

Spectator cations and catalysis with sulfonated phosphines. The role of cations in determining reaction selectivity in the aqueous phase hydroformylation of olefins

Hao Ding, Brian E. Hanson *

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212, USA

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Abstract

The hydroformylation of 1-hexene was carried out under two phase conditions with the water soluble catalyst, $\text{HRh}(\text{CO})(\text{TPPTS})_3$. The addition of different salts as a means to increase the solution ionic strength has a strong influence on reaction activity and selectivity. With monovalent cations the reaction activity decreases as ionic strength increases, while the selectivity, as measured by n/b ratios, increases as the solution ionic strength increases. The size and the charge on the cation also influence the selectivity. For example the cations Li^+ , Na^+ , Cs^+ have a positive influence on reaction selectivity compared to catalysts without additional salt. In contrast Al^{3+} has a negative influence on the reaction selectivity. It is proposed that cations play a role in determining the coordination geometry of catalytic intermediates which contributes to the diverse influence on reaction selectivity.

Keywords: Aqueous phase; Hexene; Hydroformylation; Ionic strength; Rhodium; Selectivity; TPPTS

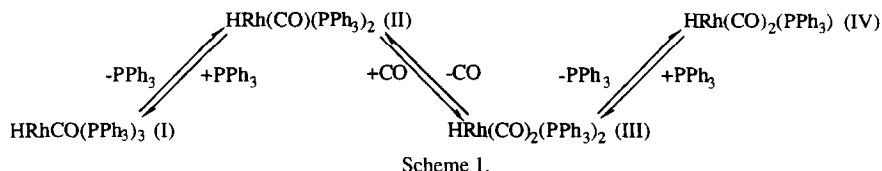
1. Introduction

The mechanism of rhodium catalyzed olefin hydroformylation with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ and related compounds has been widely investigated [1–10]. The dissociative mechanism originally proposed by Wilkinson is generally considered to be operative with oxidative addition of hydrogen as the rate determining step [8]. A large excess of triphenylphosphine is required for good selectivity to linear aldehydes, however excess phosphine also reduces the reaction rate. The reaction equilibria shown in Scheme 1 have been proposed to explain these facts [2].

High concentrations of PPh_3 favor **I** and **II** over **IV**. If catalysis proceeds via the $16 e^-$ complexes **II** and **IV** then excess phosphine forces the catalysis to go through the more sterically demanding intermediate **II**. This can explain the higher proportion of linear product obtained in the presence of excess phosphine [2].

Simple chelating phosphines such as DPPE yield rhodium hydroformylation catalysts of poor selectivity [11–13]. Since in these catalysts the P/Rh ratio is always two in all reaction intermediates it is argued that the coordination geometry of **II** is important in determining reaction selectivity. Specifically since the chelating phosphines adopt a *cis* geometry it follows that a *trans* arrangement of phosphines may be necessary for

* Corresponding author.



good product linearity. Sterically demanding chelates that can span *trans* positions, such as 2,2'-[Ph₂PCH₂]₂C₆H₄-C₆H₄[Ph₂PCH₂], BISBI, give catalysts of good selectivity [14], as does the binucleating chelate [(Et₂PCH₂CH₂)(Ph)P]₂CH₂ [12]. In the latter compound, selectivity is governed, in part, by a bimolecular elimination pathway [12].

The catalyst HRh(CO)(PPh₃)₃ is used in the commercial hydroformylation of propene [15]. This is feasible due to the relatively easy distillation of butyraldehydes from the reaction medium. With the exception of a rhodium/triphenylphosphine oxide/triphenylphosphine system for the hydroformylation of mid range olefins such as 1-octene [16] application of rhodium catalysts to the hydroformylation of higher olefins is not widely practiced commercially due to the difficulty of separating higher aldehydes from the catalyst. Many attempts have been made to immobilize rhodium catalysts [17]; these have included anchoring to polymers [11,17], inorganic solids [3,18], and dissolving in a supported liquid phase [19]. To date these methods suffer from either a lack of stability, selectivity, or poor reaction rates.

