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VERSATILE POLYMER-BOUND RHODIUM CATALYSTS.
FACILE HYDROGENATION OF AROMATIC COMPOUNDS IN THE LIQUID PHASE

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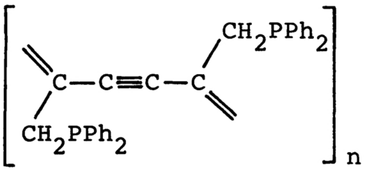
Immobilized complexes prepared from $[RhCl(nbd)]_2$ (nbd = norbornadiene) and phosphinated polydiacetylene or silica are efficient catalysts for the hydrogenation of arenes under mild conditions. However, the homologous catalyst supported on a phosphinated polystyrene is not active.

It has been established that polymers can play an important part in modifying the activity of immobilized complex catalysts.$^{1)}$ The unique characteristics observed in these catalytic reactions arise mostly from structural effects of the polymers. Polystyrene-based polymers, which possess a flexible backbone and often swell under the reaction conditions, have widely been studied as the support material. However, few repots on rigid polymer supports have appeared. From this view, we have studied the catalytic properties of complexes supported by rigid polymers such as phosphinated polydiacetylene$^{2)}$ and silica$^{3)}$. In this paper we report that such rhodium catalysts are active for the hydrogenation of benzenes at an ambient temperature. Until recently, only a few complexes have been known to be efficient for the hydrogenation of arenes in a hybrid phase$^{2,4)}$ or homogeneous state$^{5)}$.

The phosphinated supports used in the present study were prepared according to the previously reported methods.$^{2,3)}$ The phosphino group (abbreviated as P) contents of 1, 2, and 3, which were determined by elemental analysis, were 3.46, 0.56, and 0.79 mmol/g, respectively.



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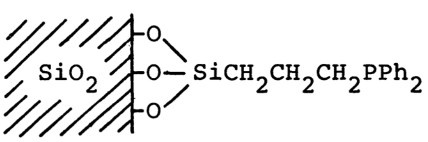

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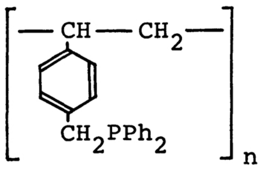

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When a suspension prepared by the addition of support 1 to a benzene solution containing $[RhCl(nbd)]_2$ (4) was allowed to stand in contact with hydrogen at 1 atm, a steady hydrogen uptake commenced after an induction period (ca 1~3h).

In this period the rhodium complex appears to be anchored and activated. Cyclohexane was detected in the solution, and its amount was stoichiometrically equivalent to the hydrogen absorbed. The rate of hydrogen uptake depended upon the ratio of P to Rh. Using the catalytic systems prepared from 1 and 4 (0.1 mmol) in benzene (10.0 ml) in the P/Rh ratios shown in parentheses, the rates, H_2 ml/min, at 25 ± 0.5°C and 1 atm were 0.51 (0.8), 0.79 (1.2), 1.35 (1.6), 1.41 (1.8), 1.21 (2.0), and 0.1 (2.4). In separate experiments, when support 1 was equilibrated with the rhodium complex in the P/Rh ratios shown in parentheses, the respective solutions contained 55 (0.8), 38 (1.2), 16 (1.8), 10 (2.0), and 3 % (2.4) of 4 used, and no other rhodium species were detected. It was also confirmed that the solid phase retained the hydrogenation activity while the filtrate did not. Furthermore, 4 itself possessed no activity for benzene hydrogenation even in the presence of triphenylphosphine. As shown above the hydrogen uptake rate reached a maximum at a P to Rh ratio of 1.8. In the solid phase, however, the ratio is estimated to be 2.1, because 16 % of 4 remained uncomplexed in the solution. Thus, the turnover rate (cycle/Rh/h) is calculated to be at least 13. This rate is superior to those of all known homogeneous6) and hybrid phase4a) catalysts.

The silica-supported catalyst prepared from 2 and 4 was also efficient for the reduction of benzene to cyclohexane under ambient conditions. The hydrogen uptake rates were 1.9 (2.1) and 0.1 ml/min (2.5 P/Rh) under the same conditions, and the induction periods were about 0.5 and 1.5 h, respectively. Over 96 % of 4 was anchored in each case. In these reactions, a light brown color appeared during the activation period and was unchanged throughout the hydrogenation. The color was similar to that of a supported complex prepared from 2 (amount of P ; 0.15 mmol) and $RhCl(PPh_3)_3$ (0.1 mmol), while this catalyst possessed poor activity for the hydrogenation of benzene (0.05 ml/min). In the catalyst system of 2 and 4, however, decrease in the P to Rh ratio (to less than 1.8) resulted in the reduction of 4 to metallic rhodium.

In contrast, the polystyrene-supported catalyst prepared from 3 and 4 in the P/Rh ratio of 2 was not active for the hydrogenation of benzene, and the rate of hydrogen uptake was not measured (less than 0.01 ml/min), though 89 % of 4 was anchored at this P/Rh ratio.

