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Fluorine/phenyl chelated boron complexes: Synthesis, fluorescence properties and catalyst for transfer hydrogenation of aromatic ketones

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ABSTRACT

The synthesis of salen/salan ligands (**L_1** and **L_2**) and their fluorine/phenyl chelated boron complexes [**$L_{(1,2)}BF_2$**] or [**$L_{(1,2)}BPh_2$**] is described in this paper. The fluorine/phenyl chelated boron complexes were synthesized from the reaction of $BF_3{\cdot}OEt_2$ or BPh_3 with the corresponding ligands in different solvent. The boron complexes display high stability and can be handled in air due to the presence of coordinative B ← N and covalent B–O bonds in their structures. The salen/salan ligands (designated as salan, a saturated version of the corresponding salen ligands) and their fluorine/phenyl chelated boron complexes have been characterized by ^1H, ^{13}C NMR and ^{19}F NMR spectra, elemental analysis, FT-IR spectra, UV–vis spectra, LC–MS spectra, melting point and fluorescence spectroscopy. The fluorescence efficiencies of BF_2–chelate boron complexes are greatly improved compared to those of the BPh_2–chelate boron analogs based on the same salen/salan ligands, probably due to the enhanced conjugation degree of the diphenyl boron chelation, which can effectively prevent molecular aggregation. The boron complexes [**$L_{(1,2)}BF_2$**] or [**$L_{(1,2)}BPh_2$**] were also applied to the transfer hydrogenation of aromatic ketones to the corresponding alcohol derivatives in the presence of *iso*-PrOH as the hydrogen source. Catalytic studies showed that all complexes are good catalytic precursors for transfer hydrogenation of aryl alkyl ketones in 0.1 M *iso*-PrOH solution. This transfer hydrogenation is characterized by low reversibility under these conditions.

1. Introduction

The fluorine/phenyl chelated boron complexes, one of the most important types of fluorescent dyes, have been extensively studied. In recent years, fluorescent materials of organic fluorine or phenyl boron complexes continue to be developed because of their utilities in many various fields of current research, and the many important applications in science and technology. Among boron compounds, as the most well-known and having excellent fluorescent properties is borondipyrromethenes (BODIPYs) with *N*,*N*-bidentate ligands [1–8]. These types of compounds are widely used as chemosensors [9,10], organic light-emitting diodes (OLEDs) [11,12], electron-transport materials [13,14], sensitizers in solar cells [15,16], nonlinear optics [17,18] as well as antibacterial properties [19] and hydrogen-transfer catalysts [20–22]. Therefore, in recent years, design and synthesis of novel boron compounds to explore their broad applications have attracted much attention. Among boron compounds, three main types of BF_2/BPh_2 chelated boron complexes are classified as *N*,*N*-bidentate, *N*,*O*-bidentate and *O*,*O*-bidentate compounds. Compared with three-coordinated boron complexes, which require bulky substituents (such as mesityl or other groups) to stabilize four-coordinated boron complexes are in general stable and can be obtained readily [23]. Also, it is known that boron is strongly electrophilic by virtue of its tendency to fill the vacant orbital and complete the octet, so in contrast to organometallic compounds, organoboron compounds are in general more stable due to the increased covalency of B–O and B ← N bonds [24]

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Catalytic transfer hydrogenation is an effective method for the reduction of ketones and aldehydes to alcohols under mild reaction conditions [25–27]. Transfer hydrogenation with the aid of a stable hydrogen donor is a useful alternative method for catalytic hydrogenation by molecular hydrogen [28,29]. In transfer hydrogenation, organic molecules such as primary and secondary alcohols [30] or formic acid and its salts [31] have been employed as the hydrogen source. The use of the hydrogen donor has some advantages over the use of molecular hydrogen since it avoids risks and constraint associated with hydrogen gas as well as the necessity for pressure vessels and other equipments. A number of transition metal complexes are known to be catalyzing hydrogen transfer from an alcohol to a ketone [32]. In the mid 1920s, Meerwein, Verley and Ponndorf (MPV-reaction), respectively, reported the first examples of hydrogen transfer from an alcohol to a ketone [33–35]. The first example of a transition metal-catalyzed transfer hydrogenation, employing an Ir-DMSO-complex, was presented in 1967 by Trocha-Grimshaw and Henbest [36]. Recently, Ikariya and coworkers have reviewed bifunctional transition metal-based molecular catalysts for transfer hydrogenation of ketones under different experimental conditions [37].

Some catalyst systems are expensive because synthesis of compounds requires many chemical synthetic steps. Hence, there is a need for economic, relatively mild and environmentally friendly catalyst system. So, we preferred the BF_2/BPh_2 chelated boron complexes as catalyst for transfer hydrogenation of aromatic ketones. As far as we know, there are few reports on BF_2/BPh_2 chelated boron complexes containing salen/salan ligands have been used as catalysts for transfer hydrogenation of aromatic ketones. Compounds of this type are considerably interesting for their simple synthesis, easily accessibility and good luminescence and fluorescence properties. Interestingly, a few of *N*,*O*-bidentate BF_2/BPh_2 chelated boron compounds are the efficient hydrogen-transfer catalysts. In this work, salen/salan ligands were selected because they can function as chelating ligands upon treatment with a boron compounds such as BPh_3 or $BF_3{\cdot}OEt_2$ conjugated π-systems that was good for studying the catalytic transfer hydrogenation of aromatic ketones. As a continuation of our previously reported work, we have synthesized BF_2/BPh_2 chelated boron complexes containing electron withdrawing or electron-donating substituents on their ligands. We show that salen/salan ligands (**L₁** and **L₂**) and their boron complexes [$\mathbf{L_{(1,2)}BF_2}$] or [$\mathbf{L_{(1,2)}BPh_2}$] display attractive fluorescence and catalytic activity.

