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Intramolecular coordination of Ln–O and Ln–N bonds in some new substituted lanthanocene complexes

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Abstract

Synthesis and intramolecular coordination chemistry of Ln–O and Ln–N bonds in some new substituted lanthanocene complexes prepared by our research group are reviewed citing ten references. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Donor functionalized Cp and Ind ligand; Polydentate Schiff base; Lanthanide; Intramolecular coordination

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1. Introduction

The chemistry of substituted metallocenes has been studied in our laboratory for about 30 years now. Recent interest of our research group is focused on the chemistry of new types of substituted metallocene complexes, which may be used as catalysts in polymerization and organic synthesis. One of the main themes of this study is an understanding of intramolecular coordination between the central metal atoms and donor atoms on the ligand. This paper summarizes our recent results in the field of substituted lanthanocene complexes. In the meantime, the intramolecular coordination chemistry of substituted titanocene, zirconocene and ruthenocene complexes are treated in our other review article [1].

The cyclopentadienyl ligand (Cp) with additional donor functionality has attracted increasing interest in the organometallic chemistry of transition and rare-earth metals. Such bi-functional ligands can coordinate to the metal with the cyclopentadienyl ring and the intramolecular donor atom, increasing the stability of highly reactive complexes. In addition, the Cp ligand is also ubiquitous in lanthanide chemistry due to its stability, it is therefore often referred to as the stabilizing backbone of organolanthanide complexes. The chemistry of lanthanide complexes based on substituted indenyl (Ind) ligands and polydentate Schiff base ligands are also of interest and are discussed.

2. Substituted-Cp and substituted-Ind based complexes

Recently a series of lanthanide sandwich complexes with mixed cyclooctatetraenyl (COT) and chelating substituted Cp or Ind ligands were synthesized in our laboratory [2] via Schemes 1 and 2.

The molecular structures of **1** and **3** have been determined, and show that the oxygen of the ligands has intramolecular coordination to the lanthanide metals, see Figs. 1 and 2.

From the molecular structures, this type of complexes may contain a THF fragment in the crystals which was, however, not observed in their MS spectra. This indicates that coordination between the lanthanide center and solvent THF is weak, which can be further proved by drying the complexes under reduced pressure for more than 1 h with the loss of THF.

In the case of **6**–**15** substituted indenyl ligands were used in place of the substituted cyclopentadienyl ligands, the results were quite similar. Suitable crystals for X-ray diffraction study were grown from THF solution. The structures of **8** and **13** show expected features (Figs. 3 and 4) [3].

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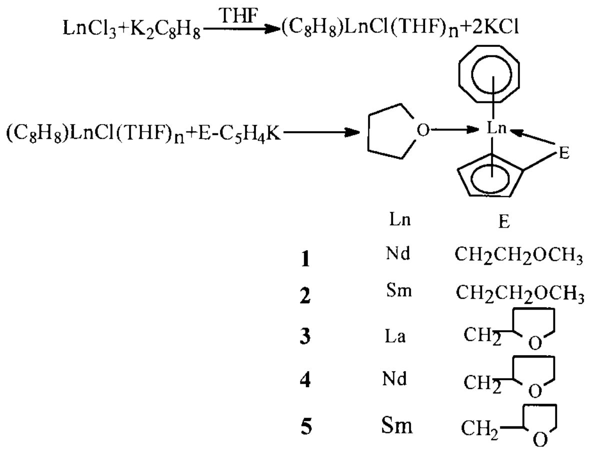
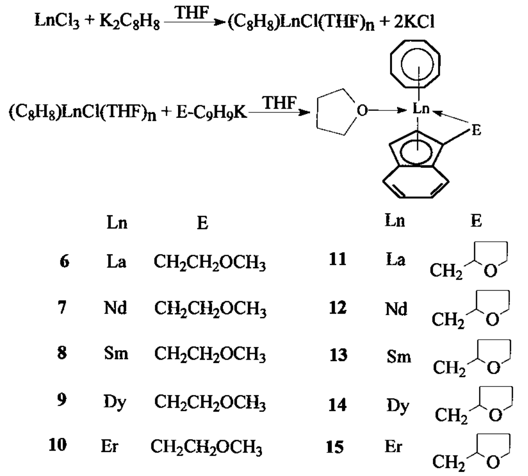


Scheme 1.



