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PREPARATION OF POLYMER-ANCHORED DINUCLEAR RHODIUM(I) CATALYSTS ATTACHED BY THE BRIDGING GROUPS

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Summary - We describe a method to anchor dinuclear rhodium(I) complexes by substitution of the chlorine bridge in $Rh_2(\mu\text{-Cl})_2L_4$ with LiSR where R represents a polymeric chain. The catalytic activity of such complexes compares well with that observed in homogeneous phase.

There is now current interest in attaching transition-metal complexes and especially those having a homogeneous catalytic activity to macromolecular supports in order to prepare insoluble materials (1-3). A great attention has been devoted to polymeric supports containing Lewis bases anchor-sites and usually the polymer $-PPh_2$ ligands are largely used in the litterature (1-3). However the loss of metal was frequently observed certainly due to the formation of coordinatively unsaturated species formed during the catalytic cycle leading to the bond-breaking of the polymer $(Ph_2)P\text{-}M$ bond. We have shown that the $[Rh_2(\mu\text{-SR})_2\{P(OR')_3\}_4]$ complexes present an excellent catalytic activity for the hydrogenation of olefins (4). We herein report results of an investigation of the anchorage of these dinuclear complexes avoiding the coordination by polymer-phosphine ligands and using "polymer-thiolato" bridging ligands instead.

As to prepare the μ-thiolato complexes it is useful to substitute the chloro bridges in $[Rh_2(\mu\text{-Cl})_2L_4]$ by the LiSR reagents (5), we have investigated the extension of this substitution to the case where R represents a polymeric chain (6).

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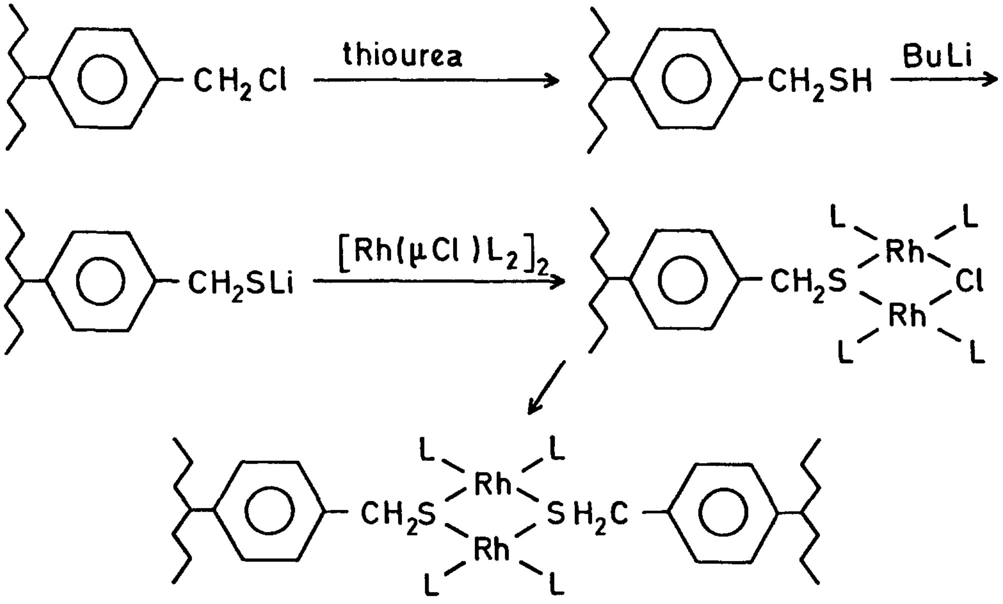
Starting from a chloromethylated-styrene resin crosslinked by divinyl-benzene groups (commercial origine duolite A 368 PR macroporous resin 20 % crosslinked C % 75.6, H % 6.7, Cl % 18.0) we have prepared the polymer mercaptan as described by the following equation :

$$\text{polymer-}C_6H_5CH_2Cl \xrightarrow{\text{thiourea}} [\text{polymer-}C_6H_5\text{-}CH_2SC(NH_2)_2]^+Cl^- \xrightarrow{\text{NaOH}} \text{polymer-}C_6H_5\text{-}CH_2SH$$

We are able to substitute almost all the chlorine groups by the sulfur ligand (C % 75.98, H % 7.79, S % 13.53, Cl % ∿ 0.1). Treatment of this resin with butyllithium in THF solution followed by the addition of the stoichiometric quantity of $[Rh_2(\mu\text{-}Cl)_2(P(OMe)_3)_4]$ in THF under an inert atmosphere (1 mole of complex for 2 at.g of resin) gave results in the incorporation of the rhodium complex to the resin : C % 67.48, H % 6.34, S % 11.18, Cl % traces, Rh % 3.82, P % 2.30. The [P]/[Rh] ratio, found to be almost 2 as in the case of the starting material, is consistent with the anchorage of the $Rh\{P(OMe)_3\}_2$ unit (scheme).



Scheme

However, since the [S]/[Rh] ratio exceeds 2 the less accessible sites presumably cannot be reached due to the too large amount of divinylbenzene groups in the polymer and the further reticulation of the resin by sulfur atoms together with loss of H_2S can be accomplished as already shown for a p-vinyl benzylthioacetate resin $^{(7)}$. If the complex $[Rh_2(\mu\text{-}Cl)_2P(OMe)_3)_4]$ is allowed to react with the polymer-SH material, the resin obtained after the procedure previously described exhibits a broad ν_{CO} band at 1990 cm^{-1} which is different from those observed for the chlorobridged dimer (ν_{CO} = 2005 VS and 1997 m cm^{-1}) even after impregnation of the polymer-$C_6H_5CH_2Cl$ resin by the chloro complex (ν_{CO} = 2005 cm^{-1} VS broad). However this 1990 cm^{-1} frequency compares quite well with that observed for the $[Rh_2(\mu\text{-}SPh)_2(CO)_2\{P(OMe)_3\}_2]$complex $^{(5)}$ (1998 VS and 1984 VS cm^{-1}). This is consistent with the retention of the dinuclear structure of the complex when attached to the resin.

In order to reduce the interactions between the SH groups we have neutralized some CH_2Cl functionnal sites in the starting material by known quantities of butyllithium. For instance from a polymer $C_6H_5CH_2SH$ resin (C % 84.88, H % 7.65, S % 4.33, Cl % 0.47) we have immobilized the $[Rh_2(\mu\text{-}Cl)_2\{P(OMe)_3\}_4]$ complex : C % 72.51, H % 7.13, S % 3.28, Cl % 0.81, Rh % 4.34, P % 1.58. In this case the [P]/[Rh] ratio is near 1.8 but it is worth while to note some residual amount of chlorine arising from the starting resin and the presence of some $[Rh_2(\mu\text{-}Cl)(\mu\text{-}S\ \text{resin})\{P(OMe)_3\}_4]$ complexes.

Moreover the catalytic hydrogenation of cyclohexene was tested for this resin. Thus the resin (100 mg) was charged in an autoclave, swelled with 10 cm^3 of benzene and pressurized at 3 bars of hydrogen at 40°C. No consumption of hydrogen was detected and no cyclohexane was observed by gpc. Introduction of 10 cm^3 of cyclohexene gave rise to hydrogenation forming cyclohexane (yield ∿ 50 % in 4 hrs). As for the homogeneous catalysts, we found for the heterogenized complex a maximum of the catalytic activity as a function of the pressure at about 5 bars.

It seems us that the dinuclear rhodium(I) complexes in solution or on polymer insoluble supports generate the same active species, since the same behaviour was observed for the hydrogenation of cyclohexene.

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