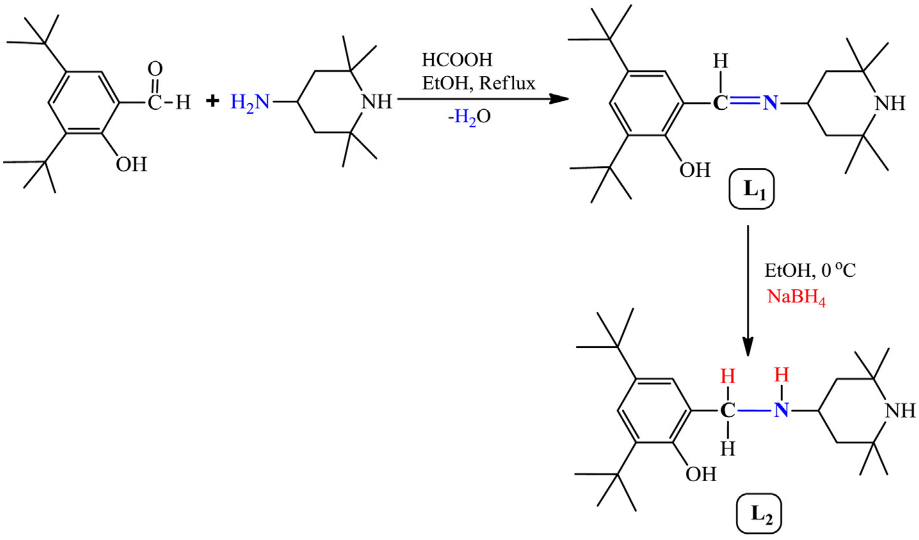
2. Results and discussion

2.1. Synthesis of compounds

As summarized in Scheme 1, the salen ligand (**L₁**) was prepared in moderate yield by refluxing the 1:1 molar ratio of 3,5-di-*tert*-butylsalicylaldehyde and 4-amino-2,2,6,6-tetramethylpiperidine in absolute ethanol and in the presence of 3-4 drops of formic acide as catalyst. The salan ligand (**L₂**) has been prepared by reduction of the corresponding salen ligand (**L₁**) with $NaBH_4$ and in EtOH solution. Both salen ligand (**L₁**) and salan ligand (**L₂**) are obtained in good yield, 86 and 78%, respectively, as yellow or white solid. The satisfactory spectroscopic results were acquired for both salen ligand (**L₁**) and salan ligand (**L₂**). As anticipated, treatment of the salen ligand (**L₁**) or salan ligand (**L₂**), with an excess of boron reagent $BF_3.OEt_2$ in anhydrous benzene and in the presence of Et_3N or with an excess of boron reagent BPh_3 in anhydrous toluene under N_2 atmosphere afforded the boron complexes [$\mathbf{L_{(1,2)}BF_2}$] or [$\mathbf{L_{(1,2)}BPh_2}$], respectively as outlined in Scheme 2. Both BF_2-chelated boron complexes [$\mathbf{L_{(1,2)}BF_2}$] and BPh_2-chelated ones [$\mathbf{L_{(1,2)}BPh_2}$] are obtained in good yield (72–65%) as yellow or white solids after purification by column chromatography. Again, the satisfactory spectroscopic results were acquired for all boron complexes. We chose to employ the the salen ligand (**L₁**) and salan ligand (**L₂**) and their boron complexes [$\mathbf{L_{(1,2)}BF_2}$] or [$\mathbf{L_{(1,2)}BPh_2}$] for several reasons: they are (1) easily prepared, (2) scarcely seen in literature, (3) to the best of our knowledge, there are few reports that boron complexes containing the salen/salan ligands used as catalyst for the transfer hydrogenation of aromatic and (4) the salen/salan ligands bind strongly to boron ions. The salen ligand (**L₁**) and salan ligand (**L₂**) and their boron complexes [$\mathbf{L_{(1,2)}BF_2}$] or [$\mathbf{L_{(1,2)}BPh_2}$] are stable in different solutions and in the solid state upon extended exposure to air. This high chemical stability in this class of compounds is attributed to the bidentate chelation of the salen ligand (**L₁**) and salan ligand (**L₂**) to the boron center. Although much effort was made to obtain single crystals of the compounds, we failed to do so. However, the ^1H, ^{13}C NMR and ^{19}F NMR spectra, elemental analysis, FT-IR spectra, UV–vis spectra, LC–MS spectra, melting points and fluorescence spectra support to the proposed structures.

2.2. Spectroscopic characterization

The ^1H and ^{13}C NMR of the salen (**L₁**) and salan (**L₂**) ligands and their fluorine/phenyl boron complexes [$\mathbf{L_{(1,2)}BF_2}$] and [$\mathbf{L_{(1,2)}BPh_2}$]



Scheme 1. Synthesis of the salen/salan ligands (**L₁** and **L₂**).