

THE SYNTHESSES OF POLYQUINOLINES WITH 2,2'-PYRIDYLQUINOLINE AND 2,6-DIQUINOLYLPYRIDINE AS LIGAND AND THEIR APPLICATIONS IN SOME CATALYTIC REACTIONS*

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ABSTRACT

The polyquinolines with 2,2'-pyridylquinoline as bidentate and 2,6-diquinolylpyridine as tridentate ligand have been prepared from 4,4'-diamino-3,3'-dibenzoyldiphenyl ether, 4,4'-diacetyldiphenyl ether and 1,4-bis(2-acetylpyridyl-6-oxy)benzene, 2,6-diacetylpyridine, respectively. These polyquinoline-supported ligands have been used in hydrogenation and hydroformylation of olefins with some transition metal complexes.

INTRODUCTION

Bipyridine and terpyridine can form complexes with metal atoms in a great range of oxidation states. So they have been comprehensively used as bidentate and tridentate ligands in organometallic compounds. Some of them could be used as homogeneous catalysts in various reactions, such as hydrogenation^[1] metathesis^[2], electrochemical oxidation^[3] and photolysis of water to get hydrogen and oxygen by solar irradiation^[4-6].

The analogues of bipyridine and terpyridine, quinoline derivatives are much less investigated so far. Although, benzo substitution adjacent to the nitrogen atoms leads to such steric crowding that the bichelated ferrous complexes show high spin, whereas that of terpyridine, low spin, less drastic alterations in the spectral properties of the complexes of the heavier metals are expected^[7]. So it is assumed that the behavior of the quinoline derivatives in organometallic chemistry should not have too much difference with that of pyridine's for the heavier metal complexes.

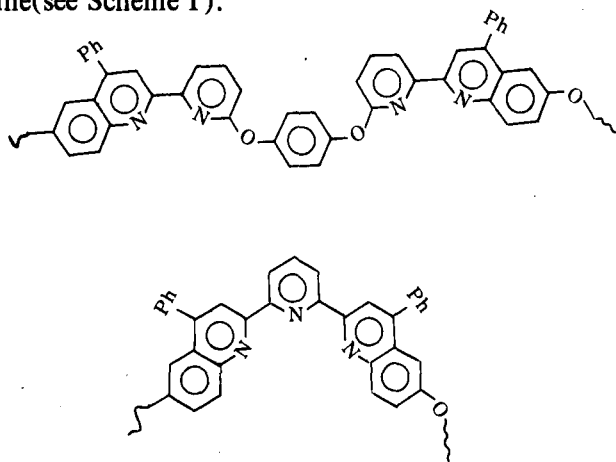
Polyquinolines, which has excellent thermal stability, heat resistance, fine chemical stability, fair affinity to some common organic solvents(soluble in cresol, chloroform and swollen in benzene) and is easy to be cross-linked^[8], inspired us to design the particular monomers to match the quinoline rings available in the backbone of

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polyquinoline as a bidentate ligand, 2,2'-pyridylquinoline, and tridentate ligand, 2,6-diquinolylpyridine (see Scheme I).



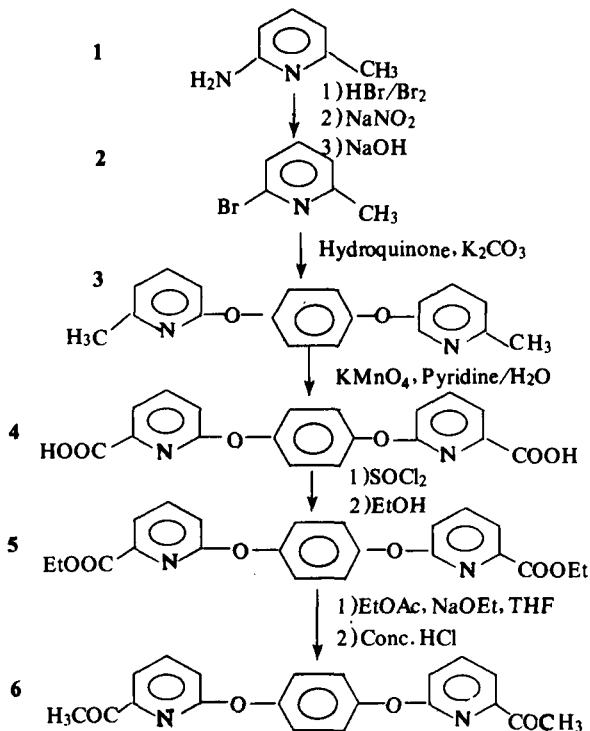
Scheme I

In this paper, we wish to report the syntheses of polyquinolines containing 2,2'-pyridylquinoline and 2,6-diquinolylpyridine and some catalytic reactions using these polymer ligands.

