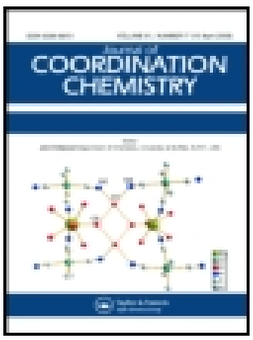

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Developments in transfer hydrogenations of aromatic ketones catalyzed by boron compounds

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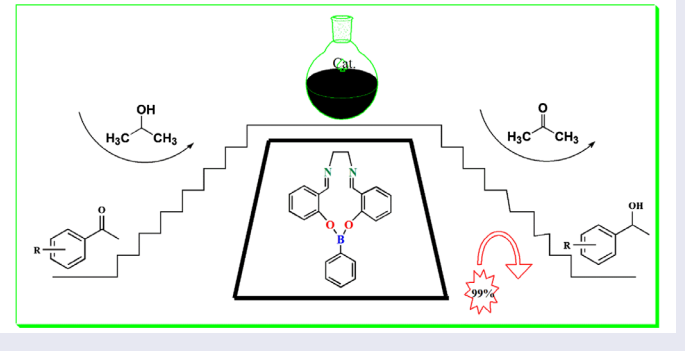
ABSTRACT

Boron complexes **BL1** and **BL2** were prepared from O-donor ligands, 2,2′-(1*E*,1′*E*)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(methane-1-yl-1-ylidene)diphenol (**L1**) and 2,2′-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methane-1-yl-1-ylidene)diphenol (**L2**). The complexes were fully characterized by ^{1}H and ^{13}C NMR, LC-MS/MS, TGA/DTA, UV-Vis, elemental analysis, SEM, and FTIR. The transfer hydrogenation of acetophenone derivatives was investigated by the boron complexes in the presence of *iso*PrOH, as the hydrogen source, under basic condition with NaOH. The results showed that the boron complexes were promising catalytic precursors for transfer hydrogenation of aromatic ketones in 0.1 M *iso*PrOH solution (up to 99%). Both steric and electronic factors of this class of molecules had a significant impact on the catalytic properties.



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Homogeneous catalysis; boron complexes; spectroscopy; aromatic ketones; catalysis; transfer hydrogenation

1. Introduction

Boron and its derivatives are used in areas from agriculture to industry, such as glass, ceramic, textile, automotive, electronics and nuclear industry, medicine, pharmaceutical and cosmetic

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industry, energy, construction industry, and communication tools and detergent [1, 2]. Due to the widespread use of boron compounds, the synthesis and application of these systems in science and technology have attracted attention. Boron complexes are stable and can be handled in air due to the presence of B←N and B–O bonds in the structures. There are three main types of BF_2/BPh_2 chelated boron complexes, which can be classified as *N*,*N*-bidentate, *N*,*O*-bidentate, and *O*,*O*-bidentate compounds [3–6].

Catalytic transfer hydrogenation with a stable hydrogen donor is a useful alternative method for catalytic hydrogenation employed with molecular hydrogen for reduction of ketones [7–10]. In the process of transfer hydrogenation, molecules such as secondary alcohols [11, 12] or formic acid and its salts [13] have been used as hydrogen sources. The hydrogen donor has some advantages over use of molecular hydrogen, preventing the risks and constraints associated with hydrogen gas as well as the necessity for pressure vessels and other equipment [14–17]. Although a number of transition metals have been used for hydrogenation reactions, there have been continuous studies to explore new metals for transfer hydrogenation reactions with excellent performance as well as cost advantages compared to the other hydrogenation metals, such as ruthenium, rhodium, and iridium [18–21].

We have reported on the synthesis and applications of a number of modified boron catalysts for transfer hydrogenation [6, 7]. Boron complexes were shown to be efficient homogeneous hydrogenation catalysts towards various substrates. Derivatization of boron-based catalysts would be important for further development of boron-catalyzed transfer hydrogenation reactions. It is our particular interest to design new ligand systems with different spacers, control the electronic attributes at boron [22–24] and investigate their coordination chemistry. In the present work, we report the synthesis and characterization of boron complexes by ^{1}H NMR (Bruker AV-400 MHz), ^{13}C NMR (Bruker AV-400 MHz), FTIR (Perkin Elmer Spectrum 100)), UV-Vis (Perkin Elmer Lambda 25), elemental analysis (Costech ECS 4010), LC-MS (Shimadzu LC/MS 8040), and their catalytic evaluation in transfer hydrogenation for aromatic ketones.

