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Synthesis of new boron complexes: application to transfer hydrogenation of acetophenone derivatives

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Two new boron complexes were synthesized from *N*-[3-(methylmercapto)aniline]-3,5-di-*tert*-butylsalicylaldimine (LH) with boron reagent BPh_3 or $BF_3.Et_2O$. These boron complexes are stable and easily soluble in protic solvents such as ethanol (C_2H_5OH) but hardly soluble in nonprotic solvents such as chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF). All new boron complexes have been fully characterized by both analytical and spectroscopic methods. The catalytic activities of complexes [$LBPh_2$], 2, and [LBF_2], 3, in the transfer hydrogenation of acetophenone derivatives were tested. Stable boron complexes were found to be efficient catalysts in the transfer hydrogenation of aromatic ketones in good conversions up to 99% in the presence of *iso*-PrOH/KOH. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: boron complexes; transfer hydrogenation; BPh_3; $BF_3.Et_2O$; synthesis

Introduction

Boron is essential for healthy plants. Its biochemical role is not fully understood even 60 years after its recognition as an essential element, although it is known to be involved in nucleic acid synthesis, possibly linked to adequate provision of pyrimidine nucleotides. Boron also plays a part in carbohydrate metabolism, hormone action and membrane formation.[1] Its complexes with conjugated light-emitting π-systems have recently received considerable attention due to their potential use in organic light-emitting devices (OLEDs)[2,3] as well as fluorescent probes for proton or heavy metal ion detection.[4] There are three main types of fluorine–boron complexes, classified as N,N bidentate, N,O bidentate and O,O bidentate compounds (Scheme 1).

For the former two kinds of fluorine-boron complexes, BODIPY (boradipyrromethane) and 1,3,2-dioxaborine are their corresponding representatives.[5] Four-coordinate organoboron compounds have been extensively investigated in the past decade as emissive materials for use in OLEDs, because of their high thermal and chemical stability.[6,7] In contrast to three-coordinate boron compounds, which can function as a Lewis acid or an electron-transport material in optoelectronic devices through the empty p orbital of the boron center,[8] four-coordinate organoboron compounds can also function as electron-transport materials by means of the boron-stabilized π^* orbital of the conjugated chelate ligands.[7,8] 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 owing to the increased covalency of B ← O and B ← N bonds. Thus, boron complexes may provide extra stability to counteract the instability of C=N bonds in salicylaldimines as catalyts compounds.

In this paper, we report the synthesis, characterization and catalytic activity in transfer hydrogenation of aromatic ketones of the two boron complexes bearing BPh_2 or BF_2 and ligand (LH). We have found that both steric and electronic factors have a significant impact on the catalytic properties of this class of molecules.

Experimental

All reagents and solvents were of reagent-grade quality and obtained from commercial suppliers (Aldrich or Merck). IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer as KBr pellets. ^{1}H (400.1 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded on a Bruker AV 400 spectrometer, with δ referenced to external tetramethylsilane (TMS). Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Electronic spectral studies were conducted on a Perkin-Elmer model Lambda 25 UV–vis spectrophotometer in the wavelength range from 200 to 1100 nm. Melting points were measured in open capillary tubes with an Electrothermal 9100 melting point apparatus and are uncorrected.

GC Analyses

GC analyses were performed on a HP 6890N gas chromatograph equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane; 30 m × 0.32 mm × 0.25 µm). The GC parameters for transfer hydrogenation of ketones were as follows: initial temperature, 110 °C; initial time, 1 min; solvent delay, 4.48 min; temperature

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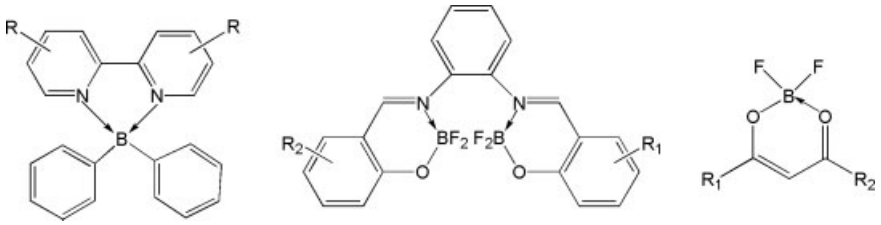


Scheme 1. The examples of N,N, N,O and O,O-type chelate boron complexes.

ramp 80 °C/min; final temperature, 200 °C; final time, 21.13 min; injector port temperature, 200 °C; detector temperature, 200 °C, injection volume, 2.0 µl.