The successful preparation of trisulfonated triphenylphosphine, TPPTS, has allowed the generation of the water soluble propene hydroformylation catalyst, HRh(CO)(TPPTS)₃, which is operated commercially [20]. Isolation of butyraldehydes can be accomplished by phase separation rather than distillation directly from the reaction mixture. Application to higher olefins however is still limited, not due to a difficult separation but rather due to poor reaction rates with water insoluble substrates.

Supported aqueous phase catalysts show good rates with higher olefin substrates but suffer from relatively poor selectivity [21]. Addition of sur-

factants to the TPPTS catalysts can give better rates but often leads to the formation of emulsions which are difficult to separate. Mildly surface active phosphines show promise in improving rates and selectivities under two phase conditions [22].

Several factors not encountered in homogeneous systems are now important in two phase catalysis with water soluble catalysts. Water solubility of the substrate in water is significant in determining the reaction rates of a two phase hydroformylation reaction. The reason for this is that hydroformylation of olefin under two phase conditions takes place in the aqueous phase [23,24]. Propene hydroformylation with Rh/TPPTS is successful industrially because propene has significant solubility in water. However, as noted above with higher olefins the rate of the hydroformylation is expected to be slower. Another factor that influences two phase hydroformylation that has only recently been realized is the ionic strength of the aqueous phase [25,26]. Solution ionic strength not only affects the solubility of olefins in water and consequently the reaction rate but also has a strong influence on the selectivity of a hydroformylation reaction. The influence on selectivity may be due to control of the geometry of catalytic intermediates.

We recently reported a series of studies on the influence of solution ionic strength on 1-octene hydroformylation with the Rh/TPPTS system [25,26]. The results revealed some interesting aspects on how ionic strength influences the reaction selectivity. For example an increase in ionic strength, through the addition of Na₂HPO₄ or Na₂SO₄, increased the reaction selectivity (*n/b* ratio) in the two phase hydroformylation of octene. Here we further elaborate the effect of solution ionic strength and investigate the role of the cations in determining reaction activity and

selectivity. Hexene-1 was chosen as the substrate for improved reaction rates compared to octene-1 in the two-phase reactions.

2. Experimental

All reactions and manipulations were carried out by standard Schlenk techniques under an atmosphere of purified nitrogen or CO. Water was deoxygenated by distillation under nitrogen prior to use. Hexene-1 and $\text{Rh}(\text{acac})(\text{CO})_2$ were purchased from Aldrich. The CO/H_2 (1/1) was received from Airco and used without further purification. TPPTS was prepared by direct sulfonation as described previously [27].

The hexene-1 hydroformylation system consisted of an aqueous layer and an organic layer. The aqueous layer was a 1.5 ml solution 5 mM in $\text{Rh}(\text{acac})(\text{CO})_2$ and 15 mM in TPPTS. The organic layer was 0.47 ml 1-hexene. The rhodium to hexene-1 ratio was 1:500 and the salts, Li_2SO_4 , Na_2SO_4 , Cs_2SO_4 or $\text{Al}_2(\text{SO}_4)_3$ were added to adjust the salt concentration to 0.033 M, 0.1 M, 0.166 M, or 0.5 M. The catalysis was done in a 30 ml stainless steel reactor equipped with a pressure gauge. The reactor was charged with CO/H_2 (1:1) to 13.6 atm (200 psi) after all the reactants were added and then placed in a silicon oil bath that had been preheated to 120°C. The stirring rate was 260 rpm. After 24 h the reaction was terminated by cooling the reactor in a ice–water bath and then depressurized.

The reaction products and starting material were analyzed by gas chromatography on a Varian 3300 chromatograph equipped with a HP1 column 25 m \times 0.32 mm \times 0.52 μm , and FID detector; He was the carrier gas; the temperature program was from 40°C (4 min) to 200°C (1 min), at a heating rate of 10°C/min.

Side reactions, such as isomerization of olefin and hydrogenation of both olefin and aldehydes, were not observed based on GC analysis.

