



Short communication

Catechol-type ligand containing new modular design dioxaborinane compounds: Use in the transfer hydrogenation of various ketones

Ahmet Kilic^{a,*}, İbrahim Halil Kaya^a, Ismail Ozaslan^a, Murat Aydemir^{b,**}, Feyyaz Durap^b^a Harran University, Chemistry Department, Art and Science Faculty, 63290 Sanliurfa, Turkey^b Dicle University, Chemistry Department, Science Faculty, 21280 Diyarbakir, Turkey

ARTICLE INFO

Keywords:

Catechol-type ligands
Dioxaborinanes
Spectroscopy
Transfer hydrogenation
Ketones

ABSTRACT

A novel class of tricoordinate dioxaborinane compounds, which have the general formula $[B_1(L_{1-5})]$ and $[B_2(L_{1-5})]$, were designed and synthesized by the corresponding catechol-type ligands (L_1-L_5) at ambient temperature. All the new compounds were fully characterized by NMR (1H , ^{13}C , and ^{11}B), FT-IR, UV-vis, LC-MS spectroscopy, and melting point analysis and microanalysis. The dioxaborinane $[B_1(L_{1-5})]$ and $[B_2(L_{1-5})]$ compounds were investigated as catalyst for the transfer hydrogenation of various ketones under suitable conditions. Particularly, it was proved that the ferrocene-based dioxaborinane $[B_1(L_{1-5})]$ molecules can afford an efficient catalytic conversion compared to corresponding 3,5-bis(trifluoromethyl)phenyl-based $[B_2(L_{1-5})]$ dioxaborinanes in transfer hydrogenation catalytic studies.

1. Introduction

Boron compounds (reagents) have become an important part of today's fine chemical industry for the preparation of highly complex functionalized molecules. Commercially available boron compounds are widely utilized in pharmaceutical polymer and electronics manufacturing [1]. Boron complexes are versatile compounds that are commonly used as regio-, chemo-, and stereoselective reducing agents of a variety of group functionalities such as aldehydes, ketones, amides, and olefins [2]. Over the past decades, environmentally friendly tri and tetracoordinate boron compounds have attracted considerable attention because of their low cytotoxicity, electronic structure, easy preparation, low cost, and air-stable properties [3]. Furthermore, boron and related compounds have important applications in many fields such as catalysis; pharmacology; toxicology; agriculture; and textile, glass, ceramic, cosmetic, energy, and construction industries, as well as in communication tool manufacturing and detergent production [4]. In contrast to tetracoordinate boron compounds, tricoordinate dioxaborinanes formed from the catechol-type ligands and boronic acid interactions have an empty p-orbital, which makes them strong electrophiles and Lewis acids, and the two covalent B–O bonds make the structure stable in air. Because of their unique features, tricoordinate dioxaborinanes are one of the most widely studied groups [5–7].

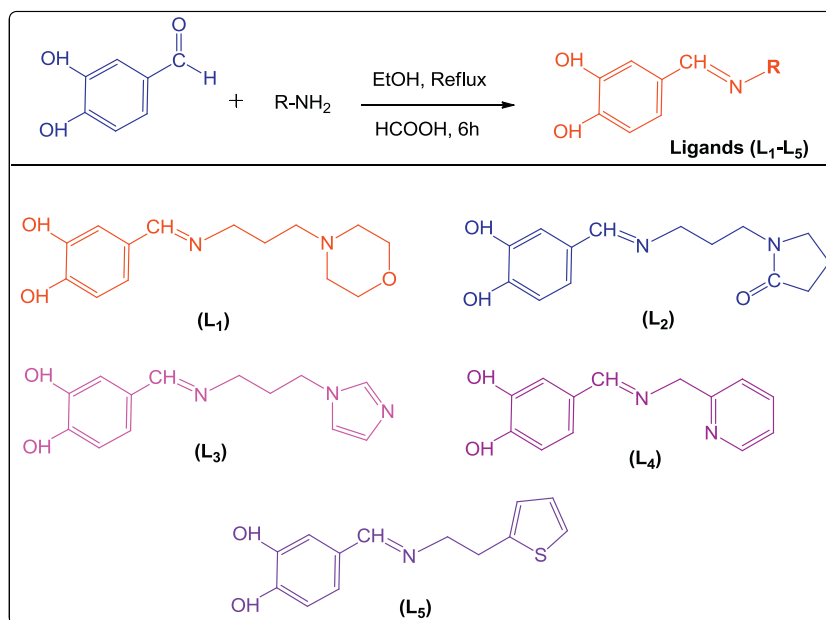
Two types of hydrogenation methods, namely the transfer hydrogenation and direct hydrogenation, have been widely used. Because of

