CHARACTERIZATION AND CATALYTIC BEHAVIOR OF WATER-SOLUBLE PHOSPHINE RHODIUM (I) COMPLEX*

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Abstract The monosulfonated triphenylphosphine ligand, $Ph_2P(m\text{-}C_6H_4SO_3K)$ (abbr. as DPM), and its rhodium complex, $HRh(CO)(DPM)_3$, have been synthesized and characterized by spectroscopic techniques (IR, NMR). The obtained data showed that the structure of $HRh(CO)(DPM)_3$ was similar to $HRh(CO)(PPh_3)_3$. The properties of $HRh(CO)(DPM)_3$ as an olefin hydroformylation catalyst in aqueous-organic solvent two-phase system are studied.

Keywords aqueous phase, sulphonated phosphine, characterization, hydroformylation

Introduction

In homogeneous catalysis, a recurrent problem is the separation of the organic products from the active catalyst. The application of water soluble transition metal complexes for catalytic reactions has recently attracted considerable attention[1~3]. The water-soluble ligands are slightly soluble in organic media, allowing the catalysis to be carried out in a two-phase system. Catalyst recovery is thus easily achieved by decantation and separation of the two phases. The tris(sodium *m*-sulfophenyl)-phosphine, $P(m\text{-}C_6H_4SO_3Na)_3$ (abbr. as TPPTS), modified rhodium catalyst system, $HRh(CO)(TPPTS)_3$, has been successfully used in large scale production of *n*-butanol[4]. On the other hand, the

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monosulfonated triphenyl-phosphine ligand (DPM), the first water soluble phosphine-based ligand, was synthesized in 1958 by Chatt and his group[5]. To our knowledge, little information is available on the structure of its rhodium complex, $HRh(CO)(DPM)_3$. In this work, FT-IR, ^1H and ^{31}P NMR have been used to characterize the structure of $HRh(CO)(DPM)_3$. The catalytic properties of $HRh(CO)(DPM)_3$ in two-phase system were also investigated.

Experimental

Preparation of the catalyst

Potassium diphenylphosphinobenzene-*m*-sulfonate (abbr. as DPM) was prepared by known methods[5]. $HRh(CO)(DPM)_3$ was prepared by referring to the literature[6]. A solution of 580 mg DPM (1.52 mmol) in 1.6 mL of deaerated distilled water was added to 70 mg acetyl-acetonatedicarbonyl-rhodium(I)($Rh(CO)_2(acac)$, 0.271 mmol) in a 75 mL steel autoclave which was previously purged with a H_2:CO (1:1) mixture. The autoclave was heated to 50°C under 3 MPa of the H_2:CO (1:1) mixture and with magnetic stirring. After 7 h, the autoclave is cooled to room temperature and slowly depressurized. The solution was filtered under nitrogen to remove the small amount of rhodium metal and 8 mL of absolute ethanol saturated with H_2:CO (1:1) was added to yield a yellow precipitate. The solid was collected, washed with absolute ethanol, and vacuum dried. The yield of $HRh(CO)(DPM)_3$ was 500 mg.

Characterization of the catalyst

Infrared spectra were measured on Nicolet 20DX-B FT-IR spectrometer using Nujol. The ^{31}P-NMR spectra were recorded on JEOL FX-90Q spectrometer at 36.2 MHz using H_2O as the solvent. Chemical shifts are expressed based on the chemical shift of H_3PO_4 solution (85%). The ^1H-NMR spectra were recorded on JEOL FX-90Q spectrometer at 89.6 MHz using D_2O as the solvent.

Hydroformylation procedure

Hydroformylation was carried out in a 75 mL steel autoclave. The reaction product analysis was done on a SP-O9 gas chromatograph equipped with a 0.25 mm×50 m capillary column. The products were further identified by GC-MS spectroscopy on an MAT31Q/SS2000 instrument.

Results and discussion

The structure of $HRh(CO)(DPM)_3$ was established by FT-IR and NMR spectroscopy (see Table 1).

Table 1 IR and NMR data for $HRh(CO)(DPM)_3$

IR (cm^{-1})		NMR			
		^1H		^{31}P	
ν(H-Rh)	ν(CO)	δ	$J_{(H-P)}$	δ	$J_{(P-Rh)}$
2007	1927	−9.56	14	43.0	155.3

