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A Remarkably Rapid Synthesis of Ruthenium(II) Polypyridine Complexes by Microwave Irradiation

Takeko MATSUMURA-INOUE, Masahiro TANABE,
Takayoshi MINAMI, and Tomoko OHASHI
Department of Chemistry, Nara University of Education, Takabatake Nara, 630

A facile synthesis method of ruthenium (II) polypyridine complexes by microwave irradiation has been developed. This method greatly reduces reaction time from 4 hours to 20 minutes with better yield(60-90%). The procedures are simple and may be used for synthesis of a variety of metal polypyridine complexes.

Microwave irradiation is known to induce some specific effects on molecular motion such as migration of ions and rotation of dipoles, which greatly accelerates reaction processes.[1) Many recent reports indicated that using microwave ovens shortens the reaction time. However, samples are placed in pressured and sealed containers.[2,3) Highly pressurized conditions in the closed system are dangerous. For safety purposes, we used an open system with a reflux condenser.[4) Here, we report a rapid synthesis method for various ruthenium (Ru) (II) polypyridine complexes using microwave oven.

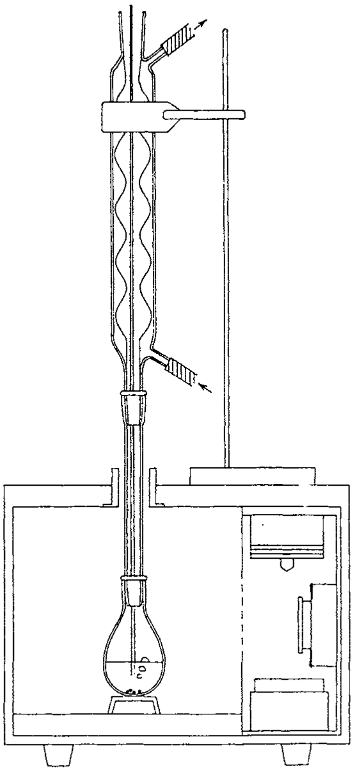
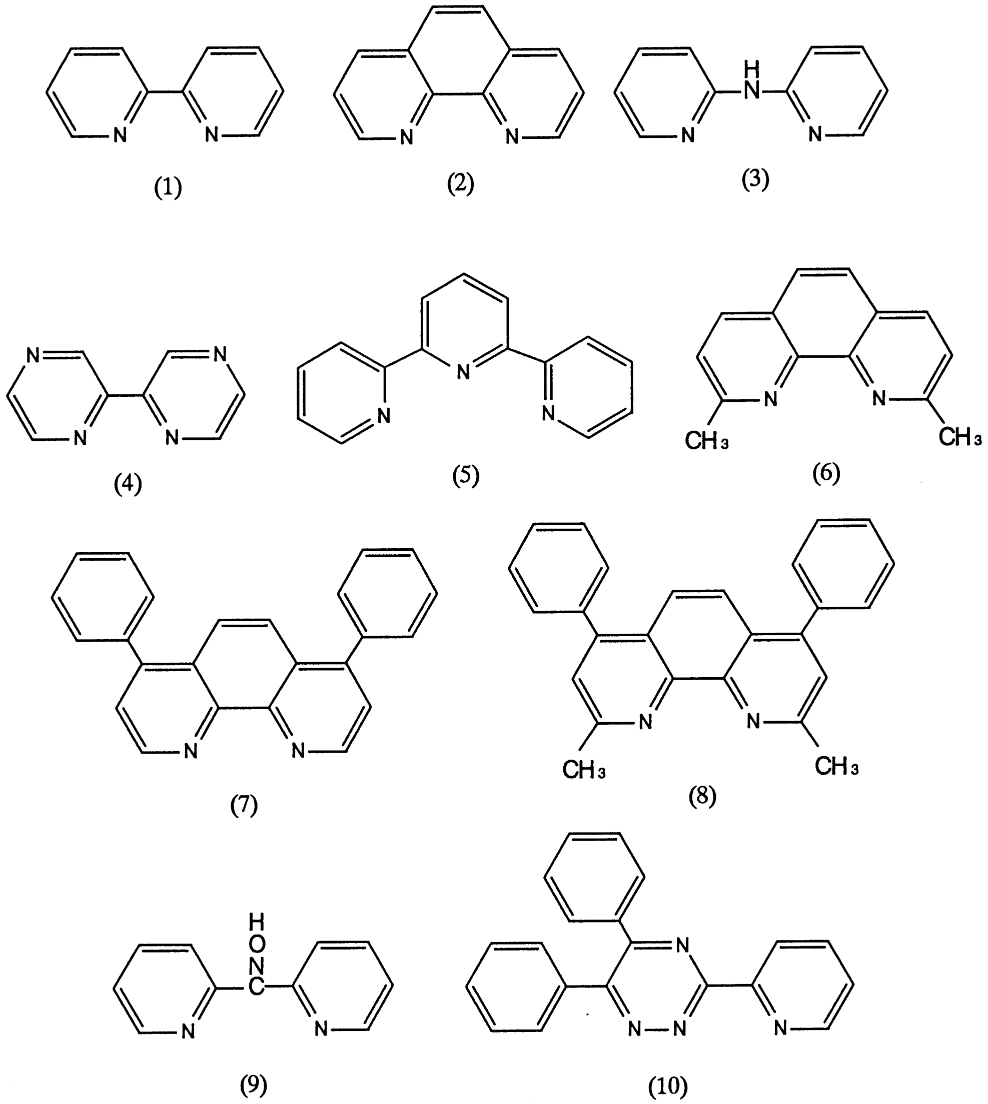


