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Note on the Preparation and Catalytic Properties of Dichlorotris[tris(*p*-methoxyphenyl)phosphine]ruthenium

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Synopsis. The procedure for the preparation of $RuCl_2[(p\text{-}MeOC_6H_4)_3P]_3$ was improved, resulting in a higher catalytic activity. The complex was thirteen and five times as active as $RuCl_2(Ph_3P)_3$ in the hydrogenation of 1,4-androstadiene-3,17-dione (I) and 4-androstene-3,17-dione (II), respectively, indicating that the methoxy complex is more selective for formation of II in the consecutive hydrogenation pathway of I.

In the preceding paper,[1] it was shown that the catalytic activity of dichlorotris(triarylphosphine)-ruthenium was enhanced by *p*-methoxy and *p*-methyl groups and reduced by *p*-fluoro group when the complex was used in the presence of an optimal amount of triethylamine. During this study it has been noticed that the complex with *p*-methoxy substituent prepared by the same procedure as for the preparation of dichlorotris-(triphenylphosphine)ruthenium[2] was often of different color and showed different catalytic activity depending on preparation. Since tris(*p*-methoxyphenyl)phosphine is much less soluble in ethanol than triphenylphosphine, it seemed that the amount of ethanol used (120 ml for 1 g of $RuCl_3 \cdot 3H_2O$ and 6 molar equivalents of the phosphine) would be too small for the preparation of the methoxy complex. The complex formed in this amount of ethanol might be contaminated with free phosphine or its hydrochloride, which would be harmful to the catalytic activity of the resulting complex.[3] From this point of view the ruthenium complex was prepared using a larger amount of ethanol and the precipitate filtered off before the reaction mixture was cooled to room temperature.[4] By this simple improvement, however, the catalytic activity of the complex was greatly increased. A rather long refluxing time (*ca.* 6 hr) was also favorable for the catalytic activity. The *p*-methoxy complex thus prepared gave satisfactory C, H, and Cl analyses corresponding to the formula $RuCl_2[(MeOC_6H_4)_3P]_3$. Application of this improvement to the preparation of the *p*-methyl complex resulted in only a moderate increase in catalytic activity and no increase in the case of the complex without substituent, as might be expected from the higher solubilities of the corresponding phosphines in ethanol. For the same reason it is advisable to use a lesser amount of ethanol for the preparation of the complex with tris(*p*-fluorophenyl)phosphine because of its much higher solubility in ethanol.

Stoichiometrically the amount of triarylphosphine required for the preparation of the ruthenium complex must be 4.5 molar equivalents if the reaction occurs by the equation:

$$RuCl_3 + \frac{9}{2}Ar_3P + \frac{1}{2}H_2O \longrightarrow RuCl_2(Ar_3P)_3 + \frac{1}{2}Ar_3P{=}O + Ar_3P \cdot HCl$$

The complexes prepared with use of 5 molar equivalents of the phosphine, however, were slightly less active than those obtained with 6 molar equivalents. Blum and Becker[5] prepared triarylphosphine ruthenium complexes by refluxing ruthenium chloride and triarylphosphine in methanol. We also prepared the complexes according to their procedure, but the resulting complexes were less active than those obtained in ethanol by the improved procedure. They describe the colors of the methoxy and methyl complexes as apparently the same, but those of our preparations are definitely different from each other (dark brown for the methoxy complex and brown for the methyl complex).

In Table 1 are summarized the results of the hydrogenation of 1,4-androstadiene-3,17-dione (I) and 4-androstene-3,17-dione (II), using the complexes obtained

Table 1. Hydrogenation of 1,4-androstadiene-3,17-dione (I) and 4-androstene-3,17-dione (II) with dichlorotris(triarylphosphine)ruthenium[a]

Compound	Catalyst X in $RuCl_2[(p\text{-}XC_6H_4)_3P]_3$	Reac. time (min)	Composition of reac. mixture (mol%)			$10^4 k_x$[c] (s^{-1})	k_x/k_H[c]
			I	II	III[b]		
I	OMe	20	3.7	90.0	6.3	27.5	13.1
I	Me	40	6.8	87.1	6.1	11.2	5.3
I	H	180	10.3	85.8	3.9	2.1	1.0
II	OMe	360	—	86.9	13.1	0.065	5.0
II	H	490	—	96.1	3.9	0.013	1.0

a) The compound (500 mg) was hydrogenated in 10 ml benzene in the presence of 0.026 mmol of the ruthenium complex and 0.034 mmol of triethylamine at 50 °C under a hydrogen pressure of 100 kg/cm². b) 5α- and 5β-androstane-3,17-dione. c) k_x and k_H denote the pseudo-first-order rate constants for the hydrogenations catalyzed by the ruthenium complexes with *p*-substituent X and with no substituent, respectively.

by the improved procedure. Pseudo-first-order rate constants were calculated by assuming that the rate of hydrogenation is first-order in the concentration of I and II.[6] It is seen that the catalytic activity of dichlorotris(triphenylphosphine)ruthenium is enhanced definitely more by the *p*-methoxy substituent than by the *p*-methyl to such an extent as would be expected from its substituent constant in the Hammett equation.

The *p*-methoxy complex is only five times as active as the complex with triphenylphosphine in the hydrogenation of II compared to thirteen times in the hydrogenation of I. Thus the ratio of the rate of hydrogenation of I to that of II is much greater for the *p*-methoxy complex. Accordingly, the *p*-methoxy complex will be more selective than the triphenylphosphine complex for formation of II in the consecutive hydrogenation pathway: I→II→saturated ketones. On the other hand, the amount of the saturated ketone formed directly from I[1,2] appears slightly increased with the methoxy complex. Therefore it is recommended to use the highly active methoxy complex at a lower temperature (*e.g.* 30 °C) to obtain a high yield of II by hydrogenation of I.

Experimental

*Preparation of Dichlorotris[tris(*p*-methoxyphenyl)phosphine]ruthenium.* A mixture of 0.425 g of $RuCl_3 \cdot 3H_2O$ (obtained from the Nippon Engelhard Co.), 3.43 g of tris(*p*-methoxyphenyl)phosphine (6 molar equivalents) and 80 ml ethanol was refluxed for 6 hr under the atmosphere of nitrogen. The crystals were filtered off before the reaction mixture was cooled to room temperature, and washed with ethanol and then with a small amount of ether. The yield was 1.83 g (92%) (Found: C, 61.37; H, 5.14; Cl, 5.96%. Calcd for $C_{63}H_{63}Cl_2O_9P_3Ru$: C, 61.56; H, 5.18; Cl, 5.77%). The same procedure is also applicable to the preparation of $RuCl_2[(p\text{-}MeC_6H_4)_3P]_3$ and results in a slightly lower yield.

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References

1) S. Nishimura, T. Ichino, A. Akimoto, and K. Tsuneda, This Bulletin, **46**, 279 (1973).
2) S. Nishimura and K. Tsuneda, This Bulletin, **42**, 852 (1969).
3) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc., A*, **1968**, 3143.
4) *Cf.* J. A. Osborn, A. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, **1966**, 1711.
5) J. Blum and Y. Becker, *J. Chem. Soc., Perkin II*, **1972**, 982.
6) It was confirmed that the rate of hydrogenation of I over the *p*-methoxy complex obeys first-order kinetics in concentration of I in the experiments employing a smaller amount of the complex.