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HYDROGENATION OF OLEFINS BY π-ARENE RUTHENIUM COMPLEXES
A ROLE OF π-ARENE LIGAND IN CATALYTIC ACTIVITY

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Abstract—The divalent ruthenium complexes bearing benzene, mesitylene and triphenylbenzene as a π-ligand were prepared and their catalytic activity for olefin hydrogenation was examined. They showed activity in the presence of a small amount of base. Particularly, the complex with triphenylbenzene was found to have extremely high activity. Discussion here is on a role of a π-arene ligand in the activity.

INTRODUCTION

Although the complexes bearing an aromatic π-ligand of zerovalent metals such as bis-π-arene- and π-arene-carbonyl-metal complexes and their derivatives have been investigated, little work has been done on the complexes of metals in relatively high oxidation states. μ-Dichloro-π-benzene-ruthenium complex, the preparation of which was reported by Winkhaus and Singer,[1] is a divalent ruthenium complex, and has been postulated to be polymeric as shown in Fig 1 because of its insolubility[1] or dimeric inferred from its IR spectrum.[2] Recently, some reaction properties of this benzene complex and its derivatives were reported by Zelonka and Baird,[2,3] and the single crystal X-ray diffraction study of the phosphine derivatives was reported by Bennett *et al.*[4] We also reported briefly the catalytic activity of the benzene complex for olefin hydrogenation.[5]

One unit of the polymeric μ-dichloro-π-benzene-ruthenium corresponds to the form in which benzene replaces three triphenylphosphines in $RuCl_2(PPh_3)_3$ known as the most active catalyst for hydrogenation of α-olefins. The phenyl groups of triphenylphosphine may be considered to play a role through a P atom as a buffer zone for charge fluctuation on the central metal participating in catalytic reaction. Therefore, it is very likely that the π-benzene ligand may also play the same role as triphenylphosphine to give the benzene complex an activity for olefin hydrogenation. It is very instructive in the same sense to know that Avilov *et al.* briefly reported a catalytic activity of some black precipitates obtained from $RhCl_3$ and substituted cyclohexadienes for olefin hydrogenation.[6]

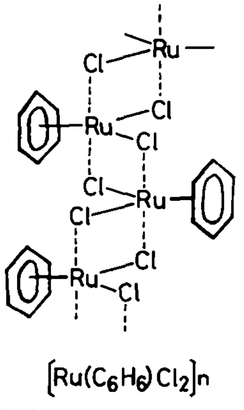

Fig 1. μ-Dichloro-π-benzene-ruthenium(II).

In this paper, we wish to report the preparation of divalent ruthenium complexes bearing benzene, mesitylene and triphenylbenzene as a π-ligand, and their catalytic activity for olefin hydrogenation studied with special interest in what effects a π-arene ligand might really exert on the catalytic activity.

EXPERIMENTAL

Preparation of complexes. Complexes were prepared from an ethanolic soln of $RuCl_3 \cdot 3H_2O$ and the corresponding 1,3- or 1,4-cyclohexadiene homologs according principally to the method reported.[1] Ppts formed were washed with MeOH and subsequently with benzene. No ppts were obtained under virtually the same conditions either by using aromatic compounds themselves instead of the corresponding dienes or by heating the ethanolic soln of $RuCl_3 \cdot 3H_2O$ alone in the presence of kieselguhr generally used as catalyst support.

1,3-Cyclohexadiene was obtained commercially. 1,4-Cyclohexadiene and 1,3,5-trimethyl-1,4-cyclohexadiene were prepared by Birch reduction[7] of benzene and mesitylene, respectively. 1,3,5-Triphenyl-1,3-cyclohexadiene was prepared by the method reported by Kohler.[8]

The benzene complex (Ru–B) was obtained as a dark brown ppt from $RuCl_3 \cdot 3H_2O$ and 1,3- or 1,4-cyclohexadiene in the abs EtOH at 35–38°. Its elemental analyses showed the formula of $[RuCl_2(C_6H_6)]_n(RuCl_2)_m$ ($m/n = 0{\cdot}2$–$0{\cdot}4$), which means that some parts of the polymer chain of $[RuCl_2(C_6H_6)]_n$ are lacking in a π-benzene ligand.