Fig. 1. The experimental apparatus; domestic microwave oven with a reflux condenser.

A domestic microwave oven(RR-12AF, 500 W, Mitsubishi Denki co. ltd.) was used. The frequency of 2450 MHz activates the OH group of water. The oven was perforated on the top to set a reflux condenser. To seal the microwave leakage, a flanged pipe (20 mm in diameter and 50 mm in length) was used (Fig.1). Leakage checked by a microwave survey meter(HI-1501, HOLADAY co.ltd.) was 1 mW/cm^2 (less than 5 mW/cm^2, the permissible leakage maximum). Nitrogen gas was bubbled into the reaction mixture. A starting material, ruthenium(III) chloride trihydrate ($RuCl_3 \cdot 3H_2O$), was prepared from ruthenium(IV) oxide (RuO_2). RuO_2 was dissolved in hydrochloric acid and the solution was evaporated to dryness. The residue, mostly ruthenium(IV) chloride ($RuCl_4$), was reduced by ethyl alcohol to yield green black $RuCl_3 \cdot 3H_2O$. Polypyridine ligands were of commercial grade. Ethelyne glycol was used as a solvent. The following procedures are recommended for the synthesis of tris(2,2'-bipyridine) ruthenium(II) perchlorate trihydrate ($[Ru(bpy)_3](ClO_4)_2 \cdot 3H_2O$) : The mixture of $RuCl_3 \cdot 3H_2O$ (0.2 g; 0.76 mmol) and 2,2'-bipyridine (bpy) (0.36 g; 2.31 mmol) in ethylene glycol (20 ml) was refluxed for 20 minutes under microwave irradiation. The green solution turns to orange red. The solution was cooled to room temperature and filtered. The filtrate was poured into a saturated aqueous solution of sodium perchlorate ($NaClO_4$) to obtain a red orange precipitate, $[Ru(bpy)_3](ClO_4)_2 \cdot 3H_2O$. Then an acetonitrile solution of the precipitate was poured into diethyl ether for recrystallization. The product showed λ_{max}=451 nm, ε_{max}=14500 $l \cdot mol^{-1} \cdot cm^{-1}$, and E_{ox}=+1.30 V (V vs. Ag/AgCl), in agreement with data described in the literature.[5,6] Anal. Found : C, 43.75; H, 3.19; N, 10.17%. Calcd for $[Ru(bpy)_3](ClO_4)_2 \cdot 3H_2O$: C, 43.80; H, 3.68;N, 10.21%. . Tris(2,2'-bipyridine) ruthenium(II) hexafluorophosphate is obtained directly similarly to perchlorate. The sulfate, $[Ru(bpy)_3]SO_4$, is obtained through the chloride, $[Ru(bpy)_3]Cl_2$. Ethylene glycol is the best choice as a solvent because of its OH group and high boiling point (198 ℃).