2. Experimental

2.1. Synthesis of L1 and L2

2,2′-(1E,1′E)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol (**L1**) and 2,2′-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methane-1-yl-1-ylidene)diphenol (**L2**) were synthesized according to literature procedures [8, 9, 25–27] (figure 1).

2.2. Synthesis of BL1 and BL2

2.2.1. General procedure

Ligand (1 mmol) was dissolved in 20 mL toluene in a round-bottom flask. Then an equivalent amount of the boron derivative which approximately corresponds to 1 mmol was added, after which the ligand solution turned completely clear. The reaction mixture was stirred at 110°C for 5 h . Different gradations of yellow precipitates were filtered, washed with excess solvent and dried in a ventilated oven. The proposed reactions for formation of **BL1** and **BL2** are depicted in figures 2 and 3 [28].

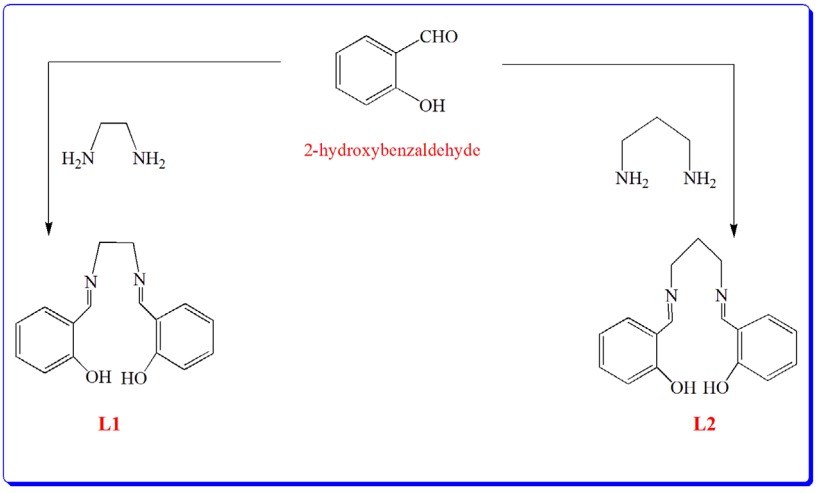


Figure 1. The synthesis of 2,2′-(1E,1′E)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene) diphenol (**L1**) and 2,2′-(propane-1,3-diyl bis(azan-1-yl-1-ylidene)) bis(methane-1-yl-1-ylidene)diphenol (**L2**).

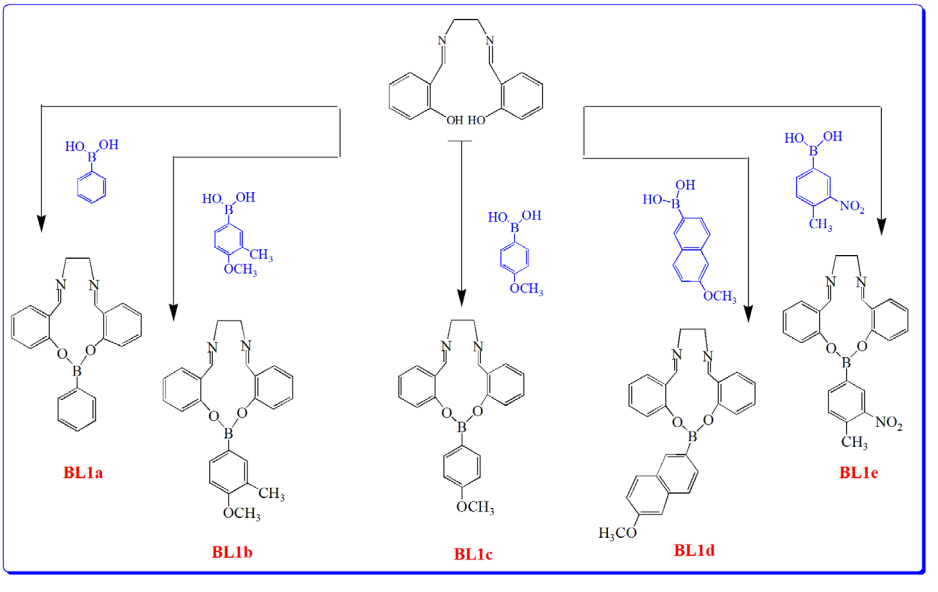


Figure 2. Proposed reactions of boron derivatives with **BL1**.