Synthesis of Ligand (LH) (1)

Ligand (LH) was synthesized according to the a previously published method.[9] Color, yellow; m.p., 93 °C; yield (%), 65; anal. calcd for [$C_{22}H_{29}NOS$] (FW: 355 g mol^{-1}), C, 74.34; H, 8.17; N, 3.94. Found, C, 74.40; H, 8.45; N, 3.71%. ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ = 13.59 (s, 1H, -O*H*, D-exchangeable), 8.63 (s, 1H, *H*C═N), 7.52–6.99 (m, 6H, Ar-C*H*), 2.53 (s, 3H, S-CH_3), 1.49 (s, 9H, C-CH_3), 1.34 (s, 9H, C-CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 163.3 (*C*H═N), 158.4, 145.9, 140.5, 137.1, 134.6, 128.3, 127.1, 126.9, 125.2, 124.8, 118.4, 117.5 (Ar-CH), 35.2, 34.2 [*C*(CH_3)$_3$], 31.5, 29.5 [C(CH_3)$_3$], 14.8 (S-CH_3); FT-IR [KBr pellets, υ_{max} (cm^{-1})], 3643–3172 υ(OH), 2955–2867 υ(Aliph-H), 1615 υ(C═N), 1467–1440 υ(C═C), 1173 υ(C–O); UV–vis [λ_{max} (nm) (logε)] 206 (4.07), 226 (4.04), 272 (3.96), 305 (3.72), 354 (3.65) in C_2H_5OH and 253 (4.20), 274 (4.40), 305 (4.21), 355 (4.14) in DMSO.

Preparation of [$LBPh_2$] (2)

0.20 g of *N*-[3-(methylmercapto)aniline]-3,5-di-*tert*-butylsalicylaldimine (LH) 1 (0.56 mmol) and 25 ml anhydrous tetrahydrofurane (THF) were added to a 50 ml reaction flask. To this solution it was added 2.5 ml of the 0.25 M solution of BPh_3 in tetrahydrofuran (THF) (~0.60 mmol) and the mixture was stirred at room temperature for 6 h. The solution was then concentrated to dryness and the residue was subjected to vacuum sublimation at 110 °C. Light yellow solid of [$LBPh_2$] was obtained from recrystallization in a mixture of chloroform ($CHCl_3$) and hexane. Color, light-yellow; m.p., 223 °C; yield (%), 68; anal. calcd for [$C_{34}H_{38}BNOS$] (FW, 519.6 g mol^{-1}), C, 78.60; H, 7.37; N, 2.70. Found, C, 78.65; H, 7.29; N, 2.73%. ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ = 8.67 (s, 1H, *H*C═N), 7.58 (d, 1H, *J* = 2.4 Hz, Ar-CH_{11}), 7.49 [d, 2H, *J* = 6.4 Hz, Ar-*Ph*(*H*)], 7.39 [d, 2H, *J* = 2.4 Hz, Ar-*Ph*(*H*)], 7.28 (s, 1H, Ar-CH_8), 7.21 (d, 1H, *J* = 7.6 Hz, Ar-CH_{12}), 7.19–7.10 [m, 6H, Ar-*Ph*(*H*)], 7.08 (d, 1H, *J* = 2.4 Hz, Ar-CH_{10}), 6.86 (d, 1H, *J* = 8.0 Hz, Ar-CH_5), 6.79 (s, 1H, Ar-CH_3), 2.55 (s, 3H, S-CH_3), 1.41 (s, 9H, C-CH_3), 1.36 (s, 9H, C-CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ = 163.5 (*C*H═N), 159.5 (Ar-C_7), 158.3 (Ar-C_1), 146.1 (Ar-C_4), 140.6 (Ar-C_2 and C_9), 139.8 [Ar-*Ph*(*C*)], 139.5 (Ar-C_{11}), 134.1 [Ar-*Ph*(*C*)], 129.6 [Ar-*Ph*(*C*)], 129.0 (Ar-C_3), 126.9 (Ar-C_{10}), 126.1 (Ar-C_5), 122.0 (Ar-C_{12}), 120.9 (Ar-C_8), 119.2 (Ar-C_6), 35.1 and 29.7 [*C*(CH_3)$_3$], 31.6 and 31.2 [C(CH_3)$_3$], 15.2 (S-CH_3); FT-IR [KBr pellets, υ_{max} (cm^{-1})]: 3054 υ(Ar-H), 2986–2848 υ(Aliph-H), 1608 υ(C═N), 1476–1427 υ(C═C), 1170 υ(C–O), 1187 υ(B–O), 1030 υ(B–N), 885 υ(B–Ph); UV–vis [λ_{max} (nm) (logε)] 212 (4.11), 233 (3.96), 274 (3.78), 303 (3.52), 435 (2.03) in C_2H_5OH and 268 (4.22), 275 (4.03), 306 (3.89), 424 (2.14) in DMSO.