Our new method also produces directly tris(2,2'-dipyridylamine) ruthenium(II) perchlorate ($[Ru(Hdpa)_3](ClO_4)_2$) from starting material($RuCl_3 \cdot 3H_2O$) in high yield (91%). In a conventional method, a synthesis of $[Ru(Hdpa)_3](ClO_4)_2$ required refluxing in the presence of hypophosphorus acid for at least 2 hours, moreover yield is as low as 30% because of impurities.[7] Mizumachi[8] recommended an alternative synthesis method of $[Ru(Hdpa)_3](ClO_4)_2$, which requires bis(2,2'-dipyridylamine) ruthenium(III) chloride monohydrate ($[Ru(Hdpa)_2Cl_2]Cl \cdot H_2O$) as an intermediate. Consequently, its overall reaction time is about 35 hours. Thus, our present method produces $[Ru(Hdpa)_3](ClO_4)_2$ rapidly in a purer state.

The synthesis of various polypyridine ruthenium(II) complexes (Fig.2) was successfully carried out in a similar way to the recommended procedure for $Ru(bpy)_3^{2+}$. The yields of these complexes are listed in Table 1. The present method is also applicable to the tris (polypyridine) osmium(Os) complexes, but the yield of Os complexes is lower than that of Ru complexes, e.g., 74% for tris(2,2'-bipyridine) osmium(II) perchlorate and 65% for tris(2,2'-dipyridylamine) osmium(II) perchlorate .


(1) (2) (3)

(4) (5) (6)

(7) (8)

(9) (10)

Fig. 2. Polypyridine ligands used in a microwave irradiation synthetic method,(1) 2,2'-bipyridine(bpy),
(2) 1,10-phenanthroline (3) 2,2'-dipyridylamine(Hdpa),
(4) 2,2'-bipyradine,(5)2,2':6',2"-tripyridine,
(6) 2,9-dimethyl-1,10-phenanthroline
(7) 4,7-diphenyl-1,10-phenanthroline,
(8) 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline
(9) 2,2'-dipyridylketon oxime
(10) 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine

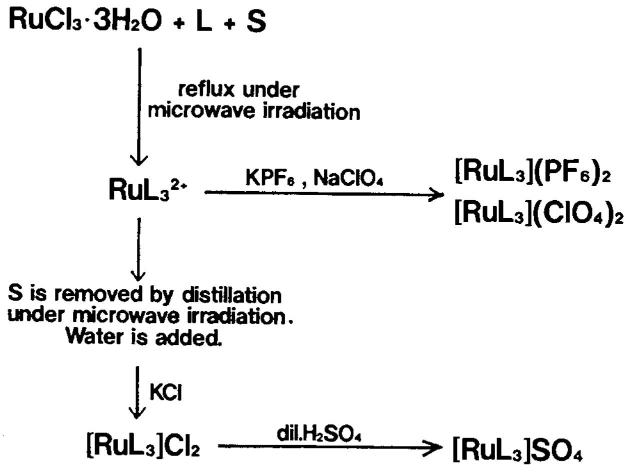


Fig. 3. Reaction scheme of the synthesis of the polypyridine complexes.
L represents a polypyridine ligand (Fig.2).
S is a solvent, ethylene glycol.

Table 1. The yields of ruthenium(II) complexes with a variety of polypyridine ligands

Ligands	Yield/%
(1)	86
(2)	69
(3)	91
(4)	57
(5)	80
(6)	65
(7)	72
(8)	67
(9)	65
(10)	95

The numbers in parentheses are the same as in Fig. 2.

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