CHEMISTRY LETTERS, pp. 995-998, 1976. Published by the Chemical Society of Japan

A NEW SYNTHETIC METHOD OF BIVALENT Rh(II) COMPLEX USING PHOSPHINATED POLYSTYRENE AND ITS CATALYTIC ACTIVITY FOR OLEFIN HYDROGENATION

Kiyotomi KANEDA, Masami TERASAWA, Toshinobu IMANAKA,
and Shiichiro TERANISHI
Department of Chemical Engineering, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560

A paramagnetic bivalent rhodium complex was selectively formed by the reaction of phosphinated polystyrene with $RhCl_3 \cdot 3H_2O$ in ethanol. The characterization of the rhodium complex was carried out by the use of IR, ESR, and ESCA spectrometers. This complex was active for hydrogenation of olefins. The remarkable features of the hydrogenation are described.

Many attempts to anchor metal complex catalysts to polymer supports have been reported in order to provide typical homogeneous catalytic chemistry plus the convenience and economy of heterogeneous catalysts.1) The polymer catalysts have been applied extensively to various types of reactions, e.g., hydrogenation, oligomerization, and deuterium exchange. We have also reported that $PdCl_2$-phosphinated polystyrene complex had high activities for hydrogenation2) and codimerization.3) In the course of our studies of heterogenization of homogeneous transition metal catalysts using polymer ligands, we found a selective formation of paramagnetic bivalent rhodium species on the treatment of alcoholic solution of $RhCl_3 \cdot 3H_2O$ with the phosphinated polystyrene, and found that this catalyst had high activities for olefin hydrogenation and H_2-D_2 exchange. It is interesting that paramagnetic bivalent rhodium, which seems to be unstable, can be selectively obtained by the use of polymer as a ligand.

This paper describes the synthesis of this bivalent rhodium complex and characterization of this complex by the use of IR, ESR, and ESCA spectrometers. Furthermore, hydrogenation of several olefinic compounds is examined for which this new catalyst exhibits the high activity.

Polymeric diphenylbenzylphosphine (PDBP) as a ligand was prepared from non crosslinked polystyrene by sequential chloromethylation (CH_2ClOCH_3, $SnCl_4$), and treatment with $(C_6H_5)_2PLi$. The PDBP contains 3.4 mmol of phosphine/g which corresponds to an equivalent ratio of diphenylphosphinomethyl group to styrene unit. A typical preparation of the rhodium complex is as follows. A mixture of $RhCl_3 \cdot 3H_2O$ (0.752 g, 2.85 mmol), PDBP (0.836 g, 2.85 mmol as diphenylbenzylphosphine group), and ethanol (20 ml) was stirred at 60°C for 14 h. After cooling, the dark-green product was recovered by filtration, washed with ethanol until the filtrate was colorless, and dried under a vacuum.

Anal. Found: C, 51.82; H, 4.00; Cl, 14.26; P, 5.37%

Calcd. for $P\cdot(RhCl_2)$: C, 52.97; H, 4.03; Cl, 14.89; P, 6.50%

The elemental analysis of each complex prepared in the ranges of 55-80°C and 12-36 h showed approximately a constant value for the elements respectively (P: polymer ligand). All the above procedures were operated under a nitrogen atmosphere. The elemental analysis shows that the complex is composed of phosphorous, chlorine, and rhodium in an atomic ratio of about 1:2:1. This indicates the elimination of one chlorine atom from the starting rhodium salt. The detailed mechanism for the elimination is under investigation.[4] The IR spectrum of the complex contains a band of terminal Rh-Cl bond at 334 cm^{-1}. No band assignable to the bridging Rh-Cl bond appears in the region 250-290 cm^{-1}. The ESR spectra of the complex and the polymer ligand are shown in Fig. I. It seems that the spectrum of the complex is derived from two species, because one species with $g = 2.001$ is also observed in the spectrum of the ligand. The signal with $g_1 = 2.103$, $g_2 = 2.026$, and $g_3 = 1.975$ is similar to those previously reported for bivalent rhodium compounds and especially its average g value ($g_{rms} = 2.094$) is in good agreement with that of trans-$RhCl_2[P(o\text{-tolyl})_3]_2$.[5] Accordingly we assign the signal of $g_{rms} = 2.094$ to bivalent rhodium. ESCA chemical shifts in the 3d levels of rhodium in the polymer complex and other compounds are given in Table I together with some related data for the chlorine 2p level. The 3d spectrum of the polymer complex is shown in Fig. II. After olefin hydrogenation, the 3d and the chlorine 2p spectra of the recovered catalyst did not change. The polymer complex has 3d binding energies similar to those of bivalent rhodium compound, trans-$RhCl_2[P(o\text{-tolyl})_3]_2$, and also the 3d peaks with no shoulder have half-width ca. 3.0 eV. Therefore, the rhodium valence state can be conclusively determined to be paramagnetic bivalent. The most likely structure of the complex seems to be three-coordinated $P\text{-}Rh^{II}\text{-}Cl_2$ with three vacant sites around the central rhodium ion.