Preparation of [LBF_2] (3)

1 ml, 8 mmol BF_3.OEt_2 and 50 ml anhydrous benzene were added to a 100 ml reaction flask. To this solution was added 0.72 g, 2 mmol of ligand **1** in 15 ml anhydrous benzene. After the reaction mixture had been heated to reflux under nitrogen for 30 min, 1 ml Et_3N was added to the reaction solution, and the mixture was heated to reflux for 12 h. A light green-yellow solid precipitated from the solution. The solid product was collected by filtration and purified by recrystallization and sublimation. Color, green-yellow; m.p., 129 °C; yield (%), 70%; anal. calcd for [$C_{22}H_{28}BF_2NOS$] (FW: 403.2 g mol^{-1}), C, 65.51; H, 7.00; N, 3.47. Found, C, 65.48; H, 6.97; N, 3.42%. ^{1}H-NMR (400.1 MHz, $CDCl_3$) δ = 8.46 (s, 1H, *H*C═N), 7.78 (d, 1H, J = 2.4 Hz, Ar-CH_{11}), 7.51 (d, 1H, J = 2.4 Hz, Ar-CH_8), 7.35 (d, 1H, J = 2.4 Hz, Ar-CH_{12}), 7.31 (d, 1H, *J* = 7.2 Hz, Ar-CH_5), 7.18 (d, 1H, J = 2.0 Hz, Ar-CH_{10}), 7.08 (s, 1H, Ar-CH_3), 2.48 (s, 3H, S-CH_3), 1.43 (s, 9H, C-CH_3), 1.35 (s, 9H, C-CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ = 164.3 (*C*H═N), 158.3 (Ar-C_7), 157.2 (Ar-C_1), 149.3 (Ar-C_4), 139.9 (Ar-C_2), 139.6 (Ar-C_9), 129.8 (Ar-C_{11}), 129.7 (Ar-C_3), 127.0 (Ar-C_{10}), 126.7 (Ar-C_5), 120.9 (Ar-C_{12}), 120.0 (Ar-C_6), 118.2 (Ar-C_8), 35.2 and 29.5 [*C*(CH_3)$_3$], 31.5 and 31.2 [C(CH_3)$_3$], 15.7 (S-CH_3); FT-IR [KBr pellets, υ_{max} (cm^{-1})], 3057 υ(Ar-H), 2955-2870 υ(Aliph-H), 1622 υ(C═N), 1473-1439 υ(C═C), 1172 υ(C–O), 1189 υ(B–O), 1045 υ(B–N), 876 υ(B–F); UV–vis [λ_{max} (nm) (logε)] 224 (4.27), 279 (3.67), 301 (3.42), 367 (2.18) in C_2H_5OH and 278 (4.33), 301 (3.78), 366 (2.05) in DMSO.