2.2.1.1. Synthesis of BL1a, BL1b, BL1c, BL1d, and BL1e. The compounds were synthesized according to the procedure in the previous section. All reactions were conducted under an atmosphere of argon. The structures were determined by various instrumentation techniques (figure 2). **BL1a**: ^{1}H NMR (ppm, DMSO-d_6): δ = 8.57 (br, 2H, C<u>H</u>=N), δ = 6.84–7.58 (m, 13H, Ar–<u>H</u>), and δ = 3.72 (t, 4H, J = 4.6 Hz, –C<u>H</u>$_2$–C<u>H</u>$_2$–), FTIR-ATR (cm^{-1}): 1316 ν(B–O), 1058 and 1027 ν(B–C), 876 ν(B–Ph), 3046 ν(Ar–CH), 2936 ν(Aliph–CH), 1636 ν(Ar–CH=CH), 1608 ν(C=N),

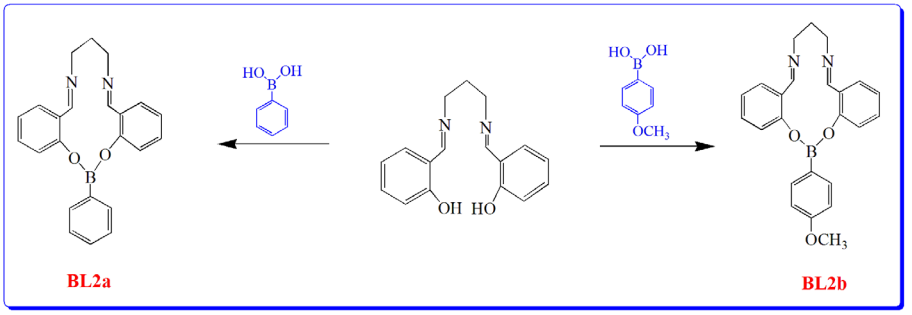


Figure 3. Proposed reactions of boron derivatives with **BL2**.