3. Results

The results from the hydroformylation of neat hexene-1 with $\text{HRhCO}(\text{TPPTS})_3$ in water without additional salt are shown in Fig. 1. At the stirring rate used the two-phase hydroformylation gives yields of up to 76% aldehyde in a 24 h reaction period. Although the selectivity, as indicated by normal to branched (n/b) ratio, generally drops as the yield increases, it remained low in the whole range of yields under these conditions; specifically the n/b ratio drops from 5.1 to 4.4 as the aldehyde yield increases from 11.8% to 76%. This is typical of some olefin isomerization [7], although in the present case internal olefins are not observed, nor is 2-ethylpentanal.

The effect of added Li_2SO_4 , Na_2SO_4 , and Cs_2SO_4 on the activity of the two-phase hydroformylation of hexene-1 is given in Fig. 2. As expected the yield of aldehydes, as an indication

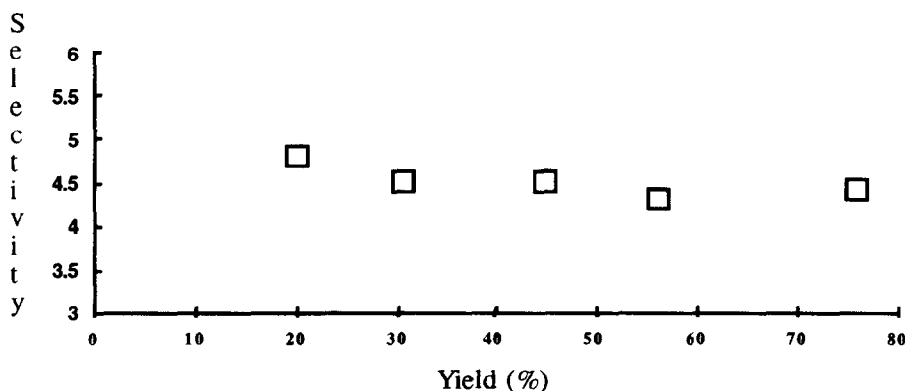


Fig. 1. Selectivity (n/b ratio) vs. yield in the hydroformylation of 1-hexene with $\text{HRh}(\text{CO})(\text{TPPTS})_3$. Reaction conditions: $\text{HRh}(\text{CO})(\text{TPPTS})_3$, 0.005 M; 1-hexene:Rh = 500:1; pressure = 20 atm; temperature = 120°C.

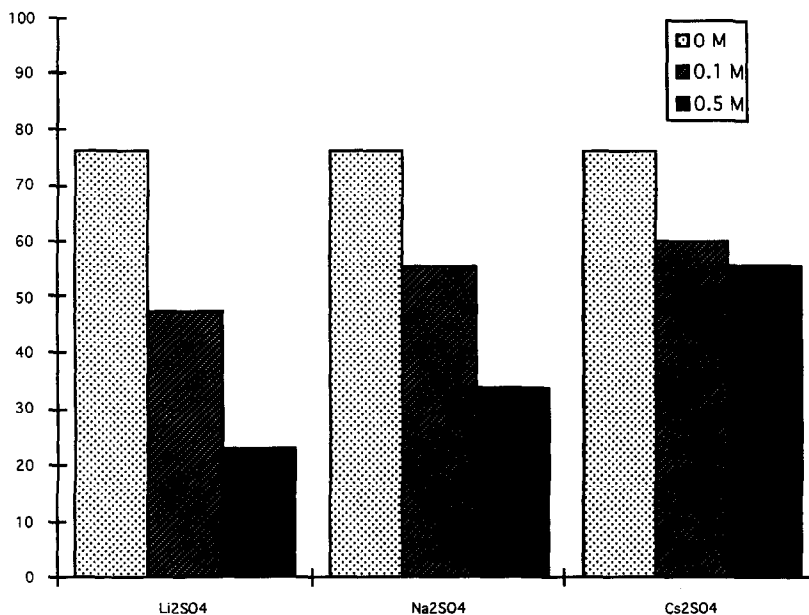


Fig. 2. The effect of alkali metal sulfates on the reaction activity of 1-hexene hydroformylation. Reaction conditions: HRh(CO)(TPPTS)₃ 0.005 M; 1-hexene:Rh = 500:1; pressure = 20 atm; temperature = 120°C; reaction time = 24 h.