Scheme 2.

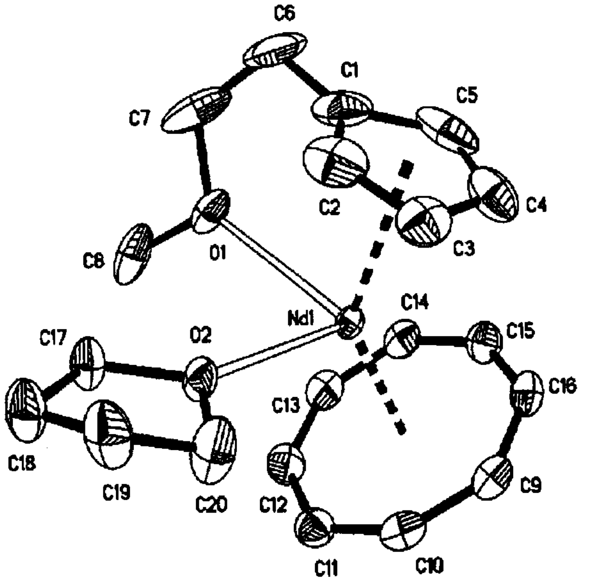


Fig. 1. Molecular structure of **1**.

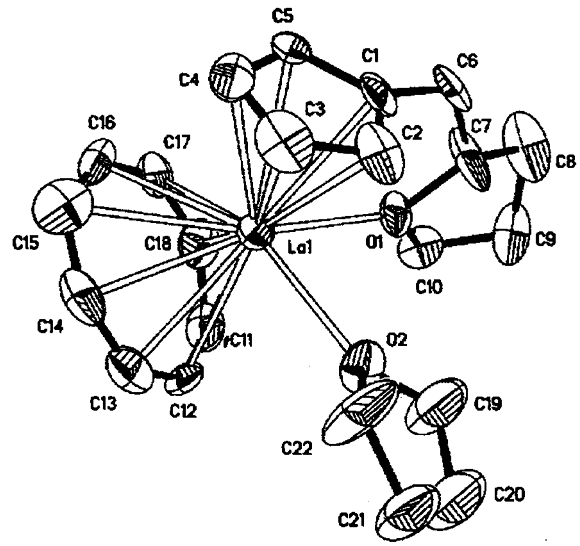


Fig. 2. Molecular structure of **3**.

Samarium is coordinated in a distorted tetrahedral configuration with the eight-membered COT ring, the five-membered indenyl ring, and two oxygens of THF and side chain group of indenyl ligand. The intramolecular coordination between the oxygen atom of the ligand and samarium does satisfy the coordination requirement of the lanthanide center. Here, as in the earlier case, there is only one THF molecule in the crystal giving a ten coordinate samarium center.

3. Polydentate Schiff base complexes

Recently, chiral lanthanide reagents have been receiving more attention due to their excellent catalytic properties in polymerization and asymmetric synthesis. We now review with emphasis on the intramolecular coordination of Ln–O and Ln–N bonds, the synthetic routes to such binuclear bis(cyclopentadienyl) lanthanides with one chelating ligand as prepared in our laboratory (Schemes 3–7) [4].

The crystal structure of **16** was determined by X-ray diffraction study (Fig. 5).

In the structure of **16**, there is no bridging THF molecule and the two samarium centers have different coordination numbers. This means that the ligand methoxyethylcyclopentadiene can not only coordinate to the central atoms but also change their coordination environment.