But by using 96% aqueous EtOH, a light brown ppt of $m \doteqdot 0$ could be obtained. When the ppt was washed repeatedly with MeOH in the light, the figure m tended to increase slowly, but every batch of ppts showed identical IR and NMR spectra as well as solubility independently of the magnitude of m. During the course of preparation neither evolution of hydrogen nor formation of aldehyde was observed, while the formation of cyclohexene and hydrogen chloride was observed in the reaction soln. The same ppt was obtained in THF and in ethanol. Through the quantitative study, it was confirmed that the hydrogen liberated by the transformation of cyclohexadiene into benzene was partly used for the formation of hydrogen chloride and partly for the reduction of cyclohexadiene to cyclohexene.

Ru-B is soluble in DMSO, partially soluble in DMF, slightly in water and acetonitrile, and substantially insoluble in other usual organic solvents. On standing Ru-B dissolved in DMSO, the dark brown soln turns light orange, and the polymer chain of the complex is cut off to yield the complex in which DMSO is coordinated to ruthenium. Evaporation of DMSO and subsequent recrystallization from water-EtOH gave red needles, d.p. above 180°. This complex is stable in air; soluble in water, DMSO, AcOH and phenol; sparingly soluble in $CHCl_3$, CH_2Cl_2 and MeOH; and almost completely insoluble in EtOH, benzene and other usual organic solvents. Elemental analyses, IR and NMR spectra[5] suggested the formula $RuCl_2(C_6H_6)[(CH_3)_2SO]$. The DMSO complex is possibly a dimer, inferred from its far IR spectrum.*

The Mesitylene complex (Ru-M) was obtained by a similar procedure to Ru-B, but required longer reaction time than Ru-B even at 37-40°. In spite of many attempts, the complex obtained was not $[RuCl_2(C_9H_{12})]_n$, but $[RuCl_2(C_9H_{12})]_n(RuCl_2)_m$ ($m/n = 0{\cdot}4$–$0{\cdot}5$). Ru-M is insoluble in the usual organic solvents except DMSO. The NMR spectrum of Ru-M in DMSO-d_6 (Fig 2) showed a singlet at δ 2·17 ppm assignable to Me protons and a singlet at δ 5·46 ppm assignable to aromatic protons. The ratio of peak area of Me protons to that of aromatic protons was 3 : 1. The signal of aromatic protons shifted to upper field in the usual manner of π-arene metal complexes. Therefore, it is quite certain that mesitylene, instead of 1,3,5-trimethyl-1,4-cyclohexadiene, is coordinated to ruthenium.

On standing Ru-M dissolved in DMSO, the dark brown soln turned light orange. The IR spectrum of the crude product after high vacuum evaporation of DMSO showed a ν_{s-o} frequency† shifting compared with that of free DMSO and suggested the formation of DMSO complex. However, the isolation of pure DMSO complex of Ru-M was unsuccessful because the coordinated DMSO was released again during recrystallization.

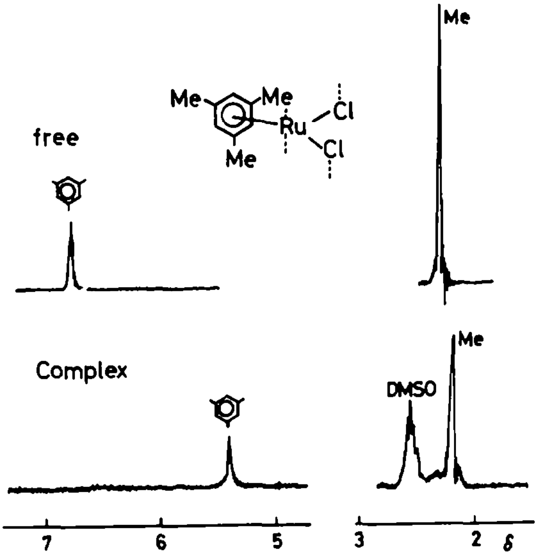

Fig 2. NMR spectra of Ru-M and free mesitylene (in DMSO-d_6, 60 MHz, TMS standard).