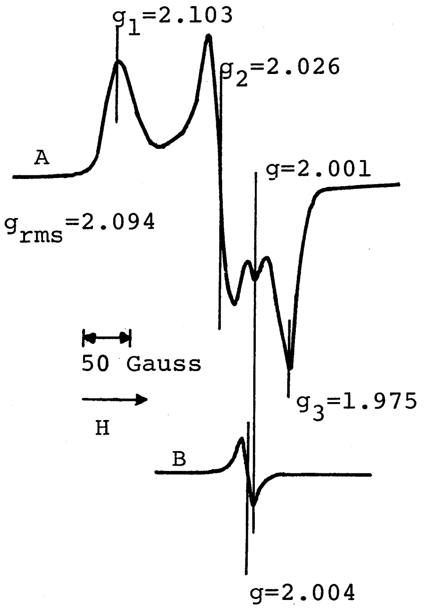

Fig. I. Electron spin resonance spectra of polymer-rhodium complex (A), and polymeric diphenylbenzylphosphine (B), measured at room temperature.

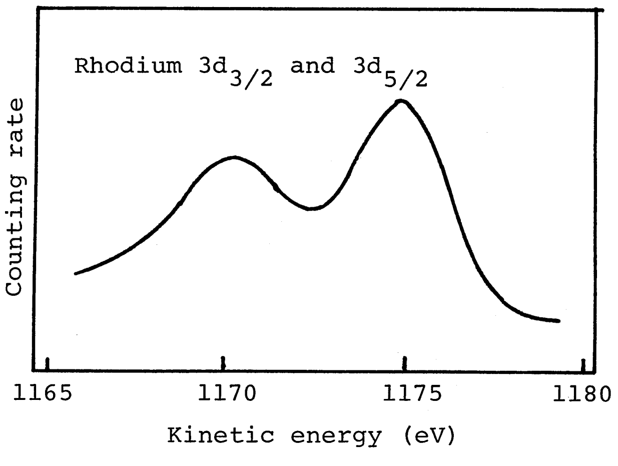

Fig. II. Rhodium 3d photoelectron spectrum of polymer-rhodium complex.

This polymer-supported Rh catalyst is so stable that it can be exposed to air for several months without any change of IR, ESR, and ESCA spectra.

Table I. Rhodium and halogen binding energies (in eV) for rhodium compounds[a]

Compound	Rh $3d_{3/2}$	Rh $3d_{5/2}$	Cl2p
PDBP·$RhCl_2$[b]	313.7	309.1	199.2
AFR·PDBP·$RhCl_2$[c]	313.7	309.1	199.2
Rhodium metal	311.8	307.1	
$RhCl(PPh_3)_3$	312.7	308.2	199.5
$RhCl(CO)(PPh_3)_2$	313.2	308.4	198.7
$RhH(CO)(PPh_3)_2$	312.9	308.1	
$RhCl_2[P(o\text{-}tolyl)_3]_2$	313.6	308.9	198.6
$RhCl_3\cdot 3H_2O$	314.4	309.7	199.5

a The E_b values are referenced to the carbon 1s (285.0 eV).

b Polymer complex used.

c After use in olefin hydrogenation.