Interest in exploring metal ion complexes with Schiff base ligands has continued to increase, since it has been recognized that many of these complexes may serve as biologically important, naturally occurring ionophores. Investigations on lanthanide complexes containing Schiff bases have been devoted to their synthesis, structural studies and their biological application for metal–

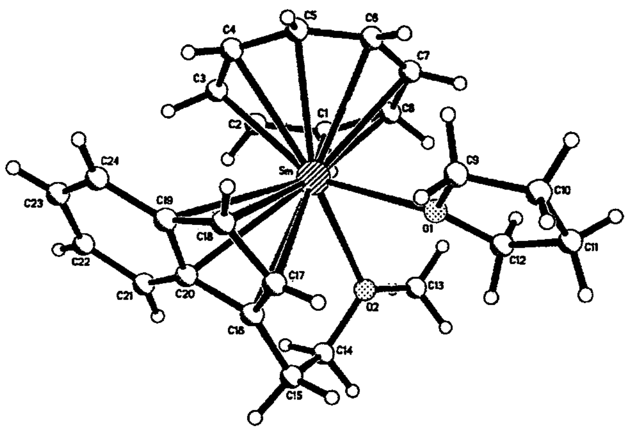
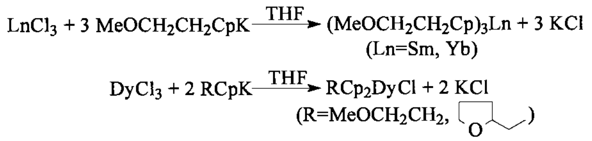


Fig. 3. Molecular structure of **8**.

enzyme or protein bonding. A large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g. their ability to reversibly bind oxygen, catalytic activity in hydrogenation and polymerization of olefins and transfer of an amino group, photochromic properties, complexing ability towards some toxic metals, etc. Thus, we are interested in the synthesis of monomeric lanthanocene complexes with a tridentate Schiff base as the ligand which is electronically equivalent to a cyclopentadienyl ligand (Schemes 8 and 9) [5,6].

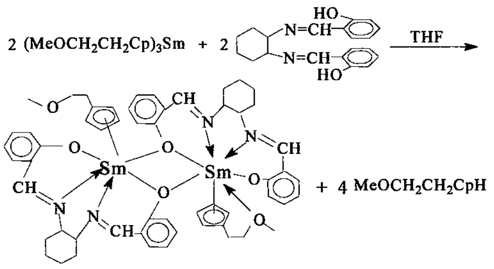
These novel complexes are monomeric and are different from the complexes derived from bidentate and tetradentate Schiff base ligands. The structure of **20** was determined by X-ray diffraction study (Fig. 6).



$LnCl_3 + 3\ MeOCH_2CH_2CpK \xrightarrow{THF} (MeOCH_2CH_2Cp)_3Ln + 3\ KCl$ (Ln=Sm, Yb)

$DyCl_3 + 2\ RCpK \xrightarrow{THF} RCp_2DyCl + 2\ KCl$ (R=MeOCH$_2$CH$_2$,)

Scheme 3.



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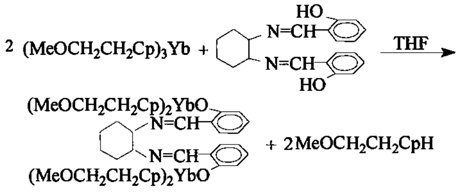
Scheme 4.



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Scheme 5.