and 1151 *v*(Ar–O). *m/z*: 355 [M + H$^+$] ***C22H19N2O2B*** (M_W: 354.15 g mol^{-1} (exact mass)). UV-Vis (nm): $\lambda_1 = 216$ ($\varepsilon = 2.16 \times 10^3$), $\lambda_2 = 279$ ($\varepsilon = 2.79 \times 10^3$), $\lambda_3 = 330$ ($\varepsilon = 3.30 \times 10^3$), and $\lambda_4 = 376$ ($\varepsilon = 3.76 \times 10^3$) (in acetone:ethanol (1 : 1)). Elemental analysis: Found (Calculated) C 74.92 (75.02), H 5.67 (5.75), and N 7.52 (7.61) %. **BL1b**: ^{1}H NMR (ppm, DMSO-d_6): $\delta = 8.57$ (br, 2H, C**H**=N), $\delta = 6.52$–7.60 (m, 11H, Ar–**H**), $\delta = 3.71$ (t, 4H, $J = 4.5$ Hz, –C**H$_2$**–C**H$_2$**–), $\delta = 3.64$ (s, 3H, Ar–OC**H$_3$**), and $\delta = 1.74$ (br, 3H, Ar–C**H$_3$**). FTIR-ATR (cm^{-1}): 1312 *v*(B–O), 1059 and 1027 *v*(B–C), 852 *v*(B–Ph), 3001 *v*(Ar–CH), 2941 *v*(Aliph-CH), 1460 *v*(Ar–CH$_3$), 1608 *v*(C=N), 1163, and 1152 *v*(Ar–O). *m/z*: 399 [M + H$^+$] ***C24H23N2O3B*** (M_W: 398.18 g mol^{-1} (exact mass)). UV-Vis (nm): $\lambda_1 = 308$ ($\varepsilon = 3.08 \times 10^3$), $\lambda_2 = 314$ ($\varepsilon = 3.14 \times 10^3$), $\lambda_3 = 328$ ($\varepsilon = 3.28 \times 10^3$), and $\lambda_4 = 368$ ($\varepsilon = 3.68 \times 10^3$) (in acetone). Elemental analysis: Found (Calculated) C 71.29 (71.38), H 4.05 (4.12), and N 5.98 (6.03) %. **BL1c**: ^{1}H NMR (ppm, DMSO-d_6): $\delta = 8.62$ (br, 2H, C**H**=N), $\delta = 6.52$–7.58 (m, 12H, Ar–**H**), $\delta = 3.77$ (s, 3H, Ar–OC**H$_3$**), and $\delta = 3.40$ (t, 4H, $J = 4.5$ Hz, –C**H$_2$**–C**H$_2$**–). FTIR-ATR (cm^{-1}): 1363 *v*(B–O), 1061 and 1024 *v*(B–C), 758 *v*(B–Ph), 3047 *v*(Ar–CH), 2990 *v*(–CH$_2$–CH$_2$–), 1636 *v*(Ar–CH=CH–), 1607 *v*(C=N), and 1151 *v*(Ar–O). *m/z*: 385 [M + H$^+$] ***C23H21N2O3B*** (M_W: 384.16 g mol^{-1} (exact mass)). UV-Vis (nm): $\lambda_1 = 216$ ($\varepsilon = 2.16 \times 10^3$), $\lambda_2 = 290$ ($\varepsilon = 2.90 \times 10^3$), and $\lambda_3 = 339$ ($\varepsilon = 3.39 \times 10^3$) (in acetone:methanol (1 : 1)). Elemental analysis: Found (Calculated) C 69.92 (70.09), H 4.07 (4.11), and N 5.51 (5.59) %. **BL1d**: ^{1}H NMR (ppm, DMSO-d$_6$): $\delta = 8.61$ (br, 2H, C**H**=N), $\delta = 6.92$–7.68 (m, 14H, Ar–**H**), $\delta = 3.81$ (s, 3H, Naph–OC**H$_3$**), and $\delta = 3.57$ (t, 4H, $J = 4.6$ Hz, –C**H$_2$**–C**H$_2$**–). FTIR-ATR (cm^{-1}): 1382 *v*(B–O), 1061 and 1027 *v*(B–C), 752 *v*(B–Ph), 3042 *v*(Ar–CH), 2993 *v*(–C**H$_2$**–C**H$_2$**–), 1632 *v*(Ar–CH=CH–), 1607 *v*(C=N), and 1150 *v*(Ar–O). *m/z*: 435 [M + H$^+$] ***C27H23N2O3B*** (M_W: 434.18 g mol^{-1} (exact mass)). UV-Vis (nm): $\lambda_1 = 311$ ($\varepsilon = 3.11 \times 10^3$), $\lambda_2 = 315$ ($\varepsilon = 3.15 \times 10^3$), $\lambda_3 = 323$ ($\varepsilon = 3.23 \times 10^3$), and $\lambda_4 = 346$ ($\varepsilon = 3.46 \times 10^3$) (in acetone). Elemental analysis: Found (Calculated) C 74.60 (74.67), H 4.30 (4.34), and N 4.98 (5.04) %. **BL1e**: ^{1}H NMR (ppm, DMSO-d$_6$): $\delta = 8.64$ (br, 2H, C**H**=N), $\delta = 6.67$–7.97 (m, 11H, Ar–**H**), $\delta = 3.70$ (t, 4H, $J = 4.5$ Hz, –C**H$_2$**–C**H$_2$**–), and $\delta = 2.34$ (br, 3H, Ar–C**H$_3$**). FTIR-ATR (cm^{-1}): 1349 *v*(B–O), 1074 and 1027 *v*(B–C), 751 *v*(B–Ph), 3046 *v*(Ar–CH), 2960 *v*(–CH$_2$–CH$_2$–), 1611 *v*(C=N), 1633 *v*(Ar–CH=CH–), and 1152 *v*(Ar–O). *m/z*: 414 [M + H$^+$] ***C23H20N3O4B*** (M_W: 413.15 g mol^{-1} (exact mass)). UV-Vis (nm): $\lambda_1 = 310$ ($\varepsilon = 3.10 \times 10^3$), $\lambda_2 = 319$ ($\varepsilon = 3.19 \times 10^3$), $\lambda_3 = 322$ ($\varepsilon = 3.22 \times 10^3$), and $\lambda_4 = 355$ ($\varepsilon = 3.55 \times 10^3$) (in acetone). Elemental analysis: Found (Calculated) C 63.77 (63.85), H 3.13 (3.18), and N 10.03 (10.17) %.

