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Preliminary Communication

The vinylation of aryl iodides catalysed by Co, Rh and Ir complexes *

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Abstract

The $CoCl(PPh_3)_3$, $RhCl(PPh_3)_3$, and $IrClCO(PPh_3)_2$ catalysed vinylation of aryl iodides proceeds to give cinnamates and stilbene in high yields.

Keywords: Cobalt; Rhodium; Iridium; Oxidative addition; Aryl halide

The Pd-catalysed vinylation of aryl halides has been extensively investigated by Heck and others because of their wide application in organic synthesis [1]. In recent years there have been a few reports on the use of nickel salts for this reaction [2]. Grigg et al. have reported an intramolecular vinylation reaction catalysed by the Wilkinson's catalyst [3]. There are no reports on the use of Co and Ir metal complexes for the vinylation of aryl halides.

The Heck reaction has been shown to proceed by the oxidative addition of Pd metal, generated in situ, to the aryl halide. The complexes $CoCl(PPh_3)_3$, $RhCl(PPh_3)_3$, $IrClCO(PPh_3)_2$ are very well known to undergo oxidative addition reactions [4]. So we decided to investigate the use of these metal complexes in the vinylation of aryl halides.

The result of our experiments is summarized in Table 1. The reaction of iodobenzene with methyl acrylate is catalysed by the Co, Rh and Ir complexes, (mentioned above) to give methyl cinnamate, in very good yields (Scheme 1).

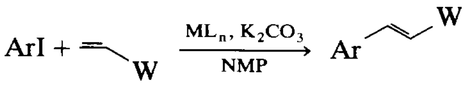
In a typical reaction, the aryl halide (2 mMol), methyl acrylate (4 mMol), K_2CO_3 (4 mMol) and the catalyst (0.025 mMol) were placed in a round bottomed flask. 1-methylpyrrolidinone (5 mL) was used as solvent and the reaction mixture heated to 110°C for 24 h. After the usual workup the reaction product was isolated by passing through a column of silica gel.

Table 1
Vinylation of aryl halides

S. No.	Aryl Iodide	Olefin	Yield %		
			Cat A	Cat B	Cat C
1	PhI	MA	84	98	80
		Styrene	83	83	80
2	4-ClPhI	MA	88	84	78 [a]
3	4-MeOPhI	MA	91	90	75 [a]
4	4-MePhI	MA	98	90	98
5	4-NO_2PhI	MA	70	90	95
6	2-ClPhI	MA	–	50 [a]	55 [a]
7	2-MePhI	MA	–	65 [a]	74 [a]

MA: Methyl acrylate. [a] Reaction temperature = 150°C. Cat A: $CoCl(PPh_3)_3$ Cat B: $RhCl(PPh_3)_3$ Cat C: $IrClCO(PPh_3)_2$. Reaction Conditions: $ArI/Olefin/K_2CO_3/Catalyst = 1/2/2/0.05$; NMP, 110°C, 24 h. All products were characterised by IR and ^1H NMR.

Different aryl iodides reacted with methyl acrylate to provide the corresponding vinylation product in very high yields. Under similar conditions, iodobenzene also reacted with styrene to form stilbene in the presence of these catalysts. The $CoCl(PPh_3)_3$ catalysed reaction was run with 0.1 mMol of catalyst and took 24 h for completion at 100°C. The $RhCl(PPh_3)_3$ catalysed reaction required only 0.025 mMol of catalyst for complete conversion in 24 h. In the case of $IrClCO(PPh_3)_2$ the



$W = CO_2Me$, Ph

$ML_n = CoCl(PPh_3)_3, RhCl(PPh_3)_3, IrCOCl(PPh_3)_2$

Scheme 1.

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reaction required slightly higher temperature (150°C) for the p-Cl and p-MeO substituted aryl iodides. The ortho substituted aryl iodides similarly needed a higher temperature (150°C) for complete conversion. While both Rh and Ir gave the expected product with the ortho substituted aryl iodides, no reaction was observed with the Co catalyst, even at higher temperature (150°C).

Bromobenzene and chlorobenzene did not react even at higher temperatures (150°C). Similarly, aliphatic halides like cyclohexyl iodide and isopropyl iodide did not undergo the vinylation reaction under these conditions.

In summary, $CoCl(PPh_3)_3$, $RhCl(PPh_3)_3$ and $IrClCO(PPh_3)_2$ have been found to be excellent catalysts for the vinylation of aryl iodides. Though the Rh and Ir complexes are expensive, the use of $CoCl(PPh_3)_3$ reveals the feasibility of a cheaper catalyst for the Heck reaction. Further work is in progress on the use of cationic Rh complexes for the Heck reaction and the asymmetric Heck reaction.

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