The triphenylbenzene complex (Ru-TPB) was formed with still more difficulty than Ru-M. It was obtained only after prolonged heating at 50-60°. In this case also, only a product corresponding to $[RuCl_2(C_6H_3Ph_3)]_n(RuCl_2)_m$ ($m/n = 1$–2) was obtained. It may be supposed from Fig 1 that triphenylbenzene is hardly coordinated side by side to adjacent metals owing to its bulkiness. The solubility of Ru-TPB is still lower than the other two complexes, and the only good solvent was sulfolane used for the extraction of aromatics. Even nitric acid could not decompose the complex completely into solution, and it was decomposed only by being treated with conc H_2SO_4. From these observations it may be thought that the surface of the polymeric complex is closely covered with triphenylbenzene molecules. The measurement of NMR spectrum of Ru-TPB in DMSO-d_6 (Fig 3) was successful only by repeated sweeps. From the ratio of peak areas of aromatic protons, it was shown that triphenylbenzene, not dienes, is coordinated. The signal of protons in the central ring of coordinated triphenylbenzene appeared at δ 7·10 ppm, 0·75 ppm higher than that of free triphenylbenzene. This suggests that the central benzene ring is coordinated to

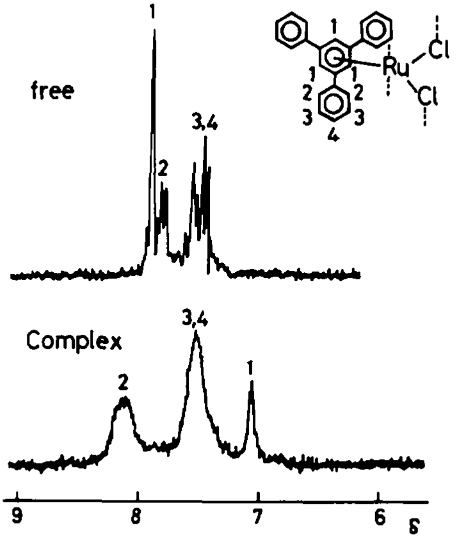

Fig 3. NMR spectra of Ru-TPB and free triphenylbenzene (in DMSO-d_6, 60 MHz, TMS standard).

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* ν_{RuCl}; 294, 276, 247, 225 cm^{-1}.

† $\nu_{s=0}$ of the crude product (KBr disk); 1110, 1010. $\nu_{s=0}$ of free DMSO (liquid film); 1055 cm^{-1}.

ruthenium. Furthermore, the signal of the ortho protons of three phenyl groups of the complex shifted to lower field, which agrees with the observations that the signal of ortho protons of monosubstituted benzene having an electron withdrawing group such as nitro group shifts to lower field. It is well known that the $Cr(CO)_3$ group of the π-arene-tricarbonyl-chromium complexes has the same extent of electron withdrawing effect as the nitro group. Therefore, it can be supported also from the lower field shift of the ortho protons that triphenylbenzene is coordinated to ruthenium.

As mentioned above, it can be inferred from IR and NMR studies that the complexes bearing benzene, mesitylene and triphenylbenzene as a π-ligand were certainly formed, although they contain some parts lacking a π-arene ligand.

Hydrogenation reaction. Hydrogenation was carried out in a glass tube inserted in a 25 ml stainless steel autoclave using a designed amount of catalyst, 0·5 ml of olefin and 3 ml of solvent under 20 kg/cm^2 of initial hydrogen pressure at $30 \pm 0{\cdot}1°$ for 4 hr with constant agitation by a TEFRON-coated magnetic rotor. Hydrogen pressure changes were recorded using an automatic pressure recorder. The products were analyzed by GLC (column packed with benzylcyanide and silver nitrate on Neopak 1A, each 4 mmμ × 3 m).