RESULTS AND DISCUSSION

Synthesis of 1,4-bis(2-acetylpyridyl-6-oxy)benzene

The synthetic route is shown in Scheme II.



Scheme II

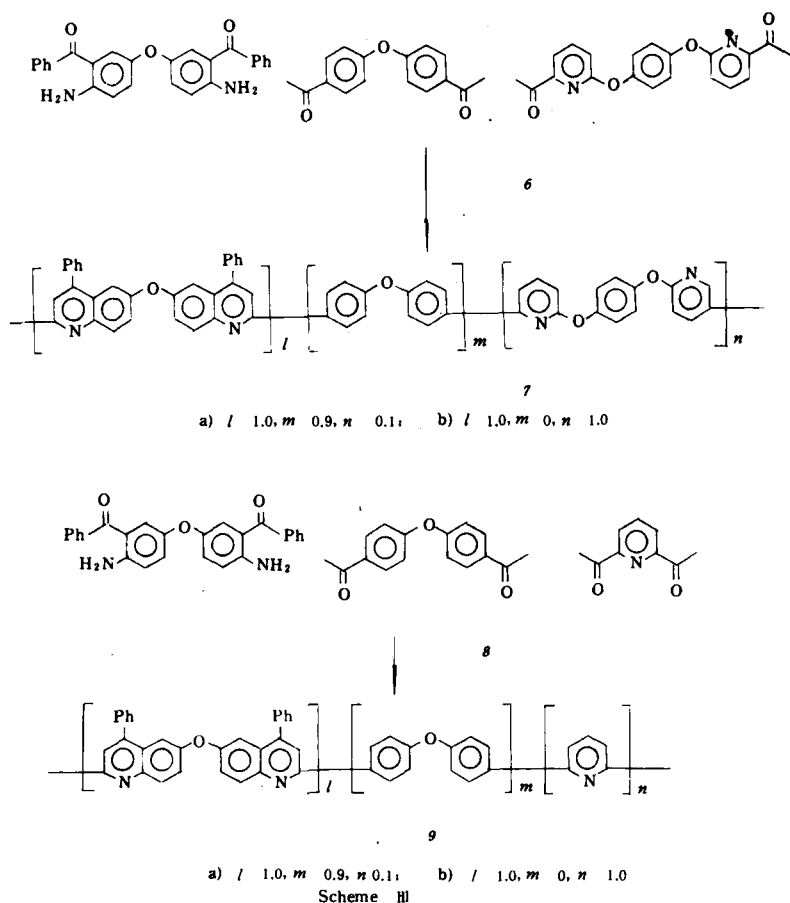
2 was prepared by the typical Sandmeyer reaction reported in ref. 9 for the preparation of 2-bromopyridine in good yield.

3 was synthesized by a similar procedure that reported in ref. 10 for phenyl pyridyl ether derivatives. The reaction temperature was critical that if it was lower than 200 °C, an intermediate, 4-hydroxy(2-methylpyridyl-6-oxy) benzene would be the main product, although the prolonged reaction time was used.

A few reports dealt with the preparation of acetyl pyridine derivatives from pyridyl acid esters. 2-acetylpyridine and 2,6-diacetylpyridine have been prepared by the treatment of ethyl picolinate^[11] and 2,6-diethoxycarbonylpyridine^[12,13] respectively with NaOMe or NaOEt, ethyl acetate in benzene. However, **6** could be prepared only by using NaOEt and ethyl acetate in THF.

Preparation of polymers

Polyquinolines with aromatic nitrogens as bidentate and tridentate ligand were prepared by the typical procedure reported^[14] (Scheme III). The intrinsic viscosities, yields and elemental analyses of the obtained polyquinolines are listed in Table 1.



The low molecular weight of **7b** and **9b** may be caused from a by-reaction, trimerization of the diacetyl monomer^[14].

Table 1 Polyquinolines with aromatic nitrogen as ligand

Polymer	$[\eta]^a$	Yield %	Elemental Analysis % ^{c)}			
			C	H	N	Residue
7a	1.48	92.7	85.01 (84.93)	4.46 (4.41)	5.11 (4.97)	
7b	0.19 ^{b)}	94.9	80.25 (80.69)	4.28 (4.12)	8.09 (8.18)	
9a	2.06	94.9	85.11 (85.28)	4.54 (4.42)	5.08 (4.86)	
9b	0.48	94.5	81.82 (84.15)	4.26 (4.24)	8.20 (8.14)	2.65

a. In CHCl_3 at 25 °Cb. Inherent viscosity, 0.5% CHCl_3 at 25 °C

c. The data in parentheses are calculated ones.