2.2.1.2. Synthesis of BL2a and BL2b. The process mentioned in Section 2.2.1 was applied for the synthesis. The obtained spectral information is summarized below:

BL2a: ^{1}H NMR (ppm, DMSO-d_6): δ = 8.54 (br, 2H, C**H**=N), δ = 6.35–7.69 (m, 13H, Ar–**H**), δ = 3.78 (m, –C**H$_2$**–CH$_2$–C**H$_2$**–), and δ = 3.51 (m, 2H, –CH$_2$–C**H$_2$**–CH$_2$–). FTIR-ATR (cm^{-1}): 1346 ν(B–O), 1065 and 1028 ν(B–C), 753 ν(B–Ph), 3064, 3046 ν(Ar–CH), 2932 ν(–CH$_2$–CH$_2$–CH$_2$-), 1608 ν(C=N), 1643 ν(Ar–CH=CH–), and 1152 ν(Ar–O). *m/z*: 369 [M + H$^+$] ***C23H21N2O2B*** (M$_W$: 368.17 g mol^{-1} (exact mass)). UV-Vis (nm): λ_1 = 313 ($\varepsilon = 3.13 \times 10^3$), λ_2 = 320 ($\varepsilon = 3.20 \times 10^3$), λ_3 = 325 ($\varepsilon = 3.25 \times 10^3$), and λ_4 = 370 ($\varepsilon = 3.7 \times 10^3$) (in acetone). Elemental analysis: Found (Calculated) C 74.97 (75.02), H 5.69 (5.75), and N 7.55 (7.61) %. **BL2b**: ^{1}H NMR (ppm, DMSO-d$_6$): δ = 8.49 (br, 2H, C**H**=N), δ = 6.33–7.89 (m, 12H, Ar–**H**), 3.79 (m, 4H, –C**H$_2$**–CH$_2$–C**H$_2$**–), δ = 3.70 (s, 3H, Ar–OC**H$_3$**), and δ = 3.53 (m, 2H, –CH$_2$–C**H$_2$**–CH$_2$–). FTIR-ATR (cm^{-1}): 1359 ν(B–O), 1068, 1028 ν(B–C), 746 ν(B–Ph), 3054 ν(Ar–CH), 2949 ν(–CH$_2$–CH$_2$–CH$_2$–), 1612 ν(C=N), 1641 ν(Ar–CH=CH–), and 1150 ν(Ar–O). *m/z*: 399 [M + H$^+$] ***C24H23N2O3B*** (M$_W$: 398.18 g mol^{-1} (exact mass)). UV-Vis (nm): λ_1 = 253 ($\varepsilon = 2.53 \times 10^3$), λ_2 = 277 ($\varepsilon = 2.77 \times 10^3$), λ_3 = 352 ($\varepsilon = 3.52 \times 10^3$) (solvent: DMSO). Elemental analysis: Found (Calculated) C 71.27 (71.38), H 4.60 (4.68), and N 5.95 (6.03) % [29].

2.3. Transfer hydrogenation of acetophenone by BL1 and BL2

The common procedure for transfer hydrogenation: particular amount of (0.04 mmol) boron complex solutions, NaOH (0.05 mmol), and acetophenone (5 mmol) in degassed *iso*PrOH (5 mL) were refluxed at 82 °C. Samples from the mixture were taken, diluted with acetone and checked for conversion at different time periods. The products were compared with the unreacted acetophenone. GC analyses were applied with a Shimadzu 2010 Plus Gas Chromatograph having a capillary column (95% dimethyl siloxane and 5% biphenyl) (30 m × 0.32 mm × 0.25 µm). The adjusted GC parameters were: initial temperature, 50 °C; solvent delay, 4.48 min; initial time, hold 1 min; final temperature, 270 °C; hold 5 min; temperature ramp 15 °C min^{-1}; injector port temperature, 200 °C; detector temperature, 200 °C, final time, 20.67 min, and injection volume, 1.5 µL.

3. Results and discussion

3.1. Spectral identification

The molecular structures of **L1** and **L2** were reported by previous studies [8, 9, 30–32] which are consistent with what we find (figure 1).

