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Intramolecular Hydrogen Bond Self-template Synthesis of Some New Robson-type Macrocyclic Ligands

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Abstract: The intramolecular hydrogen bond self-template effect was suggested in the process of directly synthesizing the first six chiral metal-free Robson-type macrocyclic ligands. These ligands were characterized by ^{1}H NMR, IR, FAB-MS.

Keywords: Self-template, macrocyclic ligands.

Binuclear macrocyclic Robson-type complexes are of interest as models of biomolecules. Many of them have been prepared and widely studied since 1970s[1,2]. These complexes are restricted mainly to those metal ions that are employed as the template reagents, although Yunqi Tian *et al*. reported the proton-template synthesis of metal –free Robson-type macrocyclic ligands by addition of acid[3] and Shaohua Gou *et al*. used Na^+ as template[4-6].

Recently, in order to explore useful information concerning molecular design of metal catalysts for enantioselective epoxidation of *trans*-disubstituted alkenes, which remains an unresolved problem in the field of metal-catalyzed asymmetric epoxidation of unfunctionalized alkenes, some Robson-type chiral ligands and mononuclear metal complexes were designed and synthesized (**Scheme 1**).

In the process we found these ligands can be synthesized without any additional template reagents. And these ligands are metal-free and proton-free. With the same quantity of diamine and 2, 6-diformal-4-substituded-phenol, the (2+2) Robson-type macrocyclic ligands were the main products if the temperature of reaction remains at 50°C and the diamine solutions was added slowly. And if the reaction temperature was increased, the (3+3) macrocyclic ligands can be produced. This result is mainly due to the contribution of the action of intramolecular hydrogen bond in the compound **2′** (**Scheme 1**) and some compound **2″** were got in our laboratory. The high temperature can make the hydrogen bond unstable, so the temperature must be controlled.

From the data of the six chiral ligands it can be found that the intramolecular hydrogen bond action is so strong that the shifts of the four protons in –CH=N– were divided into two peaks, even the four protons (Ar-H) in 2, 6-diformal-4-substituded-

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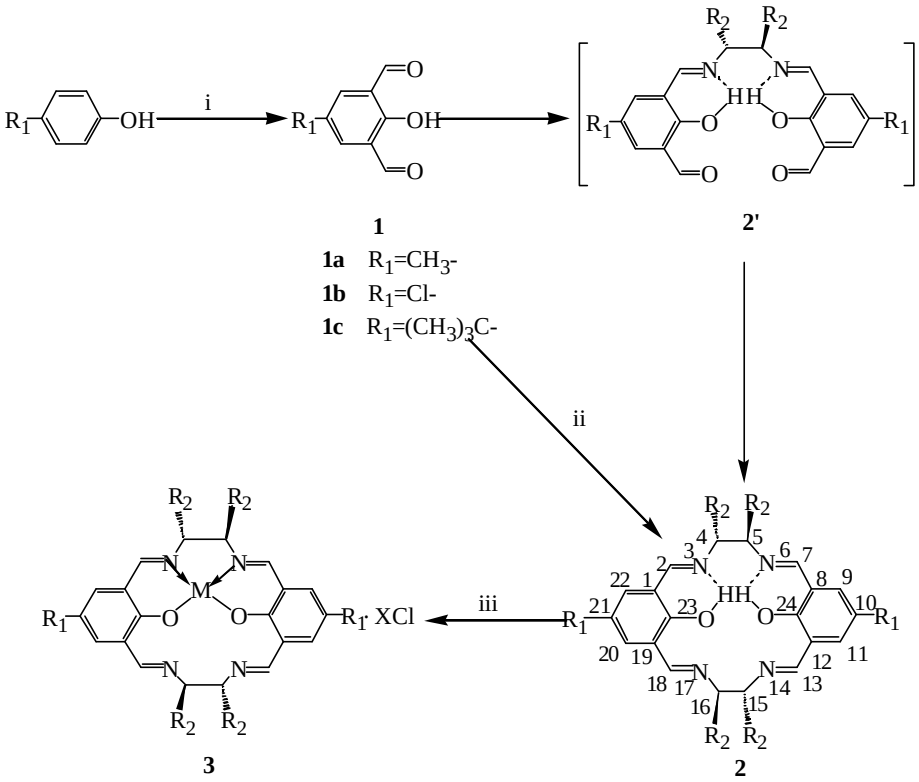
phenol were showed in different shifts.

