

STUDY OF HETEROCYCLIC POLYMER COMPLEXES

I. POLYPHENYLQUINOXALINE-PLATINUM AND RHODIUM COMPLEXES*

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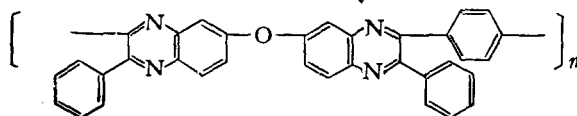
ABSTRACT

Two new polyphenylquinoxaline-platinum and rhodium complexes were synthesized and identified by X-ray photoelectron spectroscopy. Their catalytic properties on hydrosilylation and hydrogenation of olefins have been investigated. It was found that these polymer complexes possessed high selective catalytic activities, and were easily recoverable after each reaction and could be repeatedly used for more than 10 times while maintaining the same effectiveness.

INTRODUCTION

It is well known that heterocyclic polymers are good heat-resistant polymers and are usually used as structural materials. These polymers consist of hetero-atoms such as nitrogen, oxygen and / or sulfur in the main chain, each of which possesses a lone pair of electrons and acts as a donor. On the other hand, the metallic ion of a metallic compound with emptied orbits can be used as an acceptor. Since the hetero-atoms were located in conjugated ring the π -electron system greatly affected the lone pair electrons of hetero-atom by "switching effect". The electron transfer of hetero-atoms could be realized when such polymers react with metallic compounds to form polymer complexes under suitable conditions. The experimental results presented here show that polyphenylquinoxaline (PPQ) can form complex either with $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ or with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ directly without any supporter. These polymer complexes both possess chemical activities.

The chemical structure of PPQ is shown as follows:



RESULTS AND DISCUSSION

Two new polymer complexes $\text{PPQ} \cdot \text{H}_2\text{PtCl}_6$ (I) and $\text{PPQ} \cdot \text{RhCl}_3$ (II) were synthesized from the reaction of PPQ with $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ or $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in presence of anhydrous ethyl alcohol respectively. The reaction mixture was first stirred at room tem-

* Received January 3, 1984

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perature under N_2 for 35 hours and then refluxed for additional 7 hours. Afterwards (I) formed was filtered and washed thoroughly with boiling ethyl alcohol and dried under vacuum. (II) was prepared by the similar procedure except the refluxing time was changed to 17 hours. Both these two polymer complexes (I) and (II) were identified by X-ray photoelectron spectroscopy (XPS). From Table 1 the N_{1s} binding energy of (I) was 0.5 eV higher than that of PPQ while $Pt_{4f_{7/2}}$ binding energy of (I) was 2.1 eV lower than that of H_2PtCl_6 . It showed that these differences were due to the partial transfer of lone-pair electron of nitrogen atoms in PPQ to the platinum ion in H_2PtCl_6 , thus a polymer complex was formed. Similar result was obtained for polymer complex (II).

Table 1 Identification of (I) and (II) by XPS(eV)

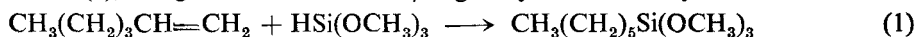
	PPQ	PPQ· H_2PtCl_6 *	H_2PtCl_6	PPQ· $RhCl_3$ **	$RhCl_3$
N_{1s}	398.8	399.3		399.4	
$Pt_{4f_{7/2}}$		73.5	75.6		
$Rh_{3d_{5/2}}$				309.7	310.6

* Orange, ** Black.

The PPQ used was prepared in our laboratory^[1].

Polymer complexes (I) and (II) can be used as catalysts in the hydrosilylation of hexene-1 with trimethoxysilane to form n-hexyltrimethoxysilane. The yield based on trimethoxysilane were 92% and 31%, b. p. 120–122°C / 60 mm, n_D^{20} 1.4092. Analysis: $C_9H_{22}SiO_3$ (Calc. C, 52.38%; H, 10.75%. Found: C, 52.09%; H, 10.55%). Lit. b. p. 202–203°C.

