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Synthesis of Polymer-Bonded Carbonyl Ruthenium (Ⅱ) and Osmium (II) Porphyrins

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Abstract: The reactions of 5- (p-hydroxyphenyl)-10, 15, 20-tris (p-methoxyphenyl) porphyrin (H_2Por) **1** respectively with triruthenium dodecacarbonyl [Ru_3 $(CO)_{12}$] and triosmium dodecacarbonyl [Os_3 $(CO)_{12}$] under N_2 gave complexes **2** and **3**. Treatment of **2** **(**and **3**) with Merrifield' peptide resin gave **4** (and **5**) respectively.

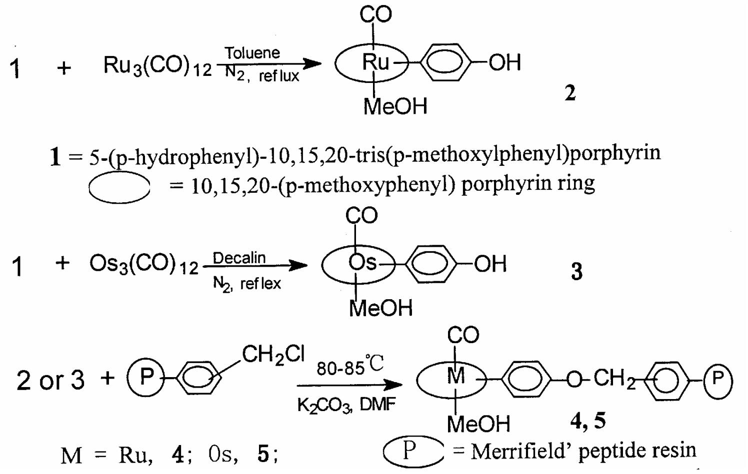
Keywords: Polymer-bonded metal porphyrin ; synthesis.

Study on metalloporphyrin complexes used as enzyme model catalyzing the oxidation of alkane and epoxidation of alkene is currently a very active research field[1]. The reactivity of ruthenium porphyrin complexes was used as oxidation catalysts because their relations to cytochrome P-450 have been studied. Machon and co-workers reported Ru (TMP) $(O)_2$ catalyzes the epoxidation of several cholest-5-ene derivatives by air in high yield and with nearly complete β-stereospecificity[2]. The epoxidation of olefins with pyridine N-oxides catalyzed by Ru (2, 6-F-TPP) (O_2)] was reported by Hirober *et al.*[3]. They also discovered that Ru (TMP) $(O)_2$ as catalyst in the presence of HCl, oxidation of cyclohexanol gave cyclohexanone; oxidation of methyl cyclohexane gave methyl cyclohexanol with Ru (TMP) (CO) as catalysts in presence of HBr. All the ruthenium porphyrin compounds are air stable in the solid state. In solution, the complexes exhibit high reactivity toward reductive agent (as Ph_3P). The study on reactivity showed that polymer-bonded metalloporphyrin as a catalyst is a new development, and it is easy to recover and reuse. Here we report the synthesis and characterization of polystyrene-bonded carbonyl ruthenium (Ⅱ) and osmium (Ⅱ) porphyrins .

The free porphyrin **1** was prepared with modification of literature procedure[4]. Complexes **2** and **3** were prepared according to literature 5, toluene (and decalin) as solvent respectively, using UV to monitor the termination of reaction (complex **2**'s Soret band moves from 422 to 414nm , B bands turn from four bands to two bands). Treatment of complex **2** **(**and **3**) with Merrifield' peptide resin under N_2 , DMF as solvent, stirred for 3 hours at 80-85℃ gave **4** (and **5**) respectively. The synthetic routes of the compounds are listed below.

These new complexes **2-5** have been identified by IR, UV-visible and ^{1}H NMR spectra and elemental analysis. Compound **2**, Anal. Calcd for $C_{49}H_{38}N_4O_6Ru$: C, 66. 29%;

H, 4. 29%; N, 7. 22%. Found: C, 65. 09%; H, 4. 21%; N, 7. 57%. UV-visible: λ_{max} 414 (Soret band). IR, υ (KBr): 1940 (Ru-C=O), 1005cm^{-1} (Oxidation State Marked Band). Compound **4**, UV: λ_{max} 418 (Soret band). IR: υ (KBr): 1938 (Ru-C=O), 1231 (Ar-O-C). Compound **5**, IR: υ (KBr): 1929 (Os-C=O), 1228 (Ar-O-C). The content of ruthenium of complex **4** is examined by AES: 1. 0mg/g.



1 = 5-(p-hydrophenyl)-10,15,20-tris(p-methoxylphenyl)porphyrin

= 10,15,20-(p-methoxyphenyl) porphyrin ring

M = Ru, **4**; Os, **5**;

P = Merrifield' peptide resin

References

1. Meunier B., *Bell. Soc. Chi. Fr.* 1986, *4*, 578.
2. J. C. Marchon , R. Ramasseul, *J. Chem. Soc., Chem. Commun.*, **1988**, *111*, 298.
3. H. Ohtale, T. Highchi, M. Hirobe, *J. Am. Chem. Soc.*, **1992**, *114*, 10660.
4. S. Q. Huang, L. M. Shun, Q. Yie, *GaoDengXueXiaoHuaXueXueBao*, **1983**, *4* (3):863.
5. Z. Y. Li, *PhD. Thesis, The Hong Kong Polytechnic University*, **1994**.

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