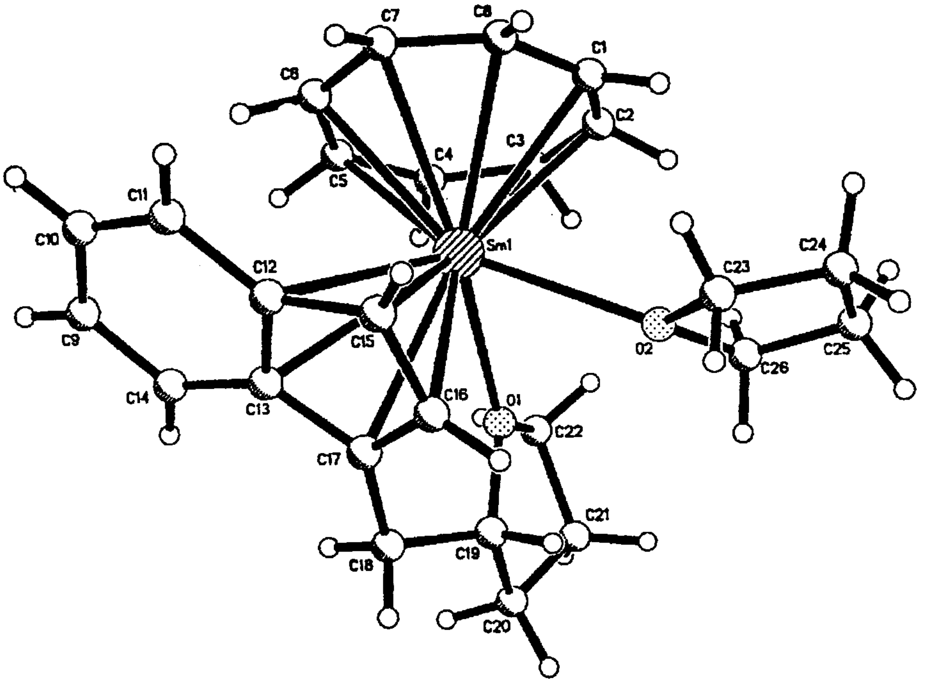
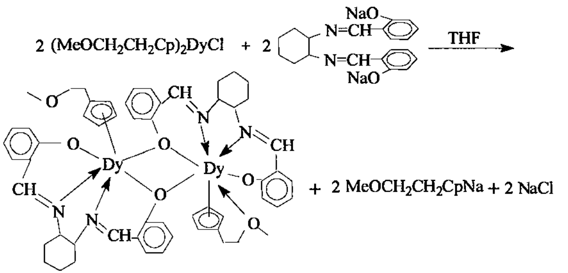


Fig. 4. Molecular structure of **13**.



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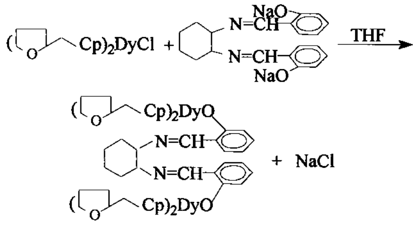
Scheme 6.



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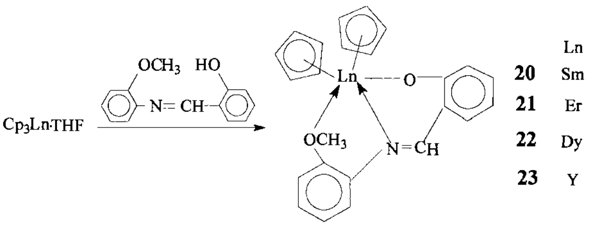
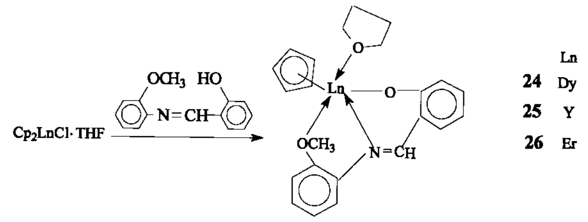
Scheme 7.



Scheme 8.



Scheme 9.

The coordination environment of these late lanthanide metal complexes is satisfied by intramolecular coordination bonds from oxygen and nitrogen atoms of the ligand to the lanthanide metal center.

This indicates that an intramolecular coordination bond is more easily formed yielding monomeric structures than an intermolecular one.

4. Conclusion

Our recent investigation in the field of intramolecular coordination of substituted lanthanocenes and other metallocene complexes has demonstrated that such co-