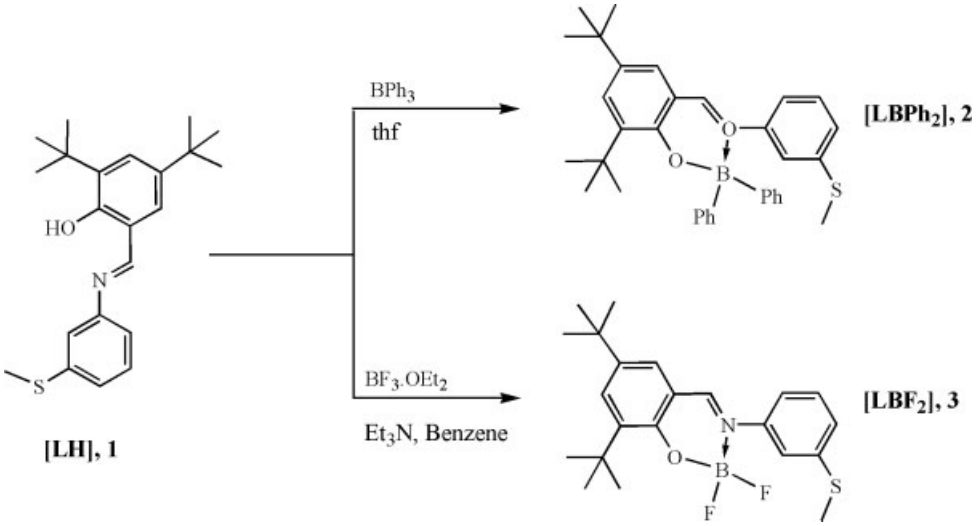
General Procedure for the Transfer Hydrogenation of Ketones

In a typical procedure for the catalytic hydrogen-transfer reaction, a solution of the boron complexes [$LBPh_2$], **2**, or [LBF_2], **3** (0.005 mmol), KOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed *iso*-PrOH (5 ml) were refluxed for 9 h. After this time, a sample of the reaction mixture was taken off, diluted with acetone and analyzed immediately by GC; the yields obtained were related to the residual unreacted ketone.

Results and Discussion

Preparation and Characterization

The ligand (**LH**), **1**, was prepared in moderate yield by refluxing the equivalent amount of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and 3-methylmercapto aniline (one equivalent ratio) in absolute methanol and three to four drops of formic acid as catalyst. The boron complexes containing substituted phenyl or fluorine moiety were synthesized according to slightly modified method reported by Hou *et al*. and Chen *et al*.[10,3] The overall synthetic scheme of the two boron complexes is shown in Scheme 2. As expected, treatment of the ligand (**LH**), **1**, with the boron reagent BPh_3 in THF solution at room temperature and with the



Scheme 2. The structure of the proposed boron complexes.

boron reagent $BF_3{}^{\bullet}OEt_2$ in benzene solution at reflux temperature gave the complexes [$LBPh_2$], **2**, and [LBF_2], **3**, respectively (Scheme 2). These two boron complexes were hardly soluble and stable in nonprotic solvents such as chloroform, dichloromethane and tetrahydrofuran, but easily soluble in protic solvents such as ethanol.

The ^{1}H NMR spectra of the ligand **(LH), 1** with two boron complexes and the chemical shifts of the different types of protons are listed in the Experimental section. In the ^{1}H-NMR spectrum of [$LBPh_2$], **2**, and [LBF_2], **3**, the resonance for the azomethine CH proton is a singlet at 8.67 ppm for [$LBPh_2$], **2**, and 8.46 ppm for [LBF_2], **3**, while the resonance ($\delta = 163.5$ for [$LBPh_2$], **2** and $\delta = 164.3$ for [LBF_2], **3**) for the imino C-atom in the ^{13}C-NMR spectra shifts to lower field in comparison with the corresponding signals of free ligand.[11] It can be stated that the position of the azomethine proton is affected by the nature of the BPh_2 and BF_2 groups. Also, the protons of the *tert*-butyl groups of ligand exhibit singlet resonances at $\delta = 1.41$ and 1.36 ppm for $LBPh_2$, **2** and $\delta = 1.43$ and 1.35 ppm for [LBF_2], **3** indicating that the *tert*-butyl protons of these compounds are magnetically nonequivalent (Scheme 2).[12]