By the use of the polymer rhodium complex the hydrogenation of a wide variety of unsaturated compounds was carried out under 1 atm of hydrogen. The hydrogenation procedure is the same as in the previous paper.[2)] This complex is active for the hydrogenation of many olefins: mono-olefins, conjugated and non-conjugated dienes, but is a poor catalyst for the reduction of acetylenic bond (Table II). Functional groups such as keto, cyano, and nitro were not found to be reduced under these conditions. As shown in Table II, this olefin hydrogenation is characterized by the following features: i) terminal olefin is reduced more rapidly than internal olefin, e.g., 1-heptene > 2-heptene; ii) cis-olefin is reduced faster than trans-olefin, e.g., dimethyl maleate > dimethyl fumarate; iii) non-conjugated diene is reduced faster than conjugated diene, e.g., 1,5-cyclooctadiene > 1,3-cyclooctadiene; iv) increasing the ring size of olefin or going from acyclic olefin to cyclic olefin, decreases the rate of hydrogenation, e.g., cyclohexene > cyclooctene, 1-octene > cyclooctene.

Table II. Hydrogenation of olefins and acetylenes[a]

Substrate	Initial rate (ml/min)	Substrate	Initial rate (ml/min)
1-Heptene	2.54	1,3-Cyclooctadiene	0.92
2-Heptene	1.37	Isoprene	1.34
1-Octene	2.13	Allyl alcohol	0.82
1-Dodecene	0.91	Dimethyl maleate	0.93
Styrene	2.02	Dimethyl fumarate	0.54
Cyclohexene	2.81	1-Pentyne	≈0.0
Cyclooctene	0.95	Phenylacetylene	≈0.0
1,5-Cyclooctadiene	1.47		

a Using polymer-rhodium complex; 4.87×10^{-5} mole, substrate; 4.94×10^{-3} mole, 1 atm of hydrogen in [13-(volume of substrate)] ml of benzene at 25°.

In comparison with the Pd-polymer catalyst,$^{2)}$ this Rh-polymer catalyst is not active for the reduction of acetylenic bonds and does not show good selectivity for the reduction of dienes to monoenes.

Solvents with moderate coordinating ability to metal such as alcohols, DMF, and acetone give fast reduction rates, while cyclohexane, n-hexane, and DMSO having weak or strong coordinating ability are extremely unfavorable solvent (Table III).

Table III. Effect of solvent on styrene hydrogenation[a]

Solvent	Initial rate (ml/min)	Solvent	Initial rate (ml/min)
Methyl alcohol	12.20	Ethyl acetate	2.99
Ethyl alcohol	7.68	THF	2.91
Propyl alcohol	5.67	Benzene	2.79
Isobutyl alcohol	5.60	Chloroform	≃0.0
Butyl alcohol	4.99	Methylene chloride	≃0.0
Isopropyl alcohol	4.47	Carbon tetrachloride	≃0.0
s-Butyl alcohol	3.16	Cyclohexane	≃0.0
t-Butyl alcohol	2.71	Hexane	≃0.0
DMF	5.36	DMSO	≃0.0
Acetone	3.39		

a Using polymer-rhodium complex; 7.31×10^{-5} mole, styrene; 4.34×10^{-3} mole 1 atm of hydrogen in 12.5 ml of solvent at 25°.

The isomerization of terminal olefins to internal olefins, or non-conjugated dienes to conjugated dienes takes place during the hydrogenation. The rate is, however, slower than the reduction rate of the corresponding olefin. The isomerization did not occur in the absence of hydrogen gas.

This complex is also active for the H_2-D_2 exchange reaction. This result supports the idea that the active species for the hydrogenation, such as a rhodium hydride intermediate, has more than two vacant coordinating sites.$^{6)}$

On the basis of kinetic studies, the mechanism of olefin hydrogenation containing bivalent rhodium species will be reported in a full paper.

The catalyst can be conveniently separated from the product solution and recycled without any appreciable loss in activity.

References and Notes

1) For recent reviews, see a) J. C. Bailar, Jr., Cat. Rev.-Sci. Eng., 10, 17 (1974); b) J. I. Crowley and H. Rapoport, Acc. Chem. Res., 9, 135 (1976).
2) K. Kaneda, M. Terasawa, T. Imanaka, and S. Teranishi, Chem. Lett., 1005 (1975).
3) K. Kanada, T. Uchiyama, M. Terasawa, T. Imanaka, and S. Teranishi, ibid., 449 (1976).
4) Two possible paths to bivalent rhodium formation can be considered: i) direct reduction of Rh(III) to Rh(II); ii) disproportionation between Rh(III) and reduced Rh(I).
5) M. A. Bennet and P. A. Longstaff, J. Amer. Chem. Soc., 91, 6266 (1969).
6) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, J. Chem. Soc. (A), 1711, (1966).

(Received July 9, 1976)