Homogeneous reactions often offer increased selectivities, activities, modification ease, milder reaction conditions, and higher yields than their heterogeneous counterparts. However, these selectivity advantages are usually offset by the need for costly separations of catalyst from product. Separations are often fraught with difficulties, resulting in costly catalyst losses. The discovery of the Wacker process by Otto Roelen of Ruhrchemie AG in 1938 marked the beginning of aqueous organometallic chemistry in an industrial setting [1].

Hydroformylation, or the addition of H-CO across a C-C double bond, is accomplished industrially via several catalysts and conditions. Hydroformylation accounts for over 5.6 million tons of aldehydic product per year. The original cobalt catalysts employed early in the Wacker process have largely been replaced with more selective and active palladium catalysts [2]. The Union Carbide Oxo Process employs rhodium(I) phosphine complexes as they are 10^2 to 10^4 times more active than the early cobalt catalysts, although poisoning from sulfur can be problematic [3]. The insolvability of these catalysts in water necessitates the use of organic solvents. Distillation is required to separate product from catalyst and often results in catalyst deactivation and productivity losses. Linear/branched (n/i) ratios are often low (3:1) [4].

A novel approach combining qualities of both heterogeneous and homogeneous processes was developed by Rhone-Poulenc in 1975. Sulfonation of the phosphine ligands affords water-soluble complexes which are currently used in the recently developed Ruhrchemie/Rhone-Poulenc bi-phasic hydroformylation process [5-14]. Three commonly used ligands, tppts (1), bisbis (2), and norbos (3), are illustrated below in Figure 1.

![Ligands](1)(2)(3)

**Figure 1. Ligands commonly used in Ruhrchemie/Rhone-Poulenc process.**

The Ruhrchemie/Rhone-Poulenc Process produces approximately 3 x 10^6 tons per year of butyraldehyde from synthesis gas (CO/H_2) and propene. Linear to branched (n/i) selectivities as high as 99/1 are obtained. Low hydrogenation rates and zero rhodium losses are characteristic of the process. Turnovers as high as 118 h^-1 are currently observed using the norbos ligand. Separations are accomplished by simple decantation of organic product from the aqueous catalyst phase. Low phosphine/rhodium ratios do not compromise catalyst longevity or activities. Milder reaction conditions and higher feed rates are also possible without sacrificing selectivities and catalyst lifetimes [15-17].

Another potentially useful homogeneous process would be the selective oxidation of alkanes to their corresponding alcohols. Currently methane is converted heterogeneously to carbon monoxide and hydrogen by Mobil and the products are used to prepare methanol for syn-fuel applications. A homogeneous system for this process has not been developed to
date. Early studies by Rudakov and Shilov demonstrated that methane could be oxidized to methyl halide and methanol catalytically in the presence of aqueous Pt$^{II}$ and Pd$^{II}$ and an appropriate oxidant [18-20]. Oxidation rates were proportional to [Pt$^{II}$] and [Pd$^{II}$]. Alkane oxidation rates were independent of added oxidant concentrations, (i.e. benzoquinone, Ce$^{IV}$, Fe$^{III}$) during the course of the experiment. The function of the added oxidant is to prevent precipitation of Pt$^{0}$ or Pd$^{0}$ after alkane functionalization. Further investigations by Horvath [21], Sen [22-24], and others [25] demonstrated that Pt$^{II}$ and Pd$^{II}$ metal species activate alkanes by an electrophilic displacement mechanism, rather than by free radical means, to afford metal-bound alkyl intermediates. The metal alkyl species, once formed, undergo nucleophilic attack by water or chloride to afford methanol and methyl chloride in low yields.

Kinetic studies conducted by Labinger and Bercaw using water-soluble alkanes support this mechanism [26]. They concluded the least sterically hindered C-H bond is the most reactive as predicted by Halpern [27]. The reaction is homogeneous, and they postulated that a $\sigma$-alkane complex may exist prior to activation of the alkane by the platinum center [28,29]. Electron transfer rather than alkyl transfer between Pt$^{II}$ and Pt$^{IV}$ centers was proposed.

Ring Opening Metathesis Polymerization or ROMP is a versatile method for obtaining polymers with unusual mechanical and optical properties. Catalyst stability during the course of polymerization plays a large role in polymer properties such as average molecular weight and microstructure. Several ROMP catalysts of early transition metals have been developed by Schrock and Grubbs, but these catalysts are often intolerant of pendant group functionalities, water, oxygen, and impurities [30,31]. Wittig-like reactions between catalyst and heteroatoms in the monomers often occur, resulting in low molecular weights and yields of polymeric material. Recently Grubbs and Novak have developed a series of water soluble late transition metal catalysts which are functional group tolerant, air and water stable, and easily separated from the resultant polymer [32]. These catalysts polymerize 7-oxa-norbornenes, isocyanides, and substituted norbornenes to yield polyoxanorbornenes [33-35], polyisocyanides [36], and polyacetylenes [37] from aqueous emulsions. The polymers are obtained in high yields, have high molecular weights, and low polydispersities. Previous studies by Grubbs and co-workers suggest that the formation of an $\eta^2$-olefin complex precedes the generation of the reactive carbene species necessary for ROMP to occur. An example of a ruthenium olefin complex is given below. Recently, well-defined ruthenium vinylidene catalysts have been prepared which initiate ROMP reactions with norbornene in protic media [38,39]. Higher polymeric yields and shorter induction delays are observed when using water as a reaction solvent. A wide range of functionalized polymers has been obtained and tailored polymers for specialty applications may be available in the near future.

In conclusion, homogeneous aqueous organometallic chemistry can often accomplish what cannot be done in non-aqueous solvents. The increased selectivity, activity, and functionality tolerances often observed in aqueous systems suggests many new and exciting transformations await discovery.

![Figure 2. Proposed catalyst precursor during aqueous ROMP reactions.](image-url)
References