The IR spectra of the two boron complexes were compared with that of the free ligand in order to determine the coordination sites that may be involved in chelation. The low- or high-frequency shift of the C═N stretchings (between 1608 and 1622 cm^{-1}), in comparison with the free ligand, was consistent with N-coordination of boron atoms to the azomethine ligand.[13] The IR spectrum of the ligand was characterized by the appearance of a band at range 3643–3172 cm^{-1}, due to the υ(O–H) groups. In the IR spectra of the boron complexes this band disappeared, as expected. This is because the O–H band of ligand disappeared upon formation of boron complexes, namely BPh_2 or BF_2. The existence of υ(B–O) and υ(B ← N) at 1187 and 1030 cm^{-1} for [$LBPh_2$], **2**, and at 1189 and 1045 cm^{-1} for [LBF_2], **3**, respectively, provides evidence for the formation of the foregoing boron complexes.

Electronic spectra of boron complexes were recorded in the 200–1100 nm range in C_2H_5OH or DMSO solution and their corresponding data are given in the Experimental section and Fig. 1. As shown in Fig. 1, the UV–vis absorption spectra of two boron complexes exhibited different spectral features with intense

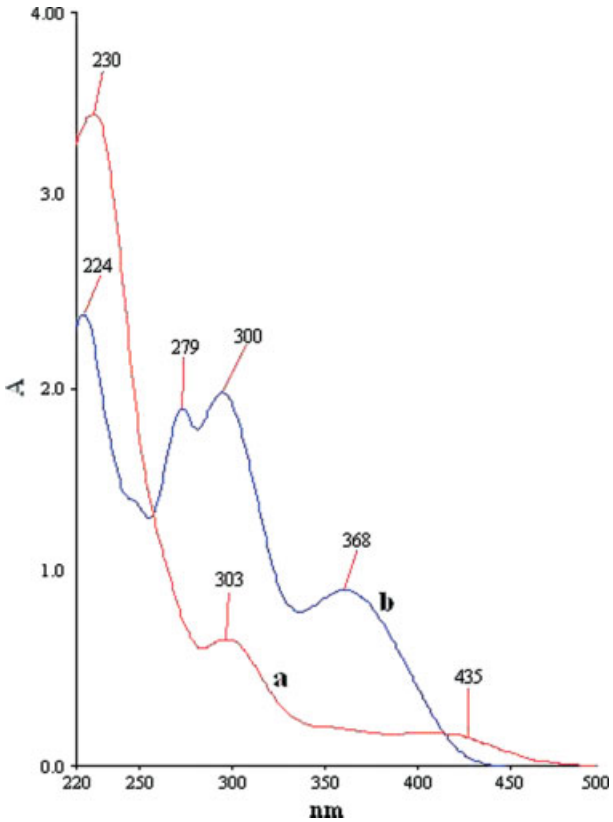
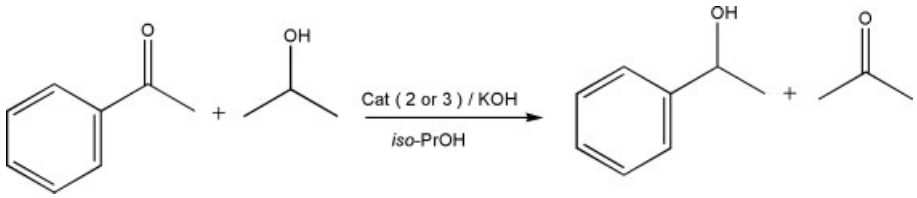


Figure 1. The UV–vis spectra of [$LBPh_2$] **2** (a) and [LBF_2] **3** (b) dissolved in C_2H_5OH at room temperature.

bands at range 212–435 nm in C_2H_5OH solution. This may have been caused by the disparate special structures of these two boron complexes. Moreover, the absorption bands for these complexes had a large molar extinction coefficient, which was insensitive to solvent polarity. Thus, the characteristic absorption bands can reasonably be assigned to ligand-centered $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ of the C═N chromophore. The absorption bands below 279 nm in two polar solvents (C_2H_5OH and DMSO) were practically identical and can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene ring or



Scheme 3. Hydrogen transfer from *iso*-PrOH to acetophenone.

