

Immobilization of a Catalytically Active Rhodium Complex by Electrostatic Interactions of Multiply Charged Phosphine Ligands with a Soluble Polyelectrolyte and Recovery by Ultrafiltration

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Summary: Binding via noncovalent electrostatic interactions of multiply sulfonated phosphine ligands with a soluble polyelectrolyte represents a convenient approach for immobilization of a catalytically active rhodium complex. As a polyelectrolyte, PDADMA- BAR^{F_4} (poly-(diallyldimethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate)) can be utilized. The polyelectrolyte-bound catalyst is active for hexene hydroformylation, and it can be recovered and recycled by ultrafiltration.

Homogeneous catalysts based on soluble transition-metal complexes¹ display high activities and selectivities under mild conditions in a variety of reactions. The catalytic properties can be optimized and adjusted to different substrates by variations of the ligands, most often phosphines, coordinating to the metal center. These advantages of homogeneous catalysts are opposed by a usually tedious separation from the products after the reaction, a problem not encountered with typical heterogeneous catalysts. In hydroformylation, as the largest scale application of homogeneous transition-metal catalysis, the separation of high-boiling side products (formed by condensation reactions) from the catalyst is often required. The development of systems combining the advantages of classical homogeneous and heterogeneous catalysts remains a challenge. Most approaches for immobilization of metal complexes have employed microporous organic or inorganic solids; however, these have met with limited success to date.² By comparison, the success of aqueous two-phase catalysis is demonstrated by its large-scale industrial application in the hydroformylation of propene.³ However, aqueous two-phase catalysis requires a low yet sufficient water solubility of the substrates, strongly limiting its scope. As a different strategy, binding of metal complexes to colloidal structures (dimensions of 1–1000 nm) is finding increasing attention. Soluble polymers,^{4,5} including dendrimers,^{6,7} have been utilized as supports. The

majority of these approaches have employed covalent attachment of ligands (e.g. of mono- or bidentate phosphines) to the polymer. As a different concept which has received relatively little attention to date,⁸ binding of the phosphine ligands of a catalytically active complex can also be achieved by electrostatic interactions (“ionic binding”) with a soluble polyelectrolyte. Hereby, the drawbacks associated with the often tedious synthesis of polymers with covalently bound ligands are circumvented. At the same time, a variety of ligands with ionic substituents (most often sulfonate groups) developed for aqueous two-phase catalysis can be drawn upon. In

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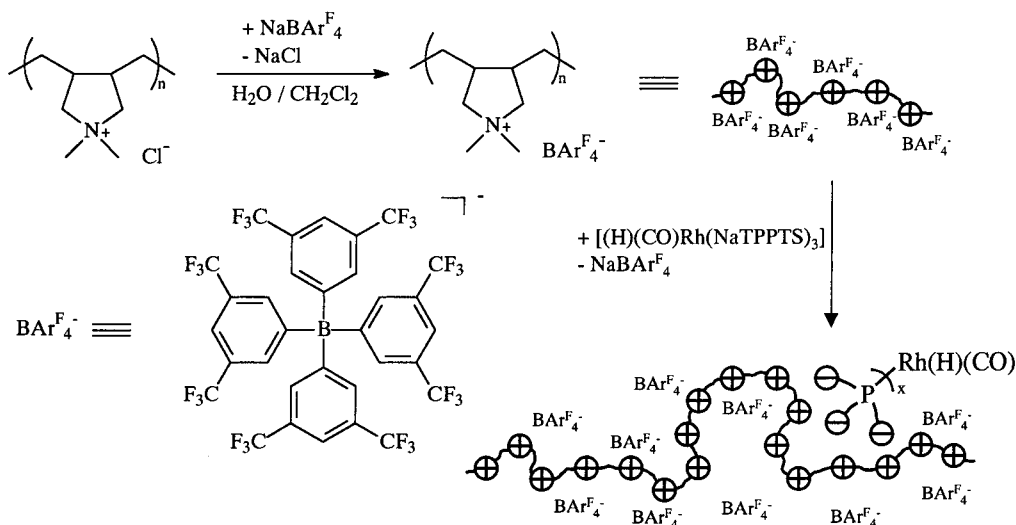
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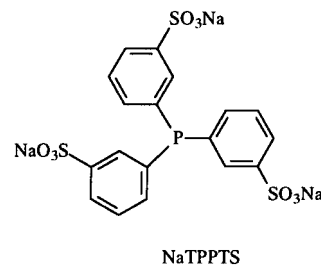
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Scheme 1. Preparation of PDADMA-BAR^F₄ and Binding of the Rhodium Complex

addition, by comparison to covalent attachment, ionic binding of ligands to the polymer offers the advantage of a strong yet reversible interaction with the polymer. Consequently, the spatial array of the polymer-bound ligands could be expected to adjust more freely to the steric requirements for coordination at the metal center instead of being dictated by the polymer. We now report a simple method for immobilization employing electrostatic interactions of multiply sulfonated phosphine ligands with a soluble polyelectrolyte and separation and recycling of a corresponding rhodium-based hydroformylation catalyst by ultrafiltration.⁹