Comparison of catalytic activity between dissolved and undissolved parts of a complex after hydrogenation run. The first hydrogenation run was carried out using 18 mg of Ru–TPB, 0·5 ml of pentene-1 and 3 ml of the solvent (benzene/pyrrolidine = 3/0·007 v/v) under 20 kg/cm^2 of initial hydrogen pressure at 30°. After H_2 uptake ceased, the mixture was separated under N_2 into liquid and solid portions using an injection-syringe with a filter at the head of its needle. Each portion was evaporated to dryness under high vacuum at room temp. Then, using each residue as a catalyst the next run was made again respectively under the operating conditions described above, and the rate of reaction was measured. Since the solid portion was partly dissolved again during the reaction, the separation into two portions was repeated, and the same operations as above were performed repeatedly.

Analysis of ruthenium. After the solution was evaporated to dryness, the residue was decomposed by being heated in conc H_2SO_4. The resulting soln was diluted with water, and a definite amount of $NaHCO_3$* was added. The atomic absorption of ruthenium in this solution was measured with a Techtron AA100 spectrophotometer using an air-acetylene flame at 349·9 nm. Ruthenium(III) acetylacetonate was used as a standard compound for calibration.

RESULTS AND DISCUSSION

The results of hydrogenation using the complexes described above are summarized in Table 1. The rate of reaction and the composition of products depended upon the kind of solvents and additives employed. In benzene alone, the complexes had low activity, but showed high activity by adding a small amount of organic base such as pyrrolidine, although the addition of a large excess of base lowered the activity. Particularly, the reaction by Ru–TPB in the presence of pyrrolidine was completed within 10 min at 30°. Its activity against equimolar amount of the metal was comparable or rather superior to that of 5% metallic ruthenium on carbon (Nippon Engelhard, Ltd.). In strongly coordinating solvents such as acetonitrile and DMSO, the reaction scarcely proceeded. In DMF, which is also a strongly coordinating solvent, isomerization was more predominant than hydrogenation (the former 85%, the latter 14%). Every complex hydrogenated not only terminal olefins such as pentene-1 but also inner olefins such as pentene-2. However, the rate of the hydrogenation of inner olefins was slower than that of terminal olefins. The difference of the rates was particularly large in the case of Ru–TPB. The difference, however, was smaller than that in the case of $RuCl_2(PPh_3)_3$, probably because the bulkiness of triphenylbenzene could not be so large as that of three molecules of triphenylphosphine. As shown in Table 2, the competitive hydrogenation of mixed substrates revealed that dienes did not retard the hydrogenation of terminal olefins, but was reduced as slow as internal olefins. For the purpose of comparison, hydrogenation was attempted using also $RuCl_3{\cdot}3H_2O$ as a catalyst under virtually the same conditions, but catalytic activity was scarcely observed.

Any complex showed no activity for hydrogenation of benzene at 30°.

Since the catalytic behavior for hydrogenation mentioned above is similar to that of $RuCl_2(PPh_3)_3$, a similar reaction scheme to that proposed on the phosphine complex has been postulated, and further, in the case of the benzene complex with DMSO the formation of its hydride complex was confirmed by NMR.[5]

The coloration of the solution after the reaction to reddish or yellowish brown suggested that a part of the catalyst was dissolved during the reaction. Although the catalysts were not completely dissolved and some ppts still remained after reaction, contamination with metallic ruthenium can be ruled out from the following facts: all the ppts remaining after reaction were completely soluble in DMSO, and moreover, metallic ruthenium catalyst showed activity independently of the presence and absence of pyrrolidine and hydrogenated not only olefins but also benzene.

The reaction mixture after a hydrogenation run was separated into liquid and solid portions under nitrogen, and the next run was carried out again using each portion as a catalyst. Both portions showed activity without induction period. The solid portion was partly dissolved again during the reaction to give a mixture of liquid and solid portions. It would be, therefore, considered that the polymer chain of a catalyst was cut off at μ-bond under the reaction conditions, and that the low molecular part was dissolved, whereas the high molecular

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*Without $NaHCO_3$, the interference by H_2SO_4 is so remarkable that the measurement is virtually impossible.