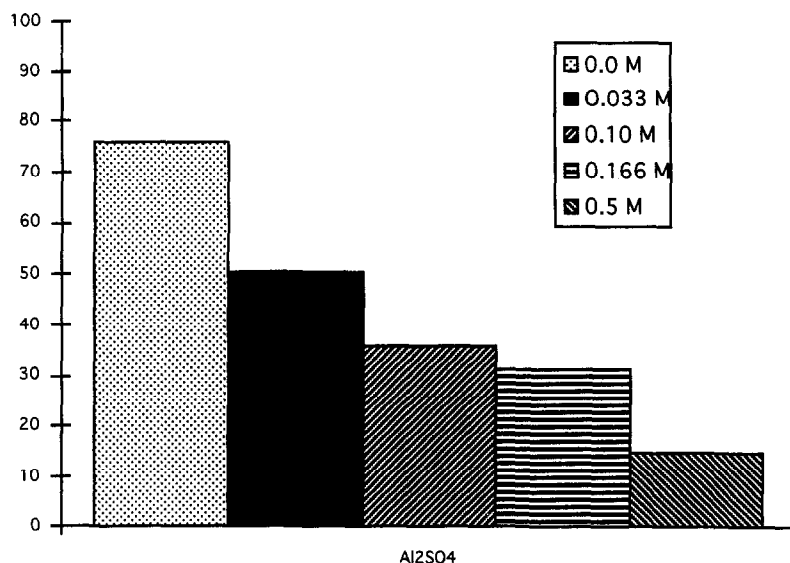


Fig. 3. The effect of Al₂(SO₄)₃ on the reaction activity of 1-hexene hydroformylation. Reaction conditions: HRh(CO)(TPPTS)₃ 0.005 M; 1-hexene:Rh = 500:1; pressure = 20 atm; temperature = 120°C; reaction time = 24 h.

of reaction activity, drops as the salt concentration increases from 0.0 M, to 0.5 M.

In Fig. 3, the effect of a trivalent salt, Al₂(SO₄)₃, on the reaction activity is presented. Similarly the yield of aldehyde drops with increasing ionic strength. In order to make a meaningful comparison between a trivalent salt and monovalent salt, concentrations of 0.033 M and 1.66 M

for Al₂(SO₄)₃ were also used in the study. No effort was made to control the pH of the catalyst that contained aluminum sulfate. At 0.5 M Al₂(SO₄)₃ prior to catalysis the pH was 4. No evidence for the formation of a precipitate in the aqueous phase was observed either prior to catalysis or after the catalytic runs.

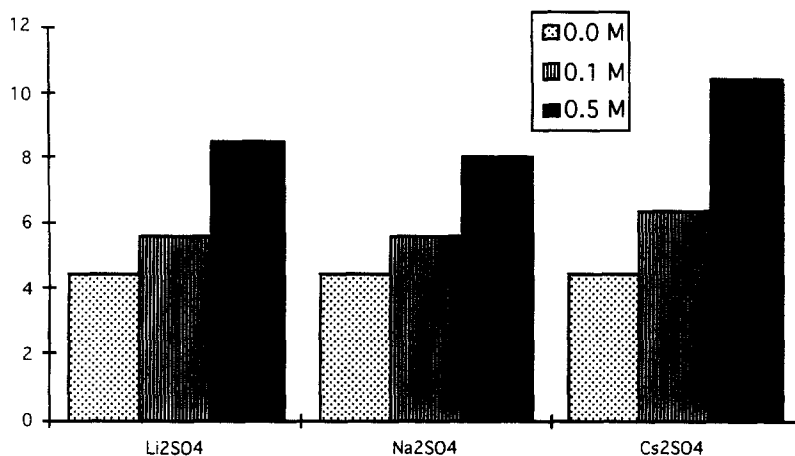


Fig. 4. The effect of alkali metal sulfates on the reaction selectivity of 1-hexene hydroformylation. Reaction conditions: HRh(CO)(TPPTS)₃, 0.005 M; 1-hexene:Rh = 500:1; pressure = 20 atm; temperature = 120°C; reaction time = 24 h.

