

Aqueous Organometallic Systems: Investigations of Hydroformylation, Ring Opening Metathesis Polymerization, and Alkane Functionalization

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Literature Seminar

March 24, 1994

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 time more active than the early cobalt catalysts, although poisoning from sulfur can be problematic [3]. The insolubility 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.

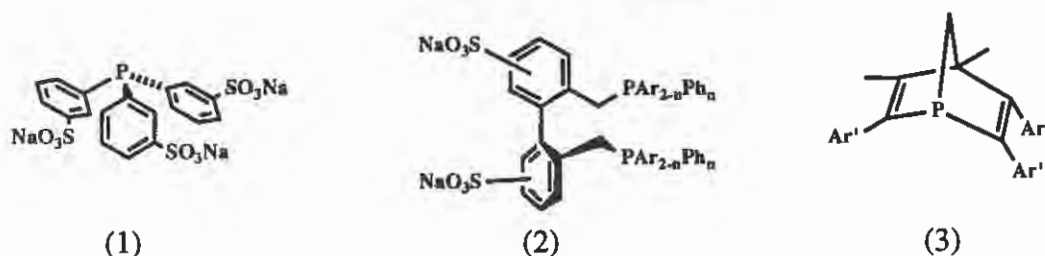


Figure 1. Ligands commonly used in Ruhrchemie/Rhone-Poulenc process.

The Ruhrchemie/Rhone-Poulenc Process produces approximately 3×10^6 tons per year of butyraldehyde from synthesis gas (CO/H₂) 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 $[\text{Pt}^{\text{II}}]$ and $[\text{Pd}^{\text{II}}]$. 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 σ -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 η^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

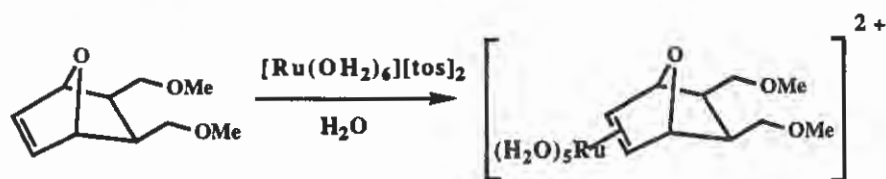


Figure 2. Proposed catalyst precursor during aqueous ROMP reactions.

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.

References

1. Masters, C. *Homogeneous Transition-Metal Catalysis-A Gentle Art*; Chapman and Hall: New York, NY, 1981.
2. Parshall, G.W. *Homogeneous Catalysis*; John Wiley & Sons: New York, NY, 1980.
3. Elschenbroich, C.; Salzer, A. *Organometallics*, 2nd ed.; VCH: New York, NY, 1992.
4. Joo, F.; Toth, E., "Catalysis by Water-Soluble Phosphine Complexes of Transition Metal Ions in Aqueous and Two-Phase Media," *J. Mol. Catal.* **1989**, *8*, 369.
5. Herd, O.; Langhans, K. P.; Stelzer, O.; Weferling, N.; Sheldrick, W. S., "A New Route to Water-Soluble Phosphanes with para-Sulfonated Phenyl Substituents. Crystal Structure of $P(C_6H_4-p-SO_3K)_3 \cdot KCl \cdot 0.5H_2O$," *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 7.
6. Herrmann, W. A.; Kulpe, J. A.; Kellner, J.; Reipl, H.; Bahrmann, K.; Konkol, W., "Water Soluble Metal Complexes of the Sulfonated Triphenylphosphane TPPTS: Preparation of the Pure Compounds and their Use in Catalysis," *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 391.
7. Herrmann, W. A.; Kohlpaintner, C. W.; Bahrmann, H.; Konkol, W., "Water-Soluble Metal Complexes and Catalysts. Part 6. A New, Efficient Water-Soluble Catalyst for Two-Phase Hydroformylation of Olefins," *J. Mol. Catal.* **1992**, *73*, 191.
8. Fache, E.; Santini, C.; Sensocq, F.; Basset, J. M., "Homogeneous Catalysis in Water Part II. Synthesis and Characterization of Ruthenium Water-Soluble Complexes," *J. Mol. Catal.* **1992**, *72*, 31.
9. Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. M.; Daigle, D. J., "Water-Soluble Organometallic Compounds. 4. Catalytic Hydrogenation of Aldehydes in an Aqueous Two-Phase System using a 1,3,5-Triaza-7-phosphaadamantane Complex of Ruthenium," *Inorg. Chem.* **1994**, *33*, 200.
10. Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A., "Water-Soluble Aqueous Two-Phase System by New Water-Soluble 1,3,5-Triaza-7-phosphaadamantane Complex of Ruthenium," *Organometallics* **1992**, *11*, 1990.
11. Herrmann, W. A.; Kellner, J.; Reipl, H., "Wasserlösliche Metallkomplexe und Katalysatoren III. Neue Wasserlösliche Metallkomplexe des Sulfonierten Triphenylphosphanes (TPPTS): Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Ag, Au.," *J. Organomet. Chem.* **1990**, *389*, 103.
12. Kulpe, J. A.; Konkol, W.; Bahrmann, H., "Wasserlösliche Metallkomplexe und Katalysatoren II. Verfahren zur Katalyserelevanten Rhodium-Komplexe," *J. Mol. Catal.* **1990**, *71*, 109.
13. Herrmann, W. A.; Kohlpaintner, C. W., "Water-Soluble Ligand, Metal Complexes, and Catalysis: Synergism of Homogeneous and Heterogeneous Catalysis," *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524.
14. Abu-Gnim, C.; Amer, I., "Phosphine vs. Phosphine Oxide Ligands in Hydroformylation Reactions," *J. Chem. Soc., Chem. Commun.* **1994**, 115.