Scheme 1



1a R_1=CH_3-
1b R_1=Cl-
1c R_1=$(CH_3)_3C$-

$3a_1$-$3f_1$	M=Mn;	X=1	**2a**	R_1 =CH_3-	R_2=Ph-
$3a_2$-$3f_2$	M=Co;	X=0	**2b**	R_1 = Cl-	R_2=Ph-
$3a_3$-$3f_3$	M=Ni;	X=0	**2c**	R_1 =$(CH_3)_3C$-	R_2=Ph-
$3a_4$-$3f_4$	M=Cu;	X=0	**2d**	R_1 =CH_3-	R_2=-$(CH_2)_4$-
			2e	R_1 = Cl-	R_2=-$(CH_2)_4$-
			2f	R_1 =$(CH_3)_3C$-	R_2= -$(CH_2)_4$-

Reagents and conditions:
i) CH_2O, NaOH, CO_2; MnO_2, $CHCl_3$, refluxed; yield 42-71%;
ii) CH_3CH_2OH, $R_2C^*H(NH_2)HC^*(NH_2)R_2$, 50°C;yield 19-55%
iii)$MCl_2 \bullet nH_2O$, yield 42-81%;

The following tables are the data for **2a-2f**:

Table 1 The ^{1}H NMR ($CDCl_3$, 80MHz, δ ppm) data for **2a-2f**

proton	Compound **2a**	Compound **2b**	Compound **2c**
4,5,15,16	4.78 s, 4H	4.78 s, 4H	4.76 s, 2H
9,22	7.15 s, 2H	7.17s, 2H	7.13 s, 2H
11,20	7.86 s, 2H	7.99 s, 2H	8.02 s, 2H
2,7	8.44 s, 2H	8.40 s, 2H	8.44 s, 2H
13,18	8.88 s, 2H	8.83 s, 2H	8.88 s, 2H
23,24	13.89 s, 2H	13.92 s, 2H	13.89 s, 2H
10,21-R_1	2.25 s, 6H		1.23 s, 18H
4,5,15,16-R_2	7.16 m, 20H	7.18 m, 20H	7.13 m, 20H

proton	Compound **2d**	Compound **2e**	Compound **2f**
4,5,15,16	3.38 s, 4H	3.36 s, 4H	3.36 s, 4H
9,22	6.93 s, 2H	7.13 d, 2H	7.16 s, 2H
11,20	7.61 s, 2H	7.76 d, 2H	7.86 s, 2H
2,7	8.20 s, 2H	8.19 s, 2H	8.27 s, 2H
13,18	8.66 s, 2H	8.59 s, 2H	8.68 s, 2H
23,24	13.86 s, 2H	14.10 s, 2H	13.89 s, 2H
10,21-R_1	2.14s, 6H		1.22 s, 18H
4,5,15,16-R_2	1.77 m,16H	1.74 m,16H	1.80 m,16H

Table 2 The IR (KBr, cm^{-1}) data for **2a-2f**

Compound	IR (KBr, cm^{-1})
2a	3422, 3028, 2310, 1636 ,1598, 1457, 1259
2b	3445, 3029, 2870, 1632, 1451, 1251
2c	3442, 2959, 2360, 1637, 1599, 1457, 1227
2d	3432, 2929, 2855, 1636, 1598, 1458, 1257
2e	3434, 2933, 2857, 1636, 1447, 1251
2f	3430, 2929, 2855, 1636, 1598, 1457, 1257

Table 3 The other data for **2a-2f**

	Colour	Yield%	MS(FAB): *m/z* (M^++1)
2a	orange solid	55	681
2b	orange solid	47	721
2c	yellow solid	24	765
2d	orange solid	51	485
2e	orange solid	45	525
2f	yellow solid	19	569

The further investigation is in progress.

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