organic phase was separated, dried (MgSO<sub>4</sub>), and distilled to give 0.455 g (95%) of pure (3), R = 2-C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>, R' = n-C<sub>4</sub>H<sub>9</sub>, b.p. 175 °C (1.0 mm) [lit.<sup>9</sup> b.p. 143.5 °C (0.2 mm)].

In conclusion, formate esters are useful alkoxy transfer agents for a variety of chlorides and bromides, using mono- and bi-metallic catalysis. These reactions occur under quite mild conditions and are simple both in execution and work-up.

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