As a source for a suitable cationic polyelectrolyte, commercially available poly(diallyldimethylammonium chloride) (PDADMAC) was employed. For catalysis the presence of inert counterions instead of chloride is desirable. In addition, large organic counterions can increase solubility of the polyelectrolyte in organic solvents. Reaction of PDADMAC with 1 equiv of NaBAR^F₄¹⁰ resulted in formation of PDADMA-BAR^F₄: utilizing a two-phase mixture of water and methylene chloride, the product precipitates selectively (Scheme 1). Washing twice with water yielded the counterion-exchanged polyelectrolyte free of chloride¹¹ in high yield (90%). As anticipated, the material possesses a high solubility in polar organic solvents, such as methanol and acetone.¹² The high-molecular-weight PDADMAC utilized as a starting compound contains low-molecular-weight fractions due to its broad molecular weight distribution. The latter were removed by ultrafiltration (vide infra) of the ion-exchanged polyelectrolyte. Utilizing PDADMA-BAR^F₄ based on a polycation with $M_w = 3 \times 10^5 \text{ g mol}^{-1}$, ca. 5% of undesired low-molecular-weight material passed the membrane.¹³ For efficient binding of a ligand to the soluble polyelectrolyte by (partial) exchange for the anionic counterions, multiple substitution of the ligand with ionic moieties is advan-

ageous. Among a variety of ligands, this prerequisite is also fulfilled by the archetypical NaTPPTS¹⁴ (NaTPPTS = tris(sodium-*m*-sulfonatophenyl)phosphane)



containing three sulfonate substituents per molecule. Stirring the well-known [(H)Rh(CO)(NaTPPTS)₃]¹⁵ with a methanol solution of PDADMA-BAR^F₄ resulted in gradual dissolution of the rhodium complex (Scheme 1).¹⁶ Typically a 4:1 to 10:1 ratio of tetraalkylammonium to sulfonate groups was utilized, such that only a part of the BAR^F₄ counterions was exchanged in order to maintain solubility of the polymer (a 1:1 adduct of the PDADMA polycation with TPPTS is completely insoluble in methanol¹⁷).

The electrostatically polymer bound complex was employed for hydroformylation of hexene. Typically 160 TO h⁻¹ were observed at 80 °C and 30 bar of CO/H₂.¹⁸ Similar activities are observed in comparative experiments with the nonimmobilized complex, which con-

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(10) (a) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920–3922. (b) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600–2604.

(11) Anal. Calcd for C₄₀H₂₈BF₂₄N: C, 48.55; H, 2.85; N, 1.41. Found: C, 48.03; H, 3.10; N, 1.34; Cl below detection limit (0.03%).

(12) For example, the solubility of PDADMA-BAR^F₄ in acetone exceeds 300 g L⁻¹, whereas PDADMAC is virtually insoluble.

(13) (a) The average molecular weight of the PDADMAC used as a starting compound was according to the supplier (Aldrich). The meaningful molecular weight determination of polyelectrolytes is far from a routine procedure; for analysis of PDADMAC, cf.: Dautzenberg, H.; Goernitz, E.; Jaeger, W. *Macromol. Chem. Phys.* **1998**, *199*, 1561–1571 and references cited therein. (b) A membrane of nominal 50 kDa MWCO was utilized.

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(16) For the exchange of the sodium counterions of NaTPPTS for low-molecular-weight mono- or difunctional alkylammonium ions and utilization for hydroformylation, cf.: Bahrmann H. In ref 1, pp 644–654.

(17) AAS analysis revealed less than 1% of the Rh employed to be present in the methanol supernatant of a 1:1 mixture (regarding ionic substituents) of PDADMA-BAR^F₄ or PDADMAC with [(H)Rh(CO)(NaTPPTS)₃].

firms the unhindered accessibility of the polymer-bound rhodium centers. After a hydroformylation run, the reaction solution was subjected to ultrafiltration¹⁹ on an asymmetric polyethersulfone membrane (nominal MWCO 50 kDa).²⁰ While the hydroformylation products and residual hexene rapidly passed the membrane, the polyelectrolyte-bound catalyst was fully retained. AAS of the retentate and filtrate demonstrated 98% rhodium recovery. This recovery corresponds to a retention of 99.8% per cell volume (the 10-fold amount of solvent with respect to the cell volume was pumped through the cell in these experiments). By comparison, the nonimmobilized complex passes the membrane under the same conditions; >90% was found in the filtrate. When the catalyst solution was recycled, virtually the same catalytic activity was observed again (165 TO h⁻¹). Subsequent ultrafiltration again afforded 93% recovery of rhodium. The catalytic activities and rhodium losses upon recycling were found to be reproducible in inde-

(18) Typical reaction conditions: 16 μ mol of Rh; 90 mL of methanol; 10 mL of hexene-1; 30 bar of CO/H₂ (1:1); 3 h; 80 °C. The *n/i* ratio was 2.5 to 3.1. In methanol, the aldehyde products largely react to give acetals, which can be converted to the aldehydes again.

(19) Ultrafiltrations were performed in a custom-made magnetically stirred stainless steel cell operated at a transmembrane pressure of 10 bar. The solution was pumped into the cell, and it was then filtered by pumping neat solvent through the cell (typically 10 cell volumes).

(20) PES membranes were supplied by Sartorius. Please note that the molecular weight cut off (MWCO) given by the supplier refers to water and also depends on the solute. Therefore, nominal MWCOs should be regarded only as a rough indication of the order of magnitude.

pendent repetitive experiments. The 2–7% loss of rhodium present in the filtrate of each run presumably results from a partial oxidation of the phosphine ligand. The batch experiments performed require excessive handling of catalyst solutions, and some exposure to air cannot be excluded. However, this is not an intrinsic problem, since in potential applications a continuous closed system or an integrated membrane reactor would be used. An increase of flow rates during ultrafiltration of the cationic polyelectrolyte and higher catalyst loading are desirable. We are currently investigating other polyelectrolytes and ligands.

In summary, in the system investigated binding of a metal complex to a polyelectrolyte via electrostatic interactions of multiply charged phosphine ligands with the polymer provides a convenient access to a polymer-bound soluble catalyst. This soluble catalyst can be recovered and recycled effectively by means of ultrafiltration.

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