Table 1. Hydrogenation of olefins by μ-dichloro-π-arene-ruthenium complexes[a]

Catalyst (mg)	Olefin (0·5 ml)	Solvent (3 ml)	Additive (ml)	Product composition[b] (%)			
				Pentane	Pentene-1	Pentene-2 *trans*	Pentene-2 *cis*
Ru-B 10	Pentene-1	Benzene	Pyrrolidine 0·007	93	0	6	1
Ru-M 10				91	0	7	2
Ru-TPB 10				100[c]	0	0	0
Ru-B 10 ($m \doteqdot 0$)				11	88	trace	1
Ru-B 10	Pentene-1	Benzene	none	5	91	0	4
Ru-M 12				3	92	1	4
Ru-TPB 19				36	25	22	17
Ru-B 10	Pentene-1	Benzene	Pyrrolidine 1·0	1	99	0	0
			Et_3N 0·01	22	46	20	12
			Et_3N 1·0	2	98	0	0
Ru-B 10	Pentene-1	Cyclohexane	Pyrrolidine 0·007	32	68	0	0
		CH_3CN	none	1	99	0	0
		DMSO	none	1	99	0	0
		DMF	none	14	1	71	14
Ru-B 10	Pentene-2[d]	Benzene	Pyrrolidine 0·007	47	0	42	11
Ru-M 12				39	0	45	16
Ru-TPB 19				89	0	10	1

[a] Initial pressure of H_2: 20 kg/cm^2. Temp.: 30 ± 0·1°. Reaction time: 4 hr.
[b] The composition of products was estimated by g.l.c.
[c] The reaction was completed within 10 min.
[d] *Trans* 52% and *cis* 48%.

Table 2. Competitive hydrogenation of mixed substrates*

Run	Substrate	(ml)	Product composition (%) Saturated	Monoenic	Recovered
1	Pentene-1	0·5	94	4 (*trans*) 2 (*cis*)	0
	1,3-Cyclooctadiene	0·25	4	16	80
2	Cyclohexene	0·25	18	0	82
	1,3-Cyclooctadiene	0·25	8	7	85
3	Cyclooctene	0·25	10	0	90
	1,5-Hexadiene	0·25	3	10	87

*Catalyst: Ru–B, 10 mg (run 1) and 7 mg (run 2,3). Solvent: 3 ml of benzene containing 0·007 ml of pyrrolidine. Reaction time: 4 hr (run 1) and 3 hr (run 2,3). The other reaction conditions are the same as described in Table 1.

part remained undissolved, which was again in part dissolved, μ-bond being further cut off in the next run. Fig 4 shows the results of the study on the catalytic activity of dissolved and undissolved portions of Ru–TPB. Catalytic activity is represented here by rate of reaction. Low activity of the dissolved part at the first separation step is ascribed to the partial decomposition of active species caused by careless aeration of the liquid portion, which immediately turned green. At the third step it could not be dissolved any further, which was indicated by weak coloration of the solution.

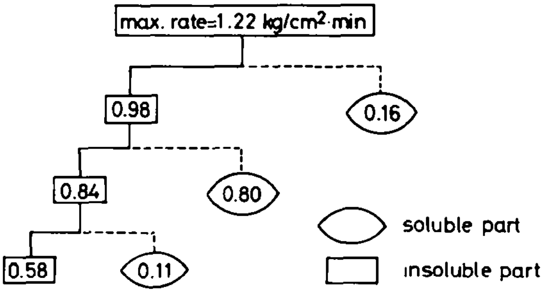

Fig 4. Catalytic activity of dissolved and undissolved portions of Ru-TPB for hydrogenation of pentene-1.

Actually its activity was low. The last part which remained undissolved was still completely soluble in DMSO. The existence of coordinated aromatic ring was confirmed by NMR in both dissolved and undissolved parts. Although a small amount of free aromatic ring was also detected, it may result from photolysis during the preparation of NMR sample, not from release during the hydrogenation reaction, because the amount of free aromatic ring detected decreased remarkably by preparing the sample in the dark with much care. Almost the same results were obtained with Ru–M.