The boron complexes have been synthesized by the condensation of **L1** and **L2** and boron precursors, and they were found to be stable in air and not hygroscopic. ^{1}H NMR spectra of the compounds showed the presence of the resonances between 8.08 and 8.64 ppm corresponding to the azomethine (C**H**=N) proton [27, 33–36]. In addition to this, disappearance of resonances due to O**H** was evidence of binding of boron to oxygen. Also, formation of the desired compounds was proved by the presence of the stretching vibrations of boron with oxygen species observed from 1312 cm^{-1} to 1378 cm^{-1} and B–Ph interaction at 751–852 cm^{-1}. The exact mass spectra of all compounds applied in positive charged scan indicated the meaningful values [27, 37]. UV-Vis analysis of the boron-based molecules demonstrated $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions due to donor and aromatic rings [6, 38-40]. The surface images of the **BL1** and **BL2** series were demonstrated as bent fibers, ground rocks,

and crumbled ice pieces (figures 2 and 3), in agreement with literature data under 16,000 times magnification [41–43] (figures 2 and 3).

3.2. SEM and EDX results of compounds

Surface morphologies of boron compounds were determined under reduced pressure at different magnifications (Supplemental Material). The EDX analyses were also taken simultaneously. Qualitative elemental analyses, especially for boron, are as expected. Existence of boron supports the complexation reaction with oxygen on ligand. **BL1a** and **BL1b** have a homogenous dispersion in image. It looks like skewed fibers and single phase. **BL1c** and **BL1d** seemed like crumbled rocks with homogenous single phase features. **BL2b** has thin and long prism shapes with 5–10 µm length. **BL1e** includes a mixture of needle and ground stone shapes. However, the clearness of images for boron complexes depends on the amorphous and crystallinity percentages and also the conductivity of the materials. If the amorphous content is more than crystallinity, the sharpness of SEM images will be excellent. Furthermore, having a conductive material also improves images.

3.3. Thermal analysis

The thermal stabilities of the compounds used for catalytic investigations were investigated. The experiment was designed by TGA/DTA under nitrogen by increasing the heat temperature at 10 °C per minute. Thermograms of boron compounds showed that they are stable up to 300 °C, since there are no weight losses till that temperature. The weight losses and the corresponding heats were evaluated for **BL1** and **BL2** with endothermic and exothermic peaks in thermograms. Acetate (CH_3COO^-), water, and small amount of humidity remaining in the solid sample give endothermic peaks; combustion or decomposition of organic structures causes exothermic curves in the thermogram (Supplemental Material). All **BL1** and **BL2** series have two-step decomposition. Thermal decompositions can be summarized as: 65.78 and 9.85% (**BL1a**); 62.23 and 10.34% (**BL1b**); 51.01 and 23.99% (**BL1c**); 60.22 and 5.53% (**BL1d**); 27.88 and 23.52% (**BL1e**); 61.90 and 13.81% (**BL2a**); 74.15 and 8.10% (**BL2b**); 81.73%. These results show that they can be favorable for higher temperature catalytic reactions [28–30, 44–46].

3.4. Catalytic transfer hydrogenation of ketones

The catalytic activities of boron complexes in transfer hydrogenation of aromatic ketones by *iso*PrOH are summarized in table 1. Transfer hydrogenation reaction chart for catalytic conversions is also depicted in figure 4. The conversions to isopropyl alcohol during the reaction showed different yields due to the different substituents. **BL1a**, **BL1b**, **BL1c**, **BL1d**, **BL1e**, and **BL2a** and **BL2b** were used as catalysts for the transfer hydrogenation reaction. Recently, we reported that boron hybrid complexes are active catalysts in the reduction of aromatic ketones [47, 48]. In a typical experiment, 0.005 mmol of the boron complex and 0.5 mmol of acetophenone were added to a solution of NaOH in *iso*PrOH (0.025 mmol of NaOH in 5 mL *iso*PrOH), refluxed at 82 °C and the reaction was monitored by gas chromatography.

Table 1. Transfer hydrogenation results of acetophenone with *iso*PrOH catalyzed by **BL1a**, **BL1b**, **BL1c**, **BL1d**, **BL1e**, and **BL2a** and **BL2b**.

