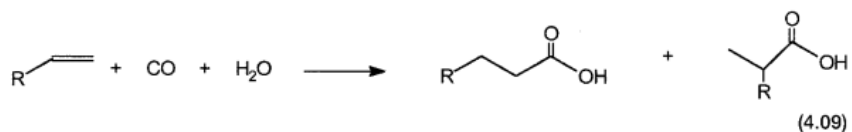


RHODIUM-CATALYZED CARBONYLATION OF OTHER ALCOHOLS

Alcohols such as ethanol, n-propanol, and I have been tested with rhodium-catalyzed carbonylation. Unlike methanol carbonylation, the reaction of alkenes with hydrido complexes, which serve as catalytic intermediates, is central to both of these reactions. Reactions where a carboxylic acid is formed from the reaction of an alkene with water and CO, as in reaction 4.9, is known as hydrocarboxylation (see Section 1.5). The outer catalytic cycle in Fig



Displays propylene hydrocarboxylation path to n-butyric and I iodide acid. The internal cycle is the n-propyl iodide carbonylation route to the iodide nbutyric acid.

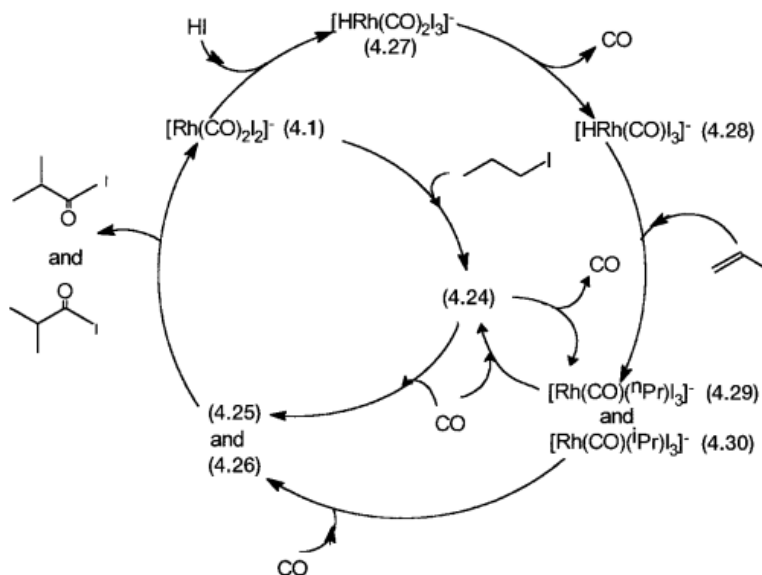
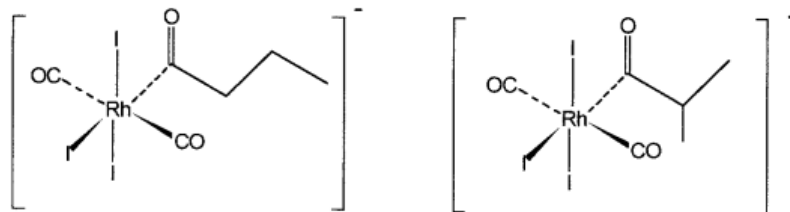


Figure. Hydrocarboxylation and carbonylation of propylene and *n*-propyl iodide

Though the cycles that seem too complex at first glance, most catalytic species are analogs of intermediates shown in Fig. 4.2. Right now. Complexes 4.24 and 4.27 are oxidative addition products of 4.1 with *n*-propyl iodide and HI, respectively. The latter complex is experiencing CO loss in order to produce 4.28 that is co-ordinately unsaturated. The conversion from 4.28 to 4.30 is the critical step which is responsible for the branched isomer formation. Obviously this reaction is possible only when propylene is present as one of the reactants, or under reaction conditions where propylene from *n*-propanol is generated in situ. Conversion of 4.28 to 4.30 is an example of alkene insertion into an M–H bond in a Markovnikov manner for a discussion on Markovnikov and anti-Markovnikov insertion.

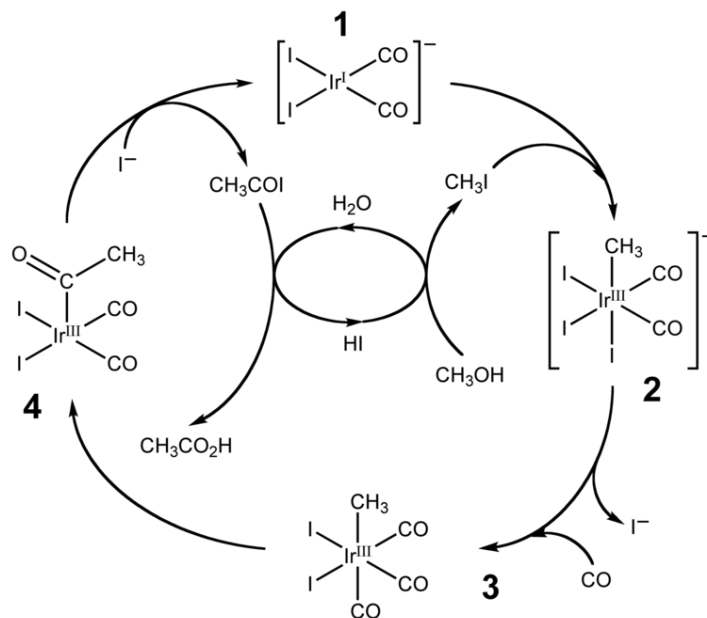


Cativa Process.

The **Cativa process** is a method for the production of acetic acid by the carbonylation of methanol. The technology, which is similar to the Monsanto process, was developed by BP Chemicals and is under license by BP Plc. The process is based on an iridium-containing catalyst, such as the complex $[\text{Ir}(\text{CO})_2\text{I}_2]^-$.

The Cativa and Monsanto processes are sufficiently similar that they can use the same chemical plant. Initial studies by Monsanto had shown iridium to be less active than rhodium for the carbonylation of methanol. Subsequent research, however, showed that the iridium catalyst could be promoted by ruthenium, and this combination leads to a catalyst that is superior to the rhodium-based systems. The switch from rhodium to iridium also allows the use of less water in the reaction mixture. This change reduces the number of drying columns necessary, decreases formation of by-products, such as propionic acid, and suppresses the water gas shift reaction.

Iridium (or an iridium and another metal mixture, normally ruthenium). The new system shows high rates at low water concentrations. The catalyst system exhibits high stability allowing a wide range of process conditions and compositions to be accessed without catalyst precipitation. In 2003 four plants are in operation using this new catalyst.



The catalytic cycle for the Cativa process, shown above, begins with the reaction of methyl iodide with the square planar active catalyst species (**1**) to form the octahedral iridium(III)

species **(2)**, the *fac*-isomer of $[\text{Ir}(\text{CO})_2(\text{CH}_3)\text{I}_3]^-$. This oxidative addition reaction involves the formal insertion of the iridium(I) centre into the carbon-iodine bond of methyl iodide. After ligand exchange (iodide for carbon monoxide), the migratory insertion of carbon monoxide into the iridium-carbon bond, step **(3)** to **(4)**, results in the formation of a square pyramidal species with a bound acetyl ligand. The active catalyst species **(1)** is regenerated by the reductive elimination of acetyl iodide from **(4)**, a de-insertion reaction.^[1] The acetyl iodide is hydrolysed to produce the acetic acid product, in the process generating hydroiodic acid which is in turn used to convert the starting material (methanol) to the methyl iodide used in the first step.