As mentioned above, the preparation of the complex m ÷ 0 was successful only in the case of Ru–B. However, this complex showed only very low activity. Therefore, it seems that the existence of some parts deficient in a π-arene ligand is essential for emergence of activity. If the activity would be attributed to this $RuCl_2$ moiety lacking a π-arene ligand and independent of the part with aromatic ligand, the observed rate of hydrogenation must be correlative with the calculated amount of $RuCl_2$ moiety of the catalyst added. As shown in Fig 5, the variation of the content of the part lacking a π-arene ligand, however, did not give so large a change in the catalytic activity in each catalyst. The activity was considerably dependent on the difference of the kind of aromatic ligands. It was extremely high in Ru-TPB containing triphenylbenzene which is a strong electron-donor and acceptor. Ru–M containing mesitylene in which electron donating property is dominant showed the lowest activity of the three. From these results it can be seen that an aromatic ligand, particularly triphenylbenzene, affords remarkable effect to the activity, although the presence of parts deficient in a π-arene ligand is essential for the emergence of activity. That parts are probably necessary for the dissolution of polymeric catalyst as a position where μ-bond of the catalyst is fissible by attacking of solvent or reagent molecules.

However, in the results shown in Fig 5 still remains the doubt that Ru–TPB is particularly apt to dissolve and the concentration of ruthenium in the reaction solution is higher in the case of Ru–TPB. Then, after hydrogenation using Ru–TPB or Ru–B, only a liquid portion was taken up by filtration and evaporated to dryness. Using the residue as a catalyst hydrogenation reactions were performed in homogeneous system in different catalyst concentrations, and the reaction rates were recorded. Then, ruthenium content in the reaction system was measured by atomic absorption analysis. The results are shown in Fig 6. Although Ru–TPB was somewhat more soluble than Ru–B, the former was about 20 times more active than the latter even at the same ruthenium concentration. The plateau at high ruthenium concentration might well result from the fact that the reaction was so rapid and the dissolution of hydrogen may become the rate-determining step* at that magnitude of catalyst concentration. If the π-arene

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*This was confirmed at the same magnitude of velocity using metallic ruthenium supported on carbon.

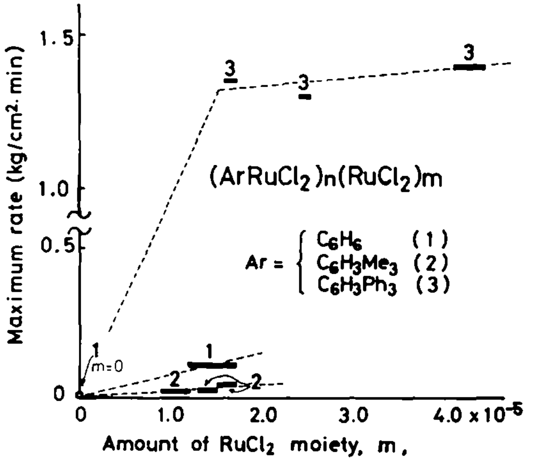

Fig 5. Plot of maximum rate of hydrogen pressure drop against amount of $RuCl_2$ moiety lacking π-arene ligand.

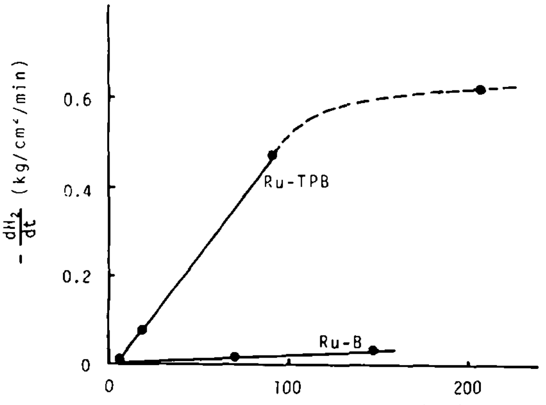

Fig 6. Comparison of activity for hydrogenation as a function of Ru concentration between Ru-TPB and Ru-B.

ligand does not contribute to the activity, there must be no difference between the activity of Ru–B and that of Ru–TPB at the same ruthenium concentration. Therefore, it can be almost certain that the π-arene ligand affects catalytic activity.

Among the π-arene ligands examined, the triphenylbenzene ligand afforded extremely high activity, which is very interesting from the similarity in both structure and function between triphenylbenzene and triphenylphosphine, considering that the compound in which the central ring of triphenylbenzene is displaced by P atom corresponds to triphenylphosphine regarded as the most effective ligand in transition metal complex catalysts.

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