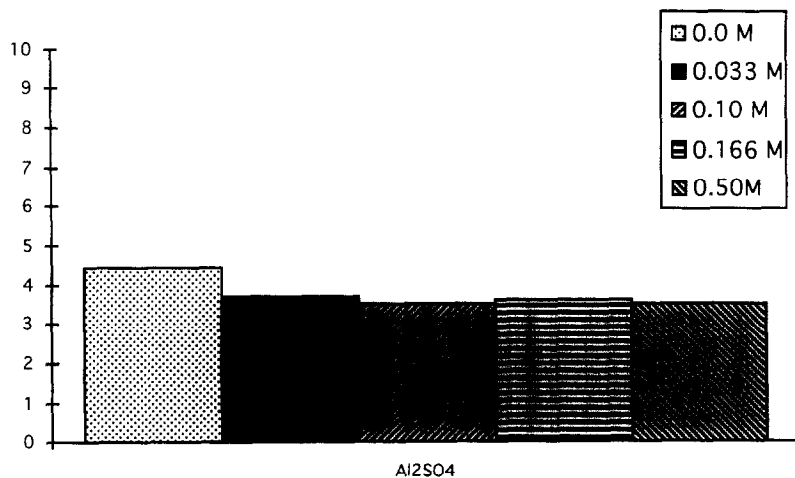


Fig. 5. The effect of Al₂(SO₄)₃ on the reaction selectivity of 1-hexene hydroformylation. Reaction conditions: HRh(CO)(TPPTS)₃, 0.005 M; 1-hexene:Rh = 500:1; pressure = 20 atm; temperature = 120°C; reaction time = 24 h.

The alkali metal salts, Li₂SO₄, Na₂SO₄, and Cs₂SO₄, have a significant influence on the reaction selectivity as shown in Fig. 4. Specifically the normal to branched aldehyde ratio increased to 8.5 at 22.6% conversion, 8.0 at 33.7% conversion and 10.4 at 55.9% conversion with Li₂SO₄, Na₂SO₄, and Cs₂SO₄ respectively. Although these comparisons are made at different conversions, it is clear that the selectivities are improved compared to that obtained at low ionic strength, Fig. 1.

Surprisingly the addition of Al₂(SO₄)₃ did not increase the reaction selectivity. As seen in Fig. 5, the n/b ratio drops slightly upon the addition of Al₂(SO₄)₃.

Neither hexane, hexene isomers, nor heptanol were detected by GC in any of the catalytic reactions. It is estimated that these products, if present, represent less than two percent of the total hexene charge.

4. Discussion

Addition of a water soluble salt to an aqueous solution increases solution ionic strength, and is expected to further diminish the limited solubility of hexene-1 in water. A drop in the yield of aldehydes then is expected when a salt is added to the aqueous catalytic solution. This effect is observed

in all cases although it is not as pronounced as cation size increases.

Addition of a salt also has a strong influence on the selectivity of hexene-1 hydroformylation. The fine control of the normal to branched aldehyde ratio (n/b) is critical to the industrial application of high olefin hydroformylation. The aldehydes produced by hydroformylation are usually further used for generating alcohols or acids, therefore a high normal to branched aldehyde ratio is normally required for an acceptable viscosity index. Interestingly the 'spectator' cation gives a measure of control on the reaction selectivity.

In homogeneous Rh/ PPh_3 based hydroformylation reaction systems, a high concentration of PPh_3 and a low partial pressure of CO generally gives the highest proportion of linear aldehyde. As shown in Scheme 1, both high concentration of PPh_3 and low partial pressure of CO favor intermediate **II** which leads to more linear aldehyde for steric reasons.