29. Bullock, R. M.; Headford, C.E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R., "Intramolecular Hydrogen Exchange among the Coordinated Methane Fragments of $\text{Cp}_2\text{W}(\text{H})\text{CH}_3$. Evidence for the Formation of a σ Complex of Methane Prior to Elimination," *J. Am. Chem. Soc.* **1989**, *111*, 3897.
30. Bazan, G. C.; Schrock, R. R.; Cho, H. N.; Gibson, V. C., "Polymerization of Functionalized Norbornenes Employing $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$ as the Initiator," *Macromolecules* **1991**, *24*, 4495.
31. Bazan, G. C.; Oskam, J. H.; Cho, H.; Park, L. Y.; Schrock, R. R., "Living Ring-Opening Metathesis Polymerization of 2,3-Difunctionalized 7-Oxanorbornenes and 7-Oxanorbornadienes by $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N-2,6-C}_6\text{H}_3\text{-}i\text{-Pr}_2)(\text{O-}t\text{-Bu})_2$ and $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N-2,6-C}_6\text{H}_3\text{-}i\text{-Pr}_2)(\text{OCMe}_2\text{CF}_3)_2$," *J. Am. Chem. Soc.* **1991**, *113*, 6899.
32. Novak, B. M.; Grubbs, R. H., "The Ring Opening Metathesis Polymerization of 7-oxabicyclo[2.2.1]hept-5-ene Derivatives: A New Acyclic Polymeric Ionophore," *J. Am. Chem. Soc.* **1988**, *110*, 960.
33. Novak, B. M.; Grubbs, R. H., "Catalytic Organometallic Chemistry in Water: The Aqueous Ring-Opening Metathesis Polymerization of 7-Oxanorbornene Derivatives," *J. Am. Chem. Soc.* **1988**, *110*, 7542.
34. Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H., "Aqueous Ring-Opening Metathesis Polymerization of Carboximide-Functionalized 7-Oxanorbornenes," *Macromolecules* **1992**, *25*, 3345.
35. Benedicto, A. D.; Novak, B. M.; Grubbs, R. H., "Microstructural Studies of Poly(7-oxabicyclo[2.2.1]hept-2-ene) Derivatives Prepared from Selected Ruthenium Catalysts," *Macromolecules* **1992**, *25*, 5893.
36. Deming, T. J.; Novak, B. M., "Organometallic Catalysis in Air and Water: Oxygen-Enhanced, Nickel-Catalyzed Polymerizations of Isocyanides," *Macromolecules* **1991**, *24*, 326.
37. Safir, A. L.; Novak, B. M., "Air- and Water-Stable 1,2-Vinyl-Insertion Polymerizations of Bicyclic Olefins: A Simple Precursor Route to Polyacetylene," *Macromolecules* **1993**, *26*, 4072.
38. Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H., "Ring-Opening Metathesis Polymerization (ROMP) of Norbornene by a Group VIII Carbene Complex in Protic Media," *J. Am. Chem. Soc.* **1992**, *114*, 3974.
39. Gagne, M. R.; Grubbs, R. H.; Feldman, J.; Ziller, J. W., "Catalytic Activity of a Well-Defined Binuclear Ruthenium Alkylidene Complex," *Organometallics* **1993**, *11*, 3933.

