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Attempt to Resolute Chiral Clusters by Optically Active Hydrazide

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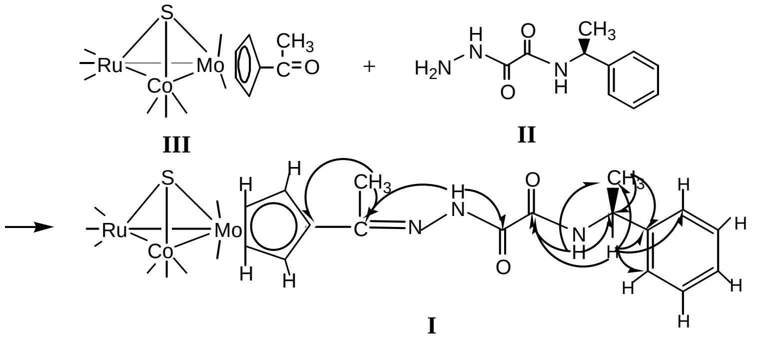
Abstract: A new kind of hydrazone (I) diastereoisomers was prepared with enantiomeric hydazide (II) and chiral cluster (III), which was characterized by HMBC. Unfortunately, the mixture could not be separated into pure diastereoisomer. This could be a direction to separate the racemic chiral clusters.

Keywords: Chiral clusters, optically active hydrazone, chiral resolution, diastereoisomer, HMBC.

Due to the framework chirality optically active clusters can provide the proof that a cluster as a whole, and not one of its fragments, acts as a catalyst, most of the work have been directed to the synthesis of tetrahedron-type chiral clusters[1-3]. However, there remains another major problem to obtain the pure enantiomers. Although Vahrenkamp had obtained some pioneering results in this area before 1990[1], only several racemic chiral clusters have been separated into pure enantiomers until now[3]. We have reported the synthesis of a number of EM_3-type chiral clusters containing carbonyl substituent in cyclopentadienyl[4-7]. It could react with optically active hydrazide to give the diastereoisomers after separated from chromatographic column. Then the auxiliary hydrazide can be removed and the pure enantiomers of chiral clusters could be obtained. In this paper, we report on the synthesis of the diastereoisomers **I** from optically active hydrazide **II** and racemic chiral cluster **III**, but we could not separate the mixture into pure diastereoisomer.

Scheme 1



III **II** **I**

To a stirred solution of chiral cluster **III** and hydrazide **II** in some anhydrous ethanol was added several drops of H_2SO_4. After stirring at room temperature for a whole day, the solvent was removed and the residue was separated on silica gel chromatography. The main product could be obtained as brown solid in 45% yield. Several attempts to separate the mixture into pure diastereoisomers have been performed, unfortunately none of which was effective.

The idea, resolution of chiral cluster using the carbonyl attached to cyclopentadienyl ring, is proposed firstly by our laboratory to our knowledge. The hydrazone containing SRuCoMo core **I** was characterized by elemental analysis, IR, ^{1}H NMR and ^{13}C NMR[8]. Since the single crystal of compound **I** was not obtained, the structure was confirmed by HMBC as shown in **Scheme 1**.

HMBC showed very strong couplings of the ^{13}C signals between δ 106.10 and 88.53 with the bonding proton signals in the region δ 5.86-5.35, which are the C-H correlations in cyclopentadienyl. And the intense couplings of the carbon signals at δ 141.66, 128.82, 127.83 and 126.12 with the ^{1}H signal at δ 7.26 are the carbon-proton correlations in benzene ring (all of them are not plotted in **Scheme 1**). The chemical shift at δ 5.01 coupling with the ^{13}C signals at δ 21.55, 126.12, 141.66 and 158.59 should be the proton in methenyl, and the ^{1}H signal at δ 7.73-7.71 should be proton resonance in Methylbenzylamine because three ^{13}C signals (δ 21.55, 49.76 and 158.59) coupled with it. All of other carbon-proton correlations can be identified from HMBC.

The study is in progress on the reactions between the optically active hydrazide with other kinds of racemic chiral clusters and the resolution of the mixture of diastereoisomers.

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8 For the compound **I**, C/H determination: Calcd., C, 37.14; H, 2.24 %. Found, C, 37.01; H, 2.35 %. IR (KBr disk, cm^{-1}): 3310w, 2081vs, 2039vs, 2004vs, 1869s, 1715m, 1670s. ^{1}H NMR ($CDCl_3$, δ): 10.08 (s, 1H, H-N), 7.73-7.71(d, 1H, H-N), 7.26(m, 5H, C_6H_5), 5.86-5.35(q, 4H, C_5H_4), 5.01(t, 1H, H-C), 2.05(s, 3H, CH_3), 1.52-1.50(d, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 224.37 ($C\equiv O$), 158.59, 155.20 (2C=O), 149.05 (C=N), 141.66, 128.82, 127.83, 126.12 (C_6H_5), 106.10, 92.60, 91.61, 90.47, 88.53 (C_5H_4), 49.76 (C-H), 21.55 (CH_3), 13.88(CH_3).

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