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# HYDROGENATION, HYDROSILYLATION AND HYDROFORMYLATION OF OLEFINS CATALYSED BY POLYMER-SUPPORTED RHODIUM COMPLEXES[1]

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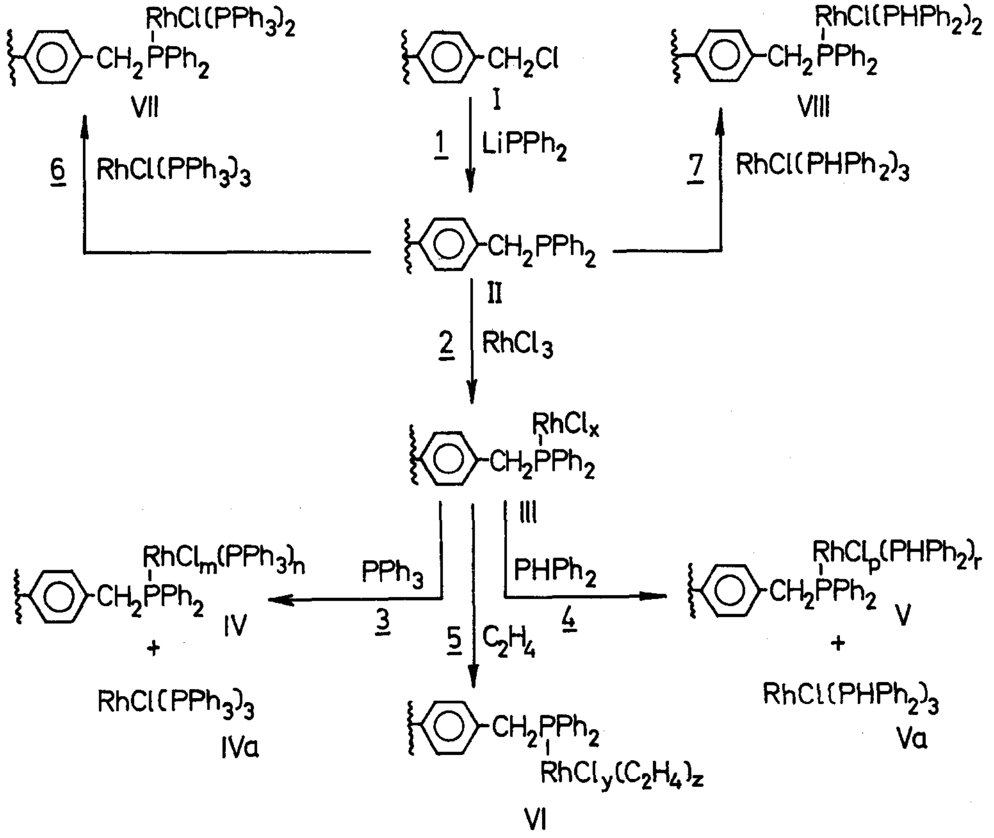
In recent years several attempts have been made to combine the advantages of homogeneous and heterogeneous catalysis[2,3]. A recent work of Grubbs and Kroll on the use of a polymer-supported rhodium(I) complex as hydrogenation catalyst[4] prompt us to report our preliminary results in this very promising field. In conjuction with our studies of hydrosilylation catalysed by soluble rhodium(I) complexes[5,6] we were also interested in catalytic activity of rhodium complexes coordinatively bonded to a polymer containing phosphine groups. In the present communication we wish to report briefly the preparation of such complexes and their catalytic activity in hydrogenation, hydrosilylation and hydroformylation of some olefins.

Preparation of Catalysts. A reaction of easily accessible macroreticular chloromethylated styrene-divinylbenzene copolymer(I) (20% crosslinking, 14,4%Cl particle size 1-2 mm) with benzene solution of lithiodiphenylphosphine[7] (reaction 1) yielded polymeric ligand II (2.4 % Cl, 9.8 % P). Treatment of ethanolic solution of $RhCl_3.3H_2O$ with polymer II (reaction 2) afforded substance III which contained rhodium fixed via Rh-P coordination to the polymer. In an attempt to prepare the analogue of Wilkinson[8] catalyst (compound VII) by reaction 3 we found that the action of triphenylphosphine on compound III in ethanol results in extensive displacement of ligand II from the coordination sphere of rhodium, the main product being Wilkinson catalyst, tris(triphenylphosphine)chlororhodium (I) (compound IVa), as proved by comparison of its IR spectrum with the spectrum of authentic sample[8].



