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PALLADIUM(0) AND RHODIUM(I) CATALYSIS OF THE CARBONYLATION OF UNACTIVATED BROMIDES

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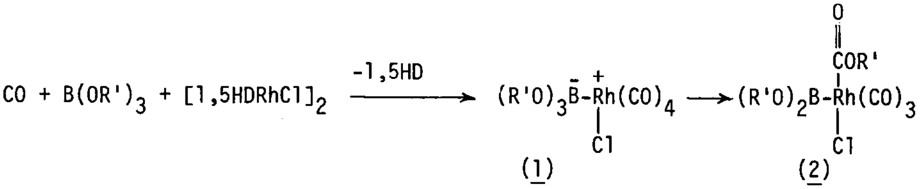
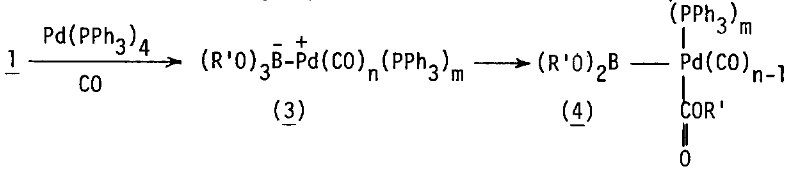
Summary: Alkyl, vinyl, and aromatic bromides react with organoborates and carbon monoxide, in the presence of catalytic quantities of 1,5-hexadienerhodium(I) chloride dimer and tetrakis(triphenylphosphine)palladium(0), to give carboxylic esters in good yields.

Recently, we reported the first examples of metal catalysis of a borate ester reaction. Benzylic bromides react with borate esters and carbon monoxide, in the presence of 1,5-hexadienerhodium(I) chloride dimer[1,5-HDRhCl]$_2$, to give esters in excellent yields. Unfortunately, no reaction occurred with less activated bromides, such as 1-bromonaphthalene or 1-bromooctane. This lack of reactivity might be due to the possibility that complex 2, obtained by reaction of the rhodium(I) catalyst (1) with borate and carbon monoxide followed by ligand migration of an OR' group, is only reactive towards activated halides. It seemed conceivable to us that a palladium analog of 2 [i.e., 4], generated by transmetalation of 1 [to give 3] and subsequent alkoxy group migration, might prove to be active towards simple bromides. Reactions catalyzed by bimetallic systems are increasingly important in catalysis[2,3]. We now describe the successful application of this bimetallic catalyzed reaction.

$$3ArCH_2Br + B(OR')_3 + 3CO \xrightarrow[75°,\ 1\ atm.]{[1,5\text{-}HDRhCl]_2} 3ArCH_2COOR' + BBr_3$$



$$CO + B(OR')_3 + [1,5HDRhCl]_2 \xrightarrow{-1,5HD} \underset{(1)}{(R'O)_3\overset{-}{B}\text{-}\underset{\displaystyle Cl}{\overset{+}{Rh}}(CO)_4} \longrightarrow \underset{(2)}{(R'O)_2B\text{-}\underset{\displaystyle Cl}{\overset{\displaystyle \overset{\displaystyle O}{\|}{C}OR'}{Rh}}(CO)_3}$$



$$\underline{1} \xrightarrow[CO]{Pd(PPh_3)_4} \underset{(3)}{(R'O)_3\overset{-}{B}\text{-}\overset{+}{Pd}(CO)_n(PPh_3)_m} \longrightarrow \underset{(4)}{(R'O)_2B — \underset{\displaystyle \underset{\displaystyle O}{\overset{\|}{C}}OR'}{\overset{\displaystyle (PPh_3)_m}{Pd}}(CO)_{n-1}}$$

Treatment of o-bromoanisole with tri-n-butyl borate and carbon monoxide, as well as catalytic amounts of the rhodium compound and tetrakis(triphenylphosphine)palladium(0), affords n-butyl o-methoxybenzoate in 94% yield. The reaction is applicable to other borates, including

$$3RBr + 3CO + B(OR')_3 \xrightarrow[Pd(PPh_3)_4]{[1,5HDRhCl]_2} 3RCOOR' + BBr_3$$

Table 1 Yields of Esters Obtained by $Pd(PPh_3)_4$-$[1,5\text{-}HDRhCl]_2$ Catalysis of the Reaction of Halides, Borate Ester and Carbon Monoxide

Halide	Borate Ester	Product	Yield,[a]%
1-Bromonaphthalene	$B(On\text{-}C_4H_9)_3$	$NpCOOC_4H_9$-n	90
	$B(OC_2H_5)_3$	$NpCOOC_2H_5$	42
	$B(Oi\text{-}C_3H_7)_3$	$NpCOOC_3H_7$-i	40
p-Bromoanisole	$B(On\text{-}C_4H_9)_3$	p-$CH_3OC_6H_4COOC_4H_9$-n	93
	$B(Ot\text{-}C_4H_9)_3$	p-$CH_3OC_6H_4COOC_4H_9$-t	95
	$B(Oi\text{-}C_3H_7)_3$	p-$CH_3OC_6H_4COOC_3H_7$-i	47
p-Bromostyrene	$B(On\text{-}C_4H_9)_3$	p-CH_2=$CHC_6H_4COOC_4H_9$-n	74
3,4-Dimethoxy-β-bromostyrene	$B(On\text{-}C_4H_9)_3$	3,4$(CH_3O)_2C_6H_3CH$=$CHCOOC_4H_9$-n	83
$PhCH_2CH_2Br$	$B(On\text{-}C_4H_9)_3$	$PhCH_2CH_2COOC_4H_9$-n	42
n-$C_8H_{17}Br$	$B(On\text{-}C_4H_9)_3$	n-$C_8H_{17}COOC_4H_9$-n	57
n-$C_{12}H_{25}Br$	$B(On\text{-}C_4H_9)_3$	n-$C_{12}H_{25}COOC_4H_9$-n	88
$Br(CH_2)_6Br$	$B(On\text{-}C_4H_9)_3$	n-$C_4H_9OCO(CH_2)_6COOC_4H_9$-n	76

[a] Yields are of isolated materials.

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tert-butyl borate, and to other aromatic bromides. Vinyl and alkyl bromides can be used as reactants, and the product yields are listed in Table 1. These reactions were effected either at 90° for 2 days, or at 150° overnight, using a 1.5/1.0 mole ratio of $[1,5HDRhCl]_2$/$Pd(PPh_3)_4$. No reaction occurs when only one of the two metal complexes is employed as the catalyst, or if $Rh(CO)(Cl)(PPh_3)_2$ is used in place of $[1,5HDRhCl]_2$. These reactions can be carried out by using borate as the solvent and reactant, or in heptane with a stoichiometric quantity of borate [i.e., 3/1 bromide/borate].

The following general procedure was used: a mixture of $[1,5HDRhCl]_2$[0.17 mmol], $Pd(PPh_3)_4$ [0.11 mmol], borate [2.0 ml. - or 0.65 mmol when heptane was used as the solvent], and bromide [2.0 mmol] was heated overnight at 150° under a carbon monoxide atmosphere. Work-up as previously described[1] gave the carboxylic esters.

In conclusion, the bimetallic catalyzed process described above, together with the reported rhodium(I) catalyzed reaction of benzylic bromides, makes the halide-borate ester carbonylation reaction a truly versatile one.

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