Catalytic reactions

(1) Hydrogenation

7a has been used as the polymer ligand with several transition metal complexes in the hydrogenation of 1-hexene (see Table 2). The hydrogenation could be satisfactorily carried out in the presence of the catalyst systems listed in Table 2 in quantitative yield to avoid the formation of metal mirror which could be formed in using $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ as the catalyst alone. So the polymer catalysts could be reused without apparent decreasing of the efficiency in the reaction.

Table 2 Hydrogenation of 1-Hexene^{a)}

Catalyst	Conversion %	Comment
$\text{Rh}(\text{CO})_2\text{Cl}_2$	45.7	Rh mirror
bipy/ $\text{Rh}(\text{CO})_2\text{Cl}_2$	100	
7a / $\text{Rh}(\text{CO})_2\text{Cl}_2$	100	
7a / $\text{Rh}(\text{CO})_2\text{Cl}_2$	100	Reused catalyst
7a / $(\text{C}_6\text{H}_5\text{CN})_2\text{PtCl}_2$	100	
7a / $(\text{C}_6\text{H}_5\text{CN})_2\text{PdCl}_2$	100	

a.) 1.0 mL of 1-hexene, 10 mL of THF, Metal: 0.016 mg atom, N:metal=2:1, temperature 100 °C, pressure 100 psi, time 16 h.

(2) Hydroformylation^[15]

The hydroformylation of 1-pentene was carried out in the presence of **7a** and **9a** as the ligand. The results are listed in Table 3. The ruthenium catalyst could give the better ratio of the linear to branched aldehyde, although the conversion of the olefin was not so high as that in the reactions using rhodium catalyst. Surprisingly that, for the system of $(\text{C}_6\text{H}_5\text{CN})_2\text{PtCl}_2 - \text{SnCl}_2$, pyridine ligand seemed to be an inhibitor for the reaction.

7a and **9a** have also been used in the hydroformylation of 1-pentene, in which the hydrogen was generated from water-gas shift reaction. The results showed that, the conversion of pentene was very poor and the ratio of linear and branched

aldehyde was 0.89 and 1.28 for **7a** and **9a**, respectively.

Table 3 Hydroformylation of 1-pentene

	Conversion %	Ratio (L/B) ^{a)}
bipy/Rh(CO) ₂ Cl ₂ ^b	95.0	0.65
7a /Rh(CO) ₂ Cl ₂ ^b	92.0	0.58
9a /Rh(CO) ₂ Cl ₂ ^b	97.4	0.99
7a /Ru(bipy) ₂ Cl ₂ ^c	36.6	1.73
bipy/(C ₆ H ₅ CN) ₂ PtCl ₂ -SnCl ₂ ^d	0	
7a /(C ₆ H ₅ CN) ₂ PtCl ₂ -SnCl ₂ ^d	trace	

a) Linear to branched aldehyde

b) 1.0 mL of 1-pentene, 10 mL of benzene, Rh, 0.016 mg atom, N:Rh = 2:1, temperature 100 — 110 °C, pressure (CO:H₂ = 1:1) 600 psi, time 16 h.

c) 1.0 mL of 1-pentene, 10 mL of benzene catalyst 0.1 g (Ru, 4.48%), temperature 120 °C, pressure (CO:H₂ = 1:1) 1800 psi, time 16 h.

d) 1.0 mL of 1-pentene, 10 mL of benzene, Pt:P:Sn = 1:2:5, temperature 100 °C, pressure (CO:H₂ = 1:1) 1800 psi, time 18 h.

EXPERIMENTAL SECTION

¹H-NMR spectra were obtained on a Varian EM360 Spectrometer using tetramethyl silane as the internal standard. Infrared spectra were taken on Beckman Acculab 3 Spectrophotometer. GLC separations were performed on a Varian 3700 on a 10% OV — 101/Chromosorb W-HP 8v/100 2m × 1/8" column. UV spectra were obtained on a Varian Techtron UV-Vis Spectrophotometer Model 635. Melting points and boiling points were uncorrected. Elemental analyses were determined by Micro-Tech laboratories and Galbraith Laboratories.

2, 6-Diacetylpyridine was purchased from Aldrich Chemical Co., and was recrystallized from toluene before use.

6-Bromopicoline(2)

This compound was prepared from 6-aminopicoline (1) by the procedure essentially analogous to that for 2-bromopyridine from 2-aminopyridine reported in ref.[9], bp 81 — 90 °C /8 mm (lit. 13: 80 — 90 °C /10 mm), ¹H NMR (CDCl₃): δ; 7.60—6.90(m, 3H, arom.), 2.50(s, 3H, CH₃).