the absence of molecular hydrogen, the transfer hydrogenation method, in which formic acid and its salts or secondary alcohols have been used as hydrogen sources, is more attractive and safer than direct the hydrogenation method [8–10]. Nowadays, several transition metals such as Au, Pt, Pd, Ir, Rh and Ru are often used as catalysts in transfer hydrogenation with high activity [11–13]. However, these metals are usually not preferred for the transfer hydrogenation, because they are expensive and cause environmental pollution. Instead of them, the development of an effective and cheaper catalyst for the transfer hydrogenation of ketones is one of the main targets for the scientists [1,2]. Boron in its tricoordinate dioxaborinane molecules is mainly interesting because it is considerably more effective and stable than tetracoordinate boron complexes for the transfer hydrogenation of ketones as catalysts [1,2]. To the best of our knowledge, there is no report on the use of tricoordinate dioxaborinane derivatives in the transfer hydrogenation. In view of the promising results, tricoordinate dioxaborinane derivatives were shown to be efficient homogeneous hydrogenation catalysts toward various substrates, and these catalysts would be a valuable material for the transfer hydrogenation. In this study, various techniques such as NMR (1H , ^{13}C , and ^{11}B), FT-IR, UV-vis, LC-MS spectroscopy, and melting point and elemental analyses were used to characterize these compounds.

* Corresponding author at: Harran University, Chemistry Department, TR-63190 Sanliurfa, Turkey.

** Corresponding author.

E-mail addresses: kilica63@harran.edu.tr (A. Kilic), aydemir@dicle.edu.tr (M. Aydemir).



Scheme 1. Synthesis of the catechol-type ligands (L₁-L₅).

2. Experimental

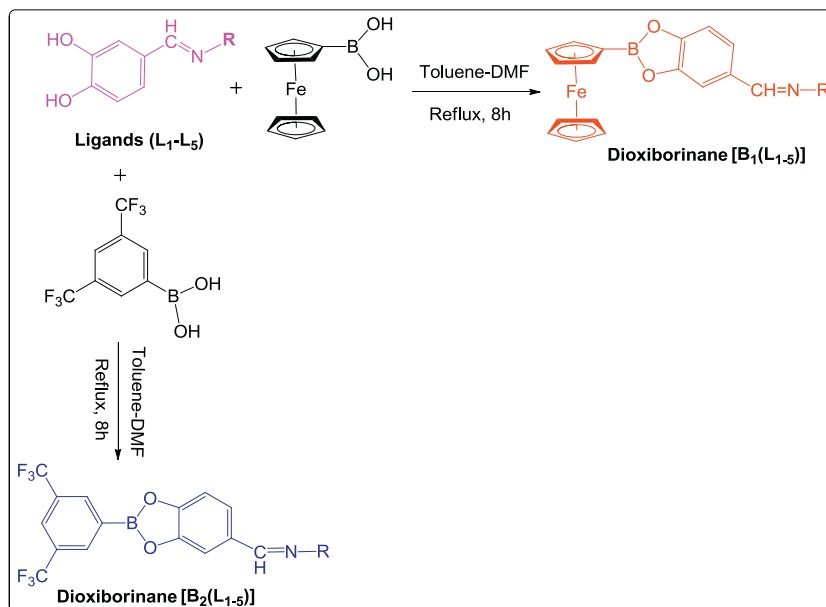
The information about the chemicals and devices used in this study is given in the supplementary information. The synthesis and spectroscopic results are also given as supplementary information for the new catechol-type ligands (L₁-L₅) and their tricoordinate dioxaborinane [B₁(L₁₋₅)] and [B₂(L₁₋₅)] compounds.

3. Results and discussion

The dark brown catechol-type ligands (L₁-L₅) were prepared in EtOH with a yield in the range 83–78%, as shown in Scheme 1. The dioxaborinane [B₁(L₁₋₅)] and [B₂(L₁₋₅)] compounds were obtained in toluene and DMF at reflux temperature over 8 h with a yield up to 78% (Scheme 2).

3.1. Characterization of the catechol-type ligands and their dioxaborinane derivatives

The bands in the range 3553–2329 cm⁻¹ were due to the stretching vibrations of intermolecular H-bond $\nu(\text{O}-\text{H}\cdots\text{OH})$ in 1,2-dihydroxy groups of catechol-type ligands, which disappeared in the FT-IR spectra of dioxaborinane [B₁(L₁₋₅)] and [B₂(L₁₋₅)] complexes (Fig. S1–S3), as expected. These results show the deprotonation of the 1,2-dihydroxy moiety owing to the coordination and confirm the formation of the dioxaborinane derivatives (Fig. S1–S3). In addition, the bands at 1650–1641 cm⁻¹ for catechol-type ligands and at 1659–1644 cm⁻¹ for dioxaborinane derivatives were due to the stretching vibrations of azomethine groups (HC=N) [14]. Furthermore, compared to the catechol-type ligands, the stretching peak of azomethine groups $\nu(\text{HC}=\text{N})$ of dioxaborinanes, [B₁(L₁₋₅)] and [B₂(L₁₋₅)], exhibited a higher



Scheme 2. Synthesis of the dioxaborinane [B₁(L₁₋₅)] and [B₂(L₁₋₅)] complexes.

Download English Version:

<https://daneshyari.com/en/article/6502966>

Download Persian Version:

<https://daneshyari.com/article/6502966>

[Daneshyari.com](https://daneshyari.com)