15. Claver, C.; Castellons, S.; Ruiz, N.; Delogu, G.; Fabbri, D.; Gladial, S., "Asymmetric Hydroformylation of Styrene by Rhodium(I) Catalysts with Chiral Ligands Containing Sulfur Donors," *J. Chem. Soc., Chem. Commun.* **1993**, 1833.
16. Siuss-Fink, G., "Cooperativity in Rh₂ Complexes: High Catalytic Activity and High Regioselectivity in the Hydroformylation of Olefins," *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 67.
17. Bayon, J. C.; Esteban, J. R.; Claver, C.; Polo, A.; Castillon, S., "Catalytic Hydroformylation of Alkenes with Cationic Dinuclear Rhodium(I) Complexes, and the Effect of Counter Ions," *J. Organomet. Chem.* **1991**, *403*, 393.
18. Rudakov, E. S.; Yarshenko, A. P.; Zamashchikov, V. V., "Kinetic Isotope Effects in the Oxidation of Hydrogen by Palladium(II), Silver(I), and Manganese(VII) in Aqueous Solutions," *React. Kinet. Catal. Lett.* **1981**, *17*, 7.
19. Rudakov, E. S.; Yarshenko, A. P.; Zamashchikov, V. V., "Kinetics of Hydrogen Oxidation in Aqueous Palladium Chloride and Bromide. Activity of Individual Pd(Cl_i) (i = 0 - 4) Complexes," *React. Kinet. Catal. Lett.* **1979**, *11*, 187.
20. Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Compounds*; Reidel: Dordrecht, 1984.
21. Horvath, I. T.; Cook, R. A.; Millar, J. M.; Kiss, G., "Low-Temperature Methane Chlorination with Aqueous Platinum Chlorides in the Presence of Chlorine," *Organometallics* **1993**, *12*, 8.
22. Kao, L.; Huston, A. C.; Sen, A., "Low-Temperature, Palladium(II)-Catalyzed, Solution-Phase Oxidation of Methane to a Methanol Derivative," *J. Am. Chem. Soc.* **1991**, *113*, 700.
23. Sen, A.; Lin, M., "A Novel Hybrid System for the Direct Oxidation of Ethane to Acetic and Glycolic Acids in Aqueous Medium," *J. Chem. Soc., Chem. Commun.* **1992**, 508.
24. Sen, A.; Benvenuto, M. A.; Lin, M.; Huston, A. C.; Basicke, N., "Activation of Methane and Ethane and Their Selective Oxidation to the Alcohols in Protic Media," *J. Am. Chem. Soc.* **1994**, *116*, 998.
25. Vargaftik, M. N.; Stolarov, I. P.; Moiseev, I. I., "Highly Selective Partial Oxidation of Methane to Methyl Trifluoroacetate," *J. Chem. Soc., Chem. Commun.* **1990**, 1049.
26. Labinger, J. A.; Herring, A. M.; Lyon, D. K.; Luinstra, G. A.; Bercaw, J. E., "Oxidation of Hydrocarbons by Aqueous Platinum Salts: Mechanism and Selectivity," *Organometallics* **1993**, *12*, 895.
27. Halpern, J., "Activation of Carbon-Hydrogen Bonds by Metal Complexes: Mechanistic, Kinetic and Thermodynamic Considerations," *Inorg. Chim. Acta.* **1985**, *100*, 41.
28. Perianna, R. A.; Bergaman, R. G., "Isomerization of the Hydridoalkylrhodium Complexes Formed on Oxidative Addition of Rhodium to Alkane C-H Bonds. Evidence for the Intermediacy of η^2 -Alkane Complexes," *J. Am. Chem. Soc.* **1986**, *108*, 7332.