1,4-Bis(2-methylpyridyl-6-oxy)benzene(3)

Into a flask assembled with mechanical stirrer, condenser and thermometer were added 47.5 g (0.276 mol) of 6-bromopicoline, 12.1 g (0.110 mol) of hydroquinone and 30.4 g (0.220 mol) of anhydrous potassium carbonate. After purging with N₂, the mixture was heated to 200 °C for 2 h, then poured into 200 mL of toluene. The inorganic salts were removed by hot filtration, and washed with hot toluene. After the removal of the toluene, the dark residue was distilled under reduced pressure to give 29.5 g (91.8%) white product, fraction 185 — 195 °C, 0.05 mm, mp 117.5—120.5 °C (from toluene), ¹H NMR (CDCl₃) δ; 7.65 — 6.45 (m, 10H, arom.), 2.45(s, 6 CH₃). Anal. Calcd. for C₁₈H₁₆N₂O₂: C, 73.95, H, 5.52, N, 9.59. Found: C, 74.21,

H, 5.50, N, 9.55.

1,4-Bis(2-carboxypyridyl-6-oxy)benzene(4)

A mixture of 1.2 g (41.1 mmol) of **3**, 200 mL of pyridine and 100 mL of water was heated to reflux. Potassium permanganate (86.0 g, 544 mmol) was added in small portions over 5 h. Manganese dioxide was removed by filtration, and washed with hot water thoroughly. The pyridine was distilled off, the aqueous solution was concentrated to about 100 mL, and then acidified with hydrochloric acid. The pale precipitate was collected by filtration, and washed with water, dried at 100 °C under reduced pressure. The diacid (9.5 g, 83.0%) was obtained and used for next step without further purification.

1,4-Bis(ethoxycarbonylpyridyl-6-oxy)benzene(5)

4 (13.0 g, 37.0 mmol) was refluxed with 20 mL of thionyl chloride overnight. After the unreacted thionyl chloride was removed by distillation, 10 mL of absolute ethanol was added and the mixture was heated to reflux for 2 h, and then cooled in ice bath. The white precipitates were collected by filtration and recrystallized from ethanol twice. Pale white needles were obtained, 3.45 g (23.9%), mp 140 — 141 °C.

¹H NMR(CDCl₃) δ; 8.10 — 6.95 (m, 10H, arom), 4.70 — 4.35 (q, 4H, CH₂), 1.52 — 1.30 (t, 6H, CH₃). Anal. Calcd for C₂₂H₂₀N₂O₆: C, 64.70, H, 4.94, N, 6.86.

Found: C, 64.48, H, 4.92, N, 6.80.

1,4-Bis(2-acetylpyridyl-6-oxy)benzene(6)

To sodium ethylate (prepared from 0.23 g, 10.0 mmol of sodium and 5 mL of absolute ethanol, the excess alcohol was removed thoroughly under vacuum before use) were added 1.0 g (2.4 mmol) of **5**, 2 mL of ethyl acetate (dried over calcium hydride) and 15 mL of THF. The mixture was heated to reflux overnight, then concentrated hydrochloric acid (15 mL) was added. The reflux was continued for 2 h. After cooling, the mixture was extracted with ether, dried over K₂CO₃. After the removal of ether, the crystals were recrystallized from toluene to afford 0.17 g (20.0%) of pale white thin needles, mp 155.5 — 156.0 °C. ¹H-NMR(CDCl₃) δ; 8.05 — 7.10 (m, 10H, arom.), 2.55 (s, 6H, CH₃). IR (KBr): 1690 cm⁻¹ (C=O). Anal. Calcd for C₂₀H₁₆N₂O₄: C, 68.95, H, 4.63, N, 8.04. Found; C, 68.73, H, 4.74, N, 8.02.

A typical procedure for the polymerization

To a resin flask were added 0.8169 g (2.00 mmol) of 4,4'-diamino-3,3'-dibenzoyldiphenyl ether, 0.4577 g (1.80 mmol) of 4,4'-diacetyldiphenyl ether, 0.0697 g (0.20 mmol) of **6**, 10 g of di-m-cresyl phosphate and 4 g of m-cresol. The flask was purged with nitrogen. The polymerization was carried out at 135 — 140 °C under mechanical stirring for 24 h. An additional portion of m-cresol was added, if the mixture became too thick for stirring. The yellow-orange viscous solution was poured slowly into 200 mL of ethanol containing 10% of triethylamine and chopped in a blender. The resulted yellow fibrous polymer was extracted with ethanol in a Soxhlet extractor for 24 h, and then dried at 100 °C under reduced pressure for 24 h.

General procedure for the catalytic reactions

All catalytic reactions were carried out in a 100 mL stainless steel bomb with a glass cylinder and a lid in it. The catalyst, substrate and solvent were charged into the cylinder. The bomb was purged with working gas 3 — 5 times before heating. After reaction, the bomb was cooled thoroughly by dry ice — isopropanol, then the pressure was released very slowly. The mixture was taken vacuum transfer, and then examined by GLC and /or other means, such as NMR, IR and so forth, if needed.

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