

Synthesis and Characterization of Chiral Organogallium and Indium Complexes with Salen Ligands

Fu Xing GAO^{1,2}, Cheng Jian ZHU^{1*}, Fang YUAN¹, Yu Hua ZHU¹, Yi PAN^{1*}

¹Department of Chemistry, Nanjing University, Nanjing 210093

²Department of Chemistry, Xinyang Normal College, Xinyang 464000

Abstract: Several new chiral organogallium and indium complexes with chiral Salen (**1** and **2**) as auxiliary ligands have been synthesized and characterized by elemental analysis, IR, ¹H NMR and Mass spectroscopy. For the gallium, mono and bimetallic complexes were obtained, whereas ring closure complexes of indium were obtained.

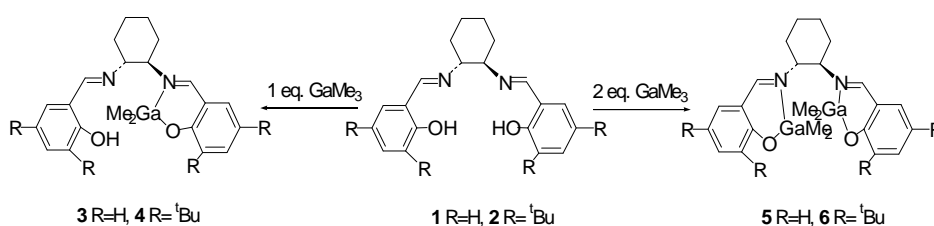
Keywords: Chiral Complex, organogallium complex, organoindium complex, Salen ligand.

The chemistry of organogallium and indium which contain either Group 15 or 16 elements has been mainly aimed at the possible application as organometallic precursors for MOCVD of semiconductor film^{1,2}. Unlike their aluminum congener, application of organogallium or indium complexes as catalysts in organic synthesis, especially as chiral catalysts, has been rarely studied. It is quite reasonable to consider that the organogallium and indium complexes would also have the activities to catalyze organic reactions in the similar manner as those of aluminum. Quite recently, Shibasaki *et al*³ reported that epoxides opening reaction can be catalyzed by heterobimetallic inorganic complexes of gallium enantioselectively. It would be worth to study the synthesis of chiral organogallium and indium complexes and their applications in organic synthesis. The Salen ligands feature two covalent and two coordinate covalent sites situated in a planar array. Salen ligands from chiral 1, 2-diaminocyclohexane have been extensively used in preparation of chiral transition-metal catalysts⁴. As part of our preliminary efforts in the preparation and application of organogallium and indium complexes, we report herein the synthesis and characterization of some novel organogallium and indium complexes with chiral Salen ligands.

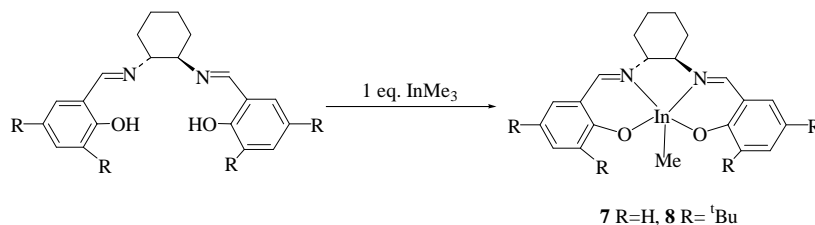
Reactions of the chiral Salen ligands **1** and **2**, which were obtained by condensation of (1R, 2R)-(–)-1,2-diaminocyclohexane with the corresponding aldehydes, with stoichiometric GaMe₃ at room temperature in benzene for 4 hours provide monometallic 'open' complexes **3** in 78% yield and **4** in 84% yield (**Scheme 1**), which are potential precursors to the synthesis of mixed metal derivatives⁵. Remarkably, the complexes could be refluxed in benzene for up to 4 h without effecting ring closure. Thus, the

*E-mail: cjzhu@netra.nju.edu.cn and yipan@netra.nju.edu.cn

$-\text{GaMe}_2$ unit appears to be very stable in the compounds. This finding follows the earlier work, which demonstrated that Me_2Ga^+ does not decompose even in aqueous sulfuric acid⁶. When two equivalents of GaMe_3 were used in the reactions, bimetallic derivatives were formed (**Scheme 1**) quantitatively, which can be used as double Lewis acids to catalyze organic reactions⁷.

Scheme 1

Mixing the ligand **1** or **2** with InMe_3 in toluene leads to ring closure monometallic chiral indium derivatives **7** and **8** in the yield of 86% and 90%, respectively (**Scheme 2**).