In the reaction (1), the gram atomic ratio N/Pt greatly affected the yield



as shown in Fig. 1. The highest yield of 92% was obtained when N/Pt was equal to 4. If the ratio was equal to 8, the yield was decreased to 73%. After each addition reaction, these polymer complexes can be easily recovered by filtration. In this way (I) was used more than 10 times as catalyst in hydrosilylation of hexene-1 with yield of 92% at the tenth time and 81% at the fifteenth time as shown in Fig. 2. Although $H_2PtCl_6 \cdot 6H_2O$ is an effective catalyst for this reaction, but it can only be used one time and has the additional disadvan-

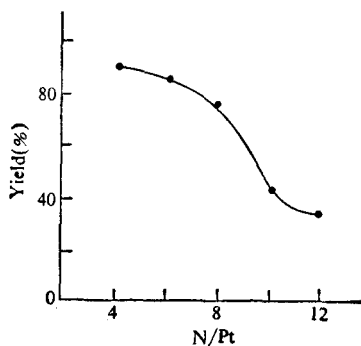


Fig. 1 Effect of gram atomic ratio N/Pt of $PPQ \cdot H_2PtCl_6$ (I) on the yield of n-hexyltrimethoxysilane

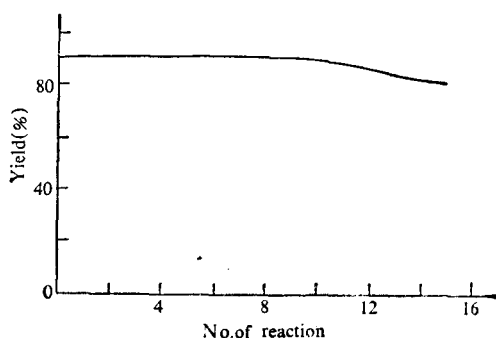


Fig. 2 Yield as a function of the repeated use of $PPQ \cdot H_2PtCl_6$ (I) for hydrosilylation of hexene-1 with trimethoxysilane

tage of absorbing moisture. In comparison, (I) possessed three advantages over $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$: (1) It does not absorb moisture. (2) It gives high yield in repeated use. (3) It is easily recoverable.

All the reactions mentioned above were carried out with 0.24 milligram-atom of platinum, 40 millimole of trimethoxysilane, 81 millimole of olefine and the reaction temperature was maintained at $62\text{--}64^\circ\text{C}$ for 2 hours or at 25°C for 24 hours with a good yield of 92%. The relation between reaction time and the yield of product is shown in Fig 3. The effect of (I) on hydrosilylation of various olefines were quite different as shown in Table 2.

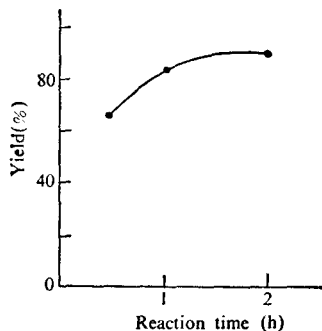


Fig. 3 Relation between time of reaction (I) and the yield of product

Table 2 Effect of $\text{PPQ} \cdot \text{H}_2\text{PtCl}_6$ (I) on hydrosilylation of different olefines with trimethoxysilane

Olefines	Hexene-1	Styrene	Decene-1	α -Pinene	Vinyl acetate	Cyclohexene
Yield (%)	92	87	81	47	27	24

When (II) was used as catalyst for the reaction (1), a lower yield of 31% was obtained. However, it shows better selective catalytic activities for hydrogenation of olefines as shown in Fig 4.

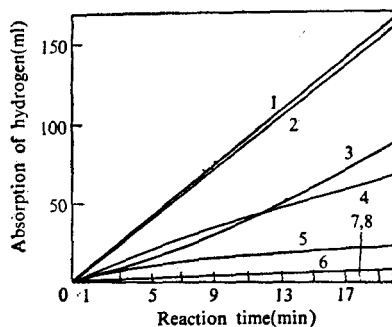


Fig. 4 Effect of $\text{PPQ} \cdot \text{RhCl}_3$ (II) on hydrogenation of various olefines

1 Cyclohexene; 2 Hexene-1; 3 Styrene; 4 Hexene-2; 5 Butyric aldehyde;
6 Allyl bromide; 7 Benzene; 8 Cyanobenzene

Conditions: 1.0×10^{-2} mole substrate; 1.0×10^{-5} mole $\text{PPQ} \cdot \text{RhCl}_3$; 5 ml anhydrous ethyl alcohol; reaction temperature: $18 \pm 1^\circ\text{C}$; hydrogen at 1 atmosphere.

REFERENCE

- [1] 卢凤才、陆秀楣、王百庚、张金彪、邢兰敏、王玉兰、高元明、白路娜等, 高分子通讯, 1980, (3), 146.