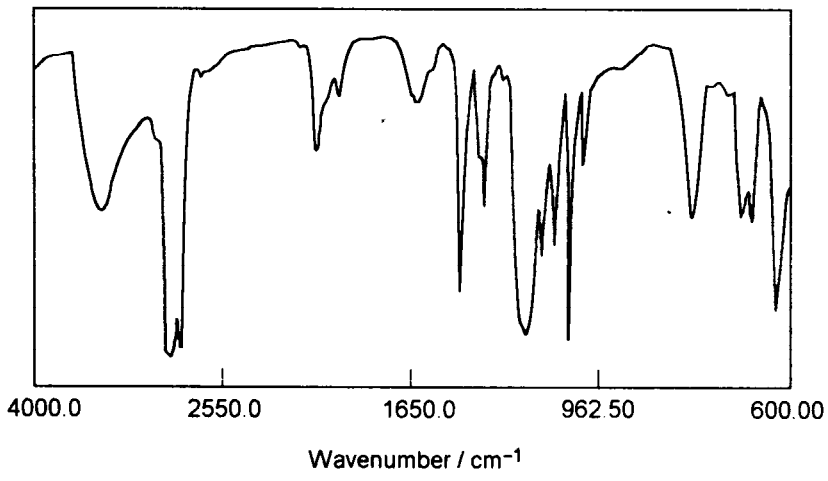

Fig.1 IR spectrum of $HRh(CO)(DPM)_3$

The FT-IR spectrum of $HRh(CO)(DPM)_3$ shows two bands at 2007 and 1927 cm^{-1}, which are attributed to rhodium-hydride and terminal carbonyl ligand vibrations. The wavenumber of 1927 cm^{-1} shows a weak characteristic absorption of the coordinated carbonyl group in the bound complex $HRh(CO)(DPM)_3$. Comparing with the corresponding IR absorption at 1924 cm^{-1} of the carbonyl group in the complex $HRh(CO)(PPh_3)_3$[7], one can attribute this increase of the wavenumber from 1924 to 1927 cm^{-1} mainly to a weaker coordination bonding between Rh and CO in the $HRh(CO)(DPM)_3$ than in the $HRh(CO)(PPh_3)_3$. This is probably caused by the electron-withdrawing effect of the meta-substituted sulfonate group in one of the benzene rings of

triphenyl-phosphine ligand, which reduces the σ electron donation ability of the phosphorus atom.

The ^{1}H-NMR spectrum of $HRh(CO)(DPM)_3$ shows a resonance peak at −9.56 (quartet, J_{H-P}=14 Hz).

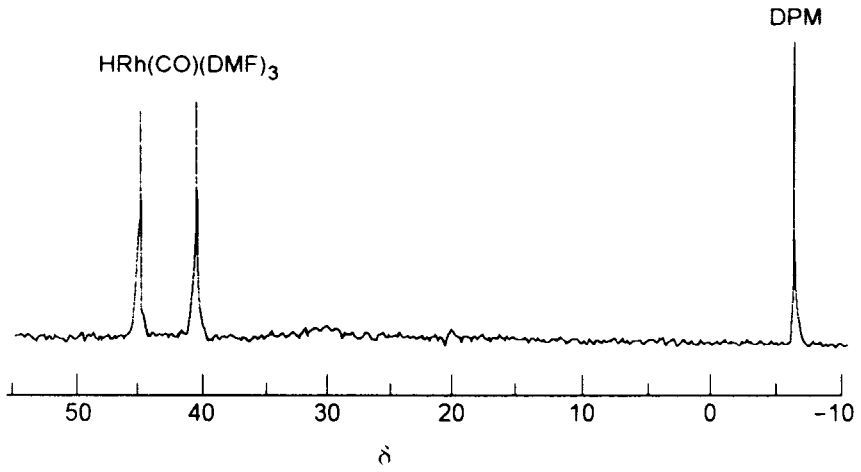

Fig. 2 ^{31}P-NMR spectra of DPM and $HRh(CO)(DPM)_3$

In fact, ^{31}P-NMR spectroscopy is a highly sensitive technique to elucidate the structures of metal-phosphine complexes. The ^{31}P-NMR spectrum of $HRh(CO)(DPM)_3$ in H_2O shows a sharp doublet at 43.0 (J_{P-Rh}=155.3 Hz), however, the resonance peak of tertiary phosphine ligand, $Ph_2P(m\text{-}C_6H_4SO_3K)$, and the phosphine oxide, $Ph_2P(O)$ ($m\text{-}C_6H_4SO_3K$), appeared at −6.7 and 33.9 respectively. Thus, the overall data show that the structure of $HRh(CO)(DPM)_3$ is very similar to $HRh(CO)(PPh_3)_3$[7].

Table 2 Hydroformylation of different olefins with $HRh(CO)(DPM)_3$

Olefin	Reaction time h	pH	Conversion %	Aldehyde yield %
1-hexene	2	6.5	99.3	85.7
styrene	3	5.5	99.4	93.6
cyclohexene	3	6.5	88.7	84.2
1-dodecene	4	6.5	74.8	66.3

Conditions: Catalyst, 3.66×10^{-6} mol/mL; olefin, 0.013 mol; V(water):V(olefin)=2:1; 100 °C; 5.0 MPa; (H_2:CO=1:1)

Table 2 summarizes the hydroformylation results for several olefins in two-phase system using $HRh(CO)(DPM)_3$ as the catalyst. It can be seen that the catalytic activity decreased in the following order: styrene, 1-hexene > cyclohexene >1-dodecene. The reason for this is that the long-chain olefins have negligible solubility in water.

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