Scheme 2

The complexes **3-8** have been characterized by elemental analysis, IR, MS and ^1H NMR. Characteristic absorption peaks in IR spectra of the complexes due to C=N bond ($1596\text{--}1626 \text{ cm}^{-1}$) and benzene ring vibrations are evidently present. The IE mass spectra of the complexes reveal the parent molecular ion M^+ and related fragments. No fragments greater than $[\text{M}]^+$ were detected, suggesting that these complexes are monomer.

^1H NMR spectra data of complexes **3-8** is shown in **Table 1**. From the ^1H NMR spectra, we found that most of the resonance signals in complexes **5-8** shift to lower field comparing to their counterpart in free ligands, since the electron density transfers from ligands to center metals by O-metal bonds and N-metal coordination bonds. It is worth to note that in complexes **5** and **6**, protons of the $-\text{GaMe}_2$ group show two sets of signals at -0.10 and -0.48 ppm for **5**, -0.15 and -0.47 ppm for **6**, respectively. These results indicate that the two $-\text{CH}_3$ groups are unequivalent, probably due to the geometric constraints of the Salen ligands.

The X-ray crystal structure analysis and their application in catalytic asymmetric organic reactions are still underway in our groups.

Table 1 ^1H NMR spectra data of compounds **3-8**

Compound	^1H NMR (δ ppm, CDCl_3)
3	7.87 (s, 1H), 7.79 (s, 1H), 7.22~6.34 (m, 8H), 3.40~3.36 (m, 2H), 2.13~1.67 (m, 8H), -0.22 (s, 3H), -0.38 (s, 3H)
4	8.30 (s, 1H), 7.99 (s, 1H), 7.35~7.33 (m, 2H), 6.99 (d, 1H, $J=2.3\text{Hz}$), 6.77 (d, 1H, $J=2.52\text{Hz}$), 3.57~3.38 (m, 2H), 1.95~1.45 (m, 8H), 1.42 (s, 9H), 1.36 (s, 9H), 1.26 (s, 9H), 1.18 (s, 9H), -0.22 (s, 3H), -0.31 (s, 3H)
5	7.72 (s, 2H), 7.30~6.34 (m, 8H), 3.41~3.37 (m, 2H), 2.19~1.20 (m, 8H), -0.10 (s, 6H), -0.48 (s, 6H)
6	7.65 (s, 2H), 7.19 (d, 2H, $J=2.6\text{Hz}$), 6.44 (d, 2H, $J=2.6\text{Hz}$), 3.36~3.31 (m, 2H), 2.14~1.28 (m, 8H), 1.25 (s, 18H), 1.01 (s, 18H), -0.15 (s, 6H), -0.47 (s, 6H)
7	8.16 (s, 1H), 8.02 (s, 1H), 7.33~6.58 (m, 8H), 3.39~3.08 (m, 1H), 2.53~1.42 (m, 8H), -0.18 (s, 3H)
8	8.12 (s, 1H), 8.08 (s, 1H), 7.40 (d, 2H, $J=2.5\text{Hz}$), 6.84 (d, 2H, $J=2.5\text{Hz}$), 3.12~3.00 (m, 2H), 2.20~1.48 (m, 8H), 1.45 (s, 18H), 1.28 (s, 18H), -0.38 (s, 3H)

Acknowledgments

We thank the National Natural Science Foundation of China (20102002), Science Foundation of Jiangsu Province (BK2001030) and the 863 High Technology Program for their financial support. The research funds for Y. Pan from Qin-Lan Program of Jiangsu Province and Kua-Shi-Ji Program of Education Ministry of PRC are also acknowledged.

References

1. M. R. Lazell, P. I O'Brien, D. J. Otway, J. Park, *Chem. Mater.*, **1999**, *11*, 3430.
2. Y. Sh. Zhong, H. W. Gu, Y. Pan, G. Dong, T. Wu, X. P. Jin, X. Y. Huang, H. W. Hu, *J. Organomet. Chem.*, **2000**, *605*, 234.
3. S. Matsunaga, J. Das, J. Roels, E. M. Vogl, N. Yamamoto, T. Iida, K. Yamaguchi and M. Shibasaki, *J. Am. Chem. Soc.*, **2000**, *112*, 2252.
4. F. Fache, E. Schulz, M. L. Tommasino, M. Lemaire, *Chem. Rev.*, **2000**, *100*, 2159.
5. D. A. Atwood, M. J. Harvey, *Chem. Rev.*, **2001**, *101*, 37.
6. O. T. Beachey, R. U. Kirss, R. J. Bianchini, T. L. Royster, *Organometallics*, **1987**, *6*, 724.
7. T. Ooi, M. Takahashi, K. Maruoka, *J. Am. Chem. Soc.*, **1996**, *118*, 11307.

Received 22 April, 2002