The hydrogenation of various aromatic compounds was carried out at an ambient temperature under 80 atm of hydrogen. Substituted benzenes with electron-releasing groups were more readily reduced than chlorobenzene and nitrobenzene. Alkylbenzenes gave the corresponding cyclohexanes in quantitative yields. It is noteworthy that cyclohexenes were not detected during the hydrogenations of benzene and *o*-xylene using the polydiacetylene-supported catalyst. Biphenyl afforded cyclohexylbenzene as a by-product, suggesting that the two benzene rings are hydrogenated one by one. Xylenes formed predominantly cis-dimethylcyclohexane. The cis-selectivity was highest in *o*-xylene, and the polydiacetylene-supported catalyst was superior to the silica-supported one. Strangely enough, our attempts to hydrogenate naphthalene and 1-methylnaphthalene were unsuccessful. In the absence of substrate, there were no detectable absorptions of hydrogen in both catalytic systems using 1 and 2. Therefore, the polydiacetylene chain and the phenyl groups of the phosphines

Table Hydrogenation of Arenes Catalyzed by Supported Rhodium Complexes [a)]

Substrate	Support	Reaction Time (h)	Products	Yield (%) [b)]
Benzene	1	0.9	Cyclohexane	100
	2	0.3	Cyclohexane	100
Toluene	1	1.5	Methylcyclohexane	100
	2	0.7	Methylcyclohexane	100
t-Butylbenzene	1	8	*t*-Butylcyclohexane	96
Biphenyl [c)]	1	5.7	Bicyclohexyl	78
			Cyclohexylbenzene	21
Anisole	1	0.7	Methoxycyclohexane	100
	2	0.8	Methoxycyclohexane	100
Aniline	1	17	Cyclohexylamine	80
Chlorobenzene	1	17	Cyclohexane	10
			Chlorocyclohexane	5
Acetophenone	1	4	1-Cyclohexylethanol	62
			Cyclohexylmethylketone	19
Nitrobenzene	1	3	Aniline	90
o-Xylene	1	1.8	1,2-Dimethylcyclohexane cis : trans = 96.0 : 4.0	100
m-Xylene	1	1.5	1,3-Dimethylcyclohexane cis : trans = 91.3 : 8.7	100
p-Xylene	1	1.5	1,4-Dimethylcyclohexane cis : trans = 86.1 : 13.9	100
	2	3	1,4-Dimethylcyclohexane cis : trans = 73.1 : 26.9	100
Cyclohexanone	1	0.4	Cyclohexanol	100

a) A mixture of support [1, 0.162g ($-PPh_2$, 0.54 mmol) or 2, 1.34g ($-PPh_2$, 0.75 mmol)] and $[RhCl(nbd)]_2$ (0.15 mmol) in heptane (3 ml) was stirred under a nitrogen atmosphere for several hours. A 65 ml stainless steel autoclave was charged with the mixture and the aromatic substrate (30 mmol) under a nitrogen atmosphere, flushed three times with hydrogen, and then pressurized to 80 atm. The hydrogenation reaction was carried out with magnetic stirring at 30 ± 1°C.

b) The yields were determined by GC methods using an internal standard.

c) Biphenyl (15 mmol) and heptane (13 ml) were used.

appeared to be unchanged in the hydrogenation.

Though it is generally difficult to pass the strict judgement on the deposition of metallic rhodium, we deduced that the catalysis is attributed to the supported complex not to the metallic rhodium from the following facts : 1) when the P/Rh ratios were changed, a maximum activity was observed ; 2) the deposition of metal was not found with the naked eye in the hydrogenation using the silica-supported catayst ; 3) naphthalenes could not be hydrogenated ; 4) after the hydrogenation the catalyst behaved like rhodium(I) species on the reaction with carbon monoxide or bis(diphenyphosphino)ethane (vide infra). These results are compatible with the catalysis of supported rhodium complex.

Because of the limited loading of the supported complex, our attempts to observe the IR absorptions of the rhodium species on 1 for the P/Rh ratio of 2 failed. On exposure to carbon monoxide (1 atm) in benzene, however, both the complexes before and after use showed two IR absorption bands due to ν_{CO} at 2065 and 1980 cm^{-1} in the intensity ratio of 1 : 2~2.5. The complex supported on 2 and 3 also exhibited similar IR bands on exposure to carbon monoxide, whereas the relative intensities were about 1 : 1.5 and 1 : 3.5, respectively. The oxidation state of the rhodium may be +1, because ligand exchange of the polydiacetylene-supported catalyst with bis(diphenylphosphino)ethane gave $RhCl(Ph_2PCH_2CH_2PPh_2)_2$ in 4% yield. Therefore the band around 2060 cm^{-1} may be assigned to ν_{CO} of complexes with a low ratio of non-removable ligands to rhodium, like $RhCl(CO)_2L$ and $Rh_2Cl_2(CO)_3L$ 7) (where L is the phosphine). The other band may be due to the complexes such as $RhCl(CO)L_2$, $Rh_2Cl_2(CO)_2L_2$, and $Rh_2Cl_2(CO)L_3$,7) where the ratio of L to Rh is higher than 1. From these considerations it is deduced that before the exposure to carbon monoxide the supported catalysts contain coordinatively unsaturated sites and/or readily removable ligands, and that the number of these sites and/or ligands is higher on 1 and 2 than on 3. This difference may reflect the natures of the polymer matrices rather than the simple electronic factors of ligand and/or steric environment around the phosphorus, because these three supports possess the same group ; $-CH_2PPh_2$. Consequently, this novel catalysis is better attributed to an effect of the rigid polymer backbone, though its nature is still unclear.

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