By analogy with the nonaqueous system, $HRh(CO)(TPPTS)_2$, the $16e^-$ square planer intermediate [9] generated from $HRh(CO)(TPPTS)_3$, is the key catalytic intermediate for hydroformylation in water. This is the water soluble analog of intermediate **II** in Scheme 1 above. A high concentration of TPPTS, then, is expected to give a higher n/b ratio by generating more $HRh(CO)(TPPTS)_2$ in the reaction equilibrium. Independent of the Rh/TPPTS ratio solution ionic strength also plays a role in determining the reaction selectivity.

Previously we have suggested that the molecule of $HRh(CO)(TPPTS)_3$, be considered as a small particle of radius 8 Å with a net charge of -9 [26]. Dissociation of TPPTS in water should be promoted due to the electronic repulsion among sulfonate groups. Solution ionic strength is expected to influence the force of intramolecular electronic repulsion. A dynamic NMR study suggested the dissociation of TPPTS from $HRh(CO)(TPPTS)_3$ is less activated at relatively low solution ionic strength [26]; the higher the ionic strength of the medium, the higher the dissociation energy is. Upon the addition of mono-

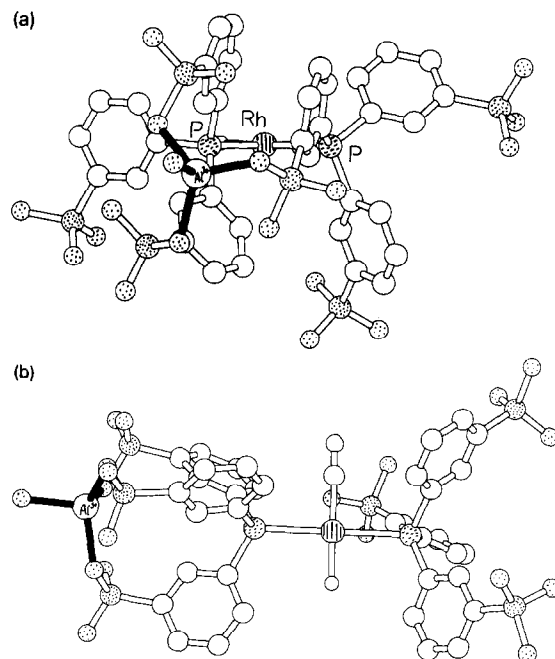


Fig. 6. Drawings generated in CAChe to represent possible modes of sulfonate group coordination to aluminum cations. (a) Two TPPTS ligands in *cis* positions are shown contributing sulfonate groups to the aluminum. (b) A single TPPTS ligand is shown directing all three sulfonate groups to an aluminum cation.

valent water soluble salt, such as Li_2SO_4 , Na_2SO_4 , and Cs_2SO_4 , high ionic strength of the aqueous medium stabilizes $HRh(CO)(TPPTS)_2$ rather than $HRh(CO)_2(TPPTS)$.

If the role of increased salt concentration is to stabilize intermediates that bear a large negative charge then $Al_2(SO_4)_3$ should behave similarly to M_2SO_4 at equivalent ionic strength. However reaction selectivity does not increase with added aluminum sulfate; in fact selectivity decreases slightly. We postulate that by stabilizing the negative charge on coordinated TPPTS aluminum cations alter either the effective dimension of the TPPTS ligand or the coordination geometry about rhodium. Two possibilities are illustrated in Fig. 6. In Fig. 6a, a *cis* arrangement of phosphine at $HRh(CO)(TPPTS)_2$ is shown. It is possible that three sulfonate groups from two phosphines chelate the aluminum ion. This creates the situation where two TPPTS ligands form an effective chelate to rhodium. Alternatively three sulfonate groups from a single phosphine can coordinate

aluminum; this is shown in Fig. 6b. Such an arrangement alters the configuration of the phosphine so that it is more compact when bound to aluminum. On the other hand, the presence of a large cation such as Cs^+ may increase the effective steric size of TPPTS. Thus in the presence of excess Cs_2SO_4 the hydroformylation of hexene goes with excellent selectivity to linear aldehydes.