Entry	Catalyst	S/C/NaOH	Time	Conversion (%)[d]	TOF (h^{-1})[e]
1	**[BL_1a]**[a]	100 : 1 : 5	48 h	<3	…..
2	**[BL_1b]**[a]	100 : 1 : 5	48 h	<3	…..
3	**[BL_1c]**[a]	100 : 1 : 5	48 h	<3	…..
4	**[BL_1d]**[a]	100 : 1 : 5	48 h	<3	…..
5	**[BL_1e]**[a]	100 : 1 : 5	48 h	<3	…..
6	**[BL_2a]**[a]	100 : 1 : 5	48 h	<3	…..
7	**[BL_2b]**[a]	100 : 1 : 5	48 h	<3	…..
8	**[BL_1a]**[b]	100 : 1	72 h	<5	…..
9	**[BL_1b]**[b]	100 : 1	72 h	<5	…..
10	**[BL_1c]**[b]	100 : 1	72 h	<5	…..
11	**[BL_1d]**[b]	100 : 1	72 h	<5	…..
12	**[BL_1e]**[b]	100 : 1	72 h	<5	…..
13	**[BL_2a]**[b]	100 : 1	72 h	<5	…..
14	**[BL_2b]**[b]	100 : 1	72 h	<5	…..
15	**[BL_1a]**[c]	100 : 1 : 5	12 h	98	<10
16	**[BL_1b]**[c]	100 : 1 : 5	24 h	99	<5
17	**[BL_1c]**[c]	100 : 1 : 5	24 h	97	<5
18	**[BL_1d]**[c]	100 : 1 : 5	24 h	99	<5
19	**[BL_1e]**[c]	100 : 1 : 5	16 h	99	<10
20	**[BL_2a]**[c]	100 : 1 : 5	24 h	98	<5
21	**[BL_2b]**[c]	100 : 1 : 5	48 h	99	<5

Reaction conditions:
[a]At room temperature; acetophenone/Cat./NaOH, 100 : 1 : 5.
[b]Refluxing in *iso*-PrOH, acetophenone/Cat, 100 : 1, in the absence of base.
[c]Refluxing in *iso*-PrOH; acetophenone/Cat/NaOH, 100 : 1 : 5.
[d]Determined by GC (three independent catalytic experiments).
[e]Referred at the reaction time indicated in column; TOF = (mol product/mol Cat.) × h^{-1}.

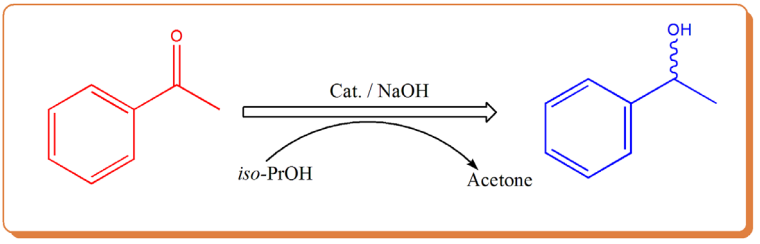


Figure 4. General reaction of transfer hydrogenation.

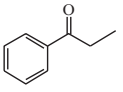
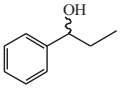
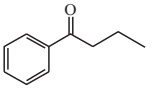
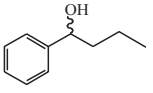
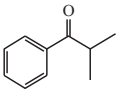
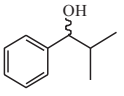
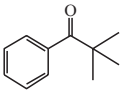
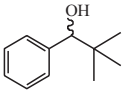
These boron hybrid complexes catalyzed the reduction of ketones to the corresponding alcohols by hydrogen transfer from *iso*PrOH. Furthermore, with a complex/NaOH ratio of 1/5, the boron complexes are active, leading to quantitative transformation of the acetophenone. The results are summarized in table 1. At room temperature no appreciable formation of 1-phenylethanol was observed (table 1, entries 1–7). As can be inferred from table 1 (entries 8–14), the precatalysts as well as NaOH are necessary to observe appreciable conversions. The base facilitates formation of boron alkoxide by abstracting proton of the alcohol and subsequently alkoxide undergoes β-elimination to give boron hydride, which is an active species in this reaction. As table 1 shows, high conversions can be achieved with **BL1a** and **BL1e** catalytic systems. The results obtained from optimization studies showed clearly that excellent conversions were achieved in reduction of acetophenone to 1-phenylethanol when **BL1a** and **BL1e** were used as catalytic precursors, with a substrate-catalyst molar ratio

Table 2. Transfer hydrogenation results for substituted acetophenones with the catalyst systems, **[BL$_1$a]** and **[BL$_1$e]**.[a]