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On the other hand, due to lower coordination ability of diphenylphosphine, reaction 4 is accompanied by the above displacement to much lesser extent. By passing ethylene through a mixture of compound III, benzene and ethanol we prepared compound VI (reaction 5) which contains coordinated ethylene. The other compounds were prepared by exchange of phosphino ligand in the corresponding soluble complexes for polymeric ligand II. Compounds VII and VIII were obtained by shaking a mixture of polymer II and methylene chloride solution of triphenyl- or diphenylphosphine for 24 h (reaction 6 and 7, respectively). All the compounds so prepared were washed several times with the solvents and dried under vacuum. All the procedures were carried out under argon.

Hydrosilylation was carried out in the following way. A mixture of catalyst (1 mg), olefin (0.5 ml) and organosilicon hydride (0.5 ml) was heated in a sealed ampoule to 80° for 2 h. Yields of hydrosilylation products were determined by g.l.c.

We have found that the addition of triethoxysilane to 1-hexene in the presence of compounds III, IV, VI and VII yields 91, 22, 99 and 19% of n-hexyltriethoxysilane, respectively. The addition of the same hydride to ethylvinyl ether acrylonitrile and trans-2-heptene catalysed by complex III (VII) afforded 88 (50), 18(14), 5(5)% of the corresponding n-alkyltriethoxysilane. Compound III turned out to be very efficient hydrosilylation catalyst. Its catalytic activity did not change after the catalyst was exposed to air for 3 days. The hydrosilylation of 1-hexene by triethoxysilane proceeded readily already at 25°C and the catalyst could be reused several times.

Hydrogenation was carried out in an autoclave. 1-Heptene was hydrogenated in the presence of 1%(w.) of catalysts (hydrogen pressure 24 atm., temperature 65°, reaction time 10 h). The reaction mixture was then allowed to stand in air

Table: Hydrogenation of 1-Heptene[a]

| Catalyst | Heptane | 1-Heptene | 2-Heptene |  | 3-Heptene |  |
|---|---|---|---|---|---|---|
|  |  |  | cis- | trans- | cis- | trans- |
| III | 98(63.6) | 0(1) | 0(7.3) | 1(16.3) | 0(2.7) | 1(9.1) |
| IV | 68.2(43.6) | 0(0.5) | 4.9(10.2) | 17.1(20.4) | 2.4(2) | 7.3(6.1) |
| V | 74.5(49.7) | 0(13.2) | 9.5(15) | 12.7(17) | 1(1.9) | 2(3.8) |
| VI | 54.2(43.6 | 3.9(9) | 15(19.5) | 20.5(24) | 1.8(1.5) | 4.7(3) |
| VII | 19.7(4.3) | 70(78.2) | 5.5(6.5) | 4.4(10.8) | 0(0) | 0(0) |
| VIII | 6(2) | 91.8(96) | 1(2) | 1(2) | 0(0) | 0(0) |

[a] Composition of reaction mixtures was determined by g.l.c.

for 30 h, the catalyst was recovered by filtration and reused under the same experimental conditions (see Table, the data in parentheses).

Some of the complexes were catalytically active at room temperature. So, for instance, in the presence of complex III 1-heptene was converted into n-heptane with 60% yield (25°, 35 atm. $H_2$, 16 h), crotonaldehyde was selectively hydrogenated to butyraldehyde (35%), vinyl acetate gave ethyl acetate (50%) and vinylethyl ether afforded diethyl ether (55%) (110°, 40 atm $H_2$, 6 h).

Hydroformylation. Compound VI was found to be good hydroformylation catalyst. Hydroformylation of 1-heptene in the presence of 5% (w.) of complex VI ($H_2$:CO=3:4, total pressure 40 atm, 20 h) gave a mixture of n-octanal (56% yield) and iso-octanal (24% yield). The reaction was accompanied by concurrent isomerisation of the unreacted olefin. Somewhat worse results were obtained with complexes IV, V and VII.

## References

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