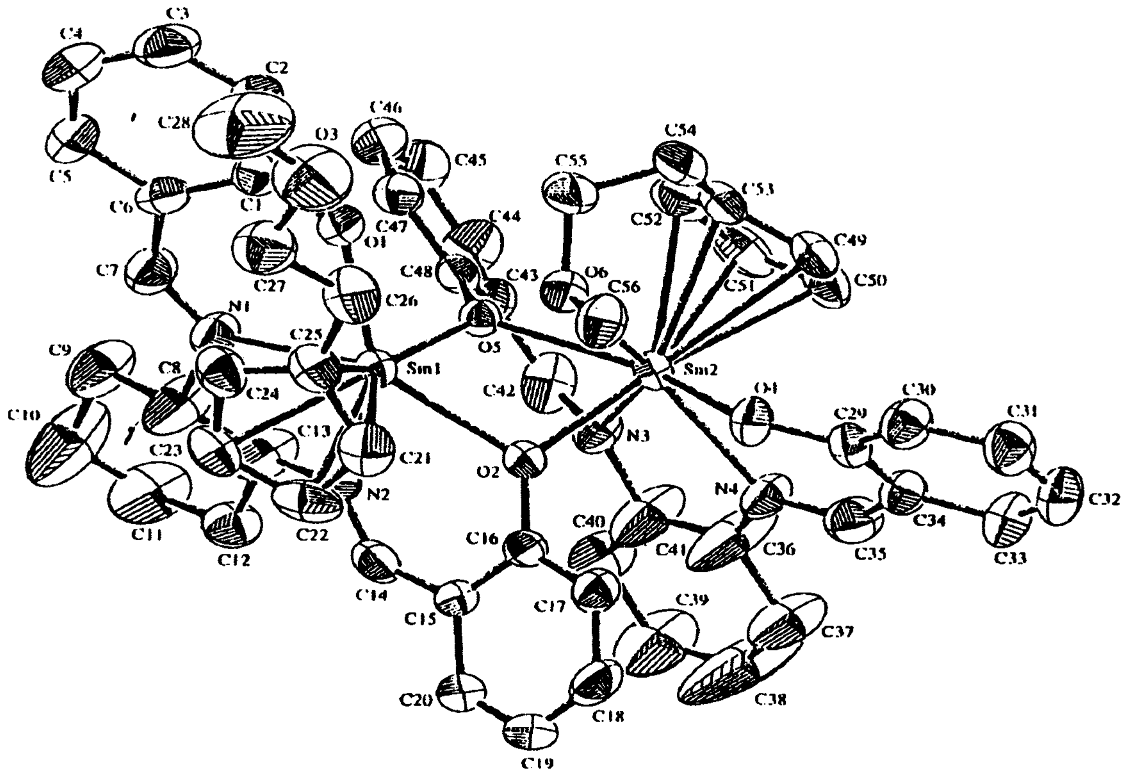


Fig. 5. Molecular structure of **16**.

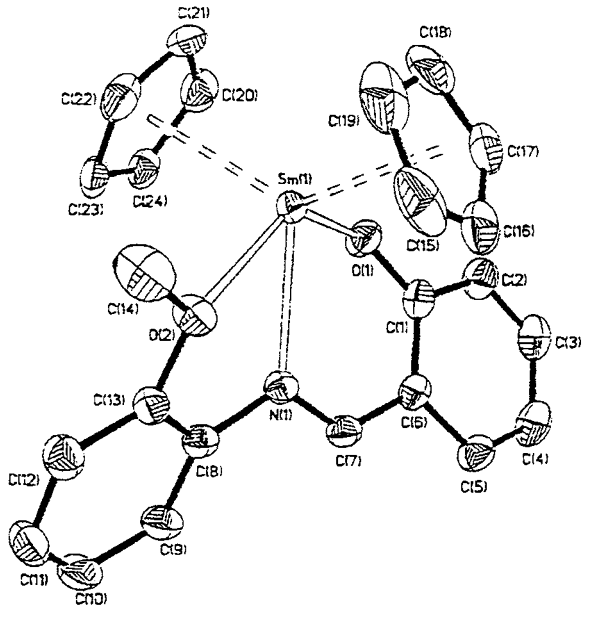


Fig. 6. Molecular structure of **20**.

ordination is one of most important factors in homogeneous organometallic catalysis. In many cases intramolecular coordination in catalysts not only influences the catalytic activity, but also controls the reaction path, and thus the selectivity. Recently we have also studied the catalytic behavior of substituted lanthanonene complexes on the polymerization of olefins and polar monomers [7–10]. A systematic study on molecular structure/catalyst property relationship in coordination catalysis is now in progress.

Acknowledgements

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