Acknowledgements

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References

- [1] (a) J.A. Osborn, J.F. Young, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, (1965) 17; (b) D. Evans, G. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, (1968) 2660; (c) D. Evans, J.A. Osborn and G. Wilkinson, *J. Chem. Soc. A*, (1968) 3133; (d) C.K. Brown and G. Wilkinson, *J. Chem. Soc. A*, (1970) 2753.
- [2] V. Kastrup, J.S. Merola and A.A. Oswald, *ACS Symp. Ser.*, 196 (1982) 43.
- [3] J.P. Collman, J.A. Belmont and J. Brauman, *J. Am. Chem. Soc.*, 105 (1983) 7288.
- [4] (a) R.M. Deshpande and R.V. Chaudhari, *Ind. Eng. Chem. Res.*, 27 (1988) 1996; (b) R.M. Deshpande, B.M. Bhanage, S.S. Divekar and R.V. Chaudhari, *J. Mol. Catal.*, 78 (1993) L37; (c) R.M. Deshpande, S.S. Divekar, R.V. Gholap and R.V. Chaudhari, *J. Mol. Catal.*, 67 (1991) 333.
- [5] J. Hjortkjaer, *J. Mol. Catal.*, 5 (1979) 377.
- [6] A. Sanger, *J. Mol. Catal.*, 3 (1977/78) 221.
- [7] B.E. Hanson and M.E. Davis, *J. Chem. Ed.*, 64 (1987) 928.
- [8] R.L. Pruett, *Adv. Organomet. Chem.*, 17 (1979) 1.
- [9] C.A. Tolman, *Chem. Soc. Rev.*, 1 (1972) 337.
- [10] K.L. Olivier and F.B. Booth, *Hydrocarbon Processing*, 49 (1978) 112.
- [11] C.U. Pittman, Jr. and A. Hirao, *J. Org. Chem.*, 43 (1978) 640.
- [12] M.E. Broussard, B. Juma, S.G. Train, W.J. Peng, S.A. Laneman and G.G. Stanley, *Science*, 260 (1993) 1784.
- [13] J.D. Unruh and J.R. Christenson, *J. Mol. Catal.*, 14 (1982) 19.
- [14] T.J. Devon, G.W. Phillips, T.A. Puckette, J.L. Stavinoha and J.J. Vanderbilt, WO 87/07600 (Dec. 17, 1987).
- [15] J. Falbe and H. Bahrmann, *J. Chem. Ed.*, 61 (1984) 961.
- [16] T. Onoda, *CHEMTECH*, 23(9), (1993) 34.
- [17] (a) C.U. Pittman, Jr., in E. Abel, F.G.A. Stone and G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 8, Pergamon, London, 1980, Chap. 55; (b) E. Bonaplata, H. Ding, B.E. Hanson and J.E. McGrath, *Polymer*, in press.
- [18] D.C. Bailey and J.H. Langer, *Chem. Rev.*, 81 (1981) 109.
- [19] P.R. Rony and J.F. Roth, U.S. Pat. (1974) 3,855,307.
- [20] E.G. Kuntz, *CHEMTECH*, 17 (1987) 570.
- [21] (a) J. P. Arhancet, M.E. Davis, J.S. Merola and B.E. Hanson, *Nature*, 339 (1989) 454; (b) J.P. Arhancet, M.E. Davis and B.E. Hanson, *J. Catal.*, 129 (1991) 94; (c) J.P. Arhancet, M.E. Davis and B.E. Hanson, *J. Catal.*, 129 (1991) 100.
- [22] H. Ding, B.E. Hanson, T. Bartik and B. Bartik, *Organometallics*, 13 (1994) 3761.
- [23] W.A. Herrmann and C.W. Kohlpaintner, *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 1524.
- [24] P. Kalck and F. Monteil, *Adv. Organomet. Chem.*, 34 (1992) 219.
- [25] H. Ding and B.E. Hanson, *J. Chem. Soc., Chem. Commun.*, (1994) 2747.
- [26] H. Ding, B.E. Hanson and T.E. Glass, *Inorg. Chim. Acta*, 229, (1995) 329.
- [27] T. Bartik, B. Bartik, T.E. Glass, W.R. Bebout and B.E. Hanson, *Inorg. Chem.*, 31, (1992) 2667.