Entry	R	Time	Conversion(%)[b]	TOF(h^{-1})[c]
Cat: [BL$_1$a]				
1	4-F	8 h	98	12
2	4-NO_2	8 h	99	12
3	4-Cl	10 h	98	10
4	4-Br	12 h	99	<10
5	2-MeO	24 h	98	<10
6	4-MeO	18 h	96	<10
Cat: [BL$_1$e]				
7	4-F	10 h	99	10
8	4-NO_2	12 h	99	<10
9	4-Cl	15 h	98	<10
10	4-Br	20 h	97	<10
11	2-MeO	30 h	98	<10
12	4-MeO	24 h	95	<10

[a]Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*PrOH (5 mL), NaOH (0.025 mmol), 82 °C, respectively, the concentration of acetophenone derivatives is 0.1 M.
[b]Purity of compounds is checked by ^{1}H NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone.
[c]TOF = (mol product/mol Cat.) × h^{-1}.

Table 3. Transfer hydrogenation results for substituted alkyl phenyl ketones with the catalyst systems, **[BL$_1$a]** and **[BL$_1$e]**.[a]

Entry	Catalyst	Time	Substrate	Product	Conversion(%)[b]	TOF(h^{-1})[c]
1	7	18 h			98	<10
2	8	26 h			98	<10
3	7	24 h			99	<10
4	8	36 h			98	<10
5	7	36 h			97	<5
6	8	48 h			98	<5
7	7	42 h			98	<5
8	8	56 h			99	<5

[a]Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), NaOH (0.025 mmol), 82 °C, respectively, the concentration of alkyl phenyl ketones is 0.1 M.
[b]Purity of compounds is checked by ^{1}H NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone.
[c]TOF = (mol product/mol Cat.) × h^{-1}.

(100 : 1) in *iso*PrOH at 82 °C (table 1, entries 15–21). As seen from table 1, the catalytic activities in the studied hydrogen transfer reactions were generally much higher for **BL1a** and **BL1e** than the other catalytic systems. For example, under identical conditions, transfer hydrogenation of acetophenone derivatives with **BL1a** led to 98% conversions within 12 h whereas with **BL1e** as the auxiliary, 99% conversions were achieved only after 16 h period (table 1, entries 15 and 19).

Due to its efficiency in transfer hydrogenation of acetophenone, **BL1a** and **BL1e** were further investigated in transfer hydrogenation of substituted acetophenone derivatives. The catalytic reductions of acetophenone derivatives were all tested with the conditions optimized for acetophenone and the results are summarized in table 2, which illustrates conversions of the reduction performed in a 0.1 M of *iso*PrOH solution containing **BL1a** and **BL1e** and NaOH (Ketone : Cat. : NaOH = 100 : 1 : 5). Electronic properties of the substituents on the phenyl ring of the ketone caused changes in the reduction rate. An *ortho*- or *para*-substituted acetophenone with an electron-donor substituent, i.e. 2-methoxy or 4-methoxy is reduced more slowly than acetophenone (table 2, entries 5, 6, 11, and 12) [49]. Additionally, the introduction of electron-withdrawing substituents, such as F, NO_2, Cl, and Br to the *para*-position of the aryl ring of the ketone decreased the electron density of the C=O bond so that the activity was improved, giving easier hydrogenation [50, 51]. The examination of the results indicates clearly that the best yield was achieved in the reduction of acetophenone derivatives when **BL1a** was used as the catalyst precursor (table 2, entries 1 and 2).

We also carried out experiments to explore the effect of bulkiness of the alkyl groups on the catalytic activity and the results are given in table 3 (entries 1–12). A variety of simple aryl alkyl ketones were transformed to the corresponding secondary alcohols. Catalytic activity is highly dependent on the steric bulk of the alkyl group. The reactivity regularly decreased by increasing the bulkiness of the alkyl groups [52–55]. Catalytic activity of **BL1a** was generally much higher in the studied hydrogen transfer reactions than that of **BL1e**.

4. Conclusion

In the present study, we have synthesized ligands including O donors and their boron complexes. The compounds were characterized with various techniques. All complexes can be implemented for conversions of aromatic ketone to corresponding alcohols. The boron compounds are catalytically active and preferred instead of expensive catalysts like rhodium, ruthenium, and iridium. The construction of these catalysts and their flexibility towards transfer hydrogenation make these systems for further study. Further work and possible use of asymmetric versions of these complexes for catalytic purposes are in progress.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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