Table 1. Transfer hydrogenation of acetophenone with *iso-Pr*OH catalyzed by [$LBPh_2$], **2**, and [LBF_2], **3**

Entry	Catalyst	S–catalyst–KOH	Time	Conversion (%)[e]	TON (h^{-1})[f]
1	2[a]	100 : 1 : 5	24 h	<1	–
2	3[a]	100 : 1 : 5	24 h	<1	–
3	2[b]	100 : 1	12 h	<5	–
4	3[b]	100 : 1	12 h	<5	–
5	2[c]	500 : 1 : 5	24 h	98	20
6	3[c]	500 : 1 : 5	24 h	99	20
7	2[d]	100 : 1 : 5	9 h	98	98
8	3[d]	100 : 1 : 5	9 h	97	97

Reaction conditions: [a] at room temperature, acetophenone–catalyst–KOH, 100 : 1 : 5; [b] refluxing in *iso*-PrOH, acetophenone–catalyst, 100 : 1, in the absence of base; [c] refluxing in *iso*-PrOH, acetophenone–catalyst–KOH, 500 : 1 : 5; [d] refluxing in *iso*-PrOH, acetophenone–catalyst–KOH, 100 : 1 : 5. [e] Determined by GC (three independent catalytic experiments). [f] Referred to the reaction time indicated in column 4. TON (mol product mol^{-1} catalyst).

azomethine (-C═N) group for boron complexes. The absorption bands observed within the range of 301–367 nm in two polar solvents (C_2H_5OH and DMSO) were most probably due to the transition of $n \rightarrow \pi^*$ of the imine group corresponding to the boron complexes. Also, the absorption bands observed at 424 and 435 nm in two polar solvent for [$LBPh_2$], **2**, were most probably due to the charge transfer.

Catalytic Transfer Hydrogenation of Acetophenone Derivatives

iso-PrOH is the conventional hydrogen source having favorable properties; it is stable, easy to handle (b.p. 82 °C), non-toxic, environmentally friendly, inexpensive and the acetone product is readily removable.[14] In this context, complexes **2** and **3** were selected as catalysts, *iso*-PrOH/KOH as the reducing system and acetophenone as a model substrate (Scheme 3); the results are listed in Table 1.

At room temperature no appreciable formation of 1-phenylethanol was observed (Table 1, entries 1 and 2). As can be inferred from the Table 1 (entries 3 and 4), the catalysts as well as the presence of KOH are necessary to observe appreciable conversions. The base facilitates the formation of alkoxide by abstracting proton of the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. This is the mechanism proposed by several workers on the studies of ruthenium-catalyzed transfer hydrogenation reaction by metal hydride intermediates.[15,16] Similarly this may the mechanism proposed for the boron catalyzed transfer hydrogenation reaction by boron hydride intermediates.[17,18]

As shown in Table 1, increasing the substrate-to-catalyst ratio does not lower the conversions of the product in most cases. In addition, we have expanded the substrate-to-catalyst ratio to observe the effect on the catalytic efficiency. As shown in Table 1, increasing the substrate-to-catalyst ratio does not damage the conversions of the product in most cases except time of the reaction lengthened. Remarkably, the transfer hydrogenation of acetophenone could be achieved to 99% yield even when the substrate-to-catalyst ratio reached 500 : 1.

In Table 1, entries 7 and 8, when the reaction temperature was increased to 82 °C smooth reduction of acetophenone into 1-phenylethanol occurred, with conversion ranging from 98 to 97% after 9 h for [$LBPh_2$], **(2)** and for [LBF_2], **3** of reaction. Results obtained from optimization studies indicate clearly that both complexes are active and efficient catalysts leading to nearly quantitative conversions, with no significant difference between the catalytic activities. The catalytic reduction of acetophenone derivatives was all tested with the conditions optimized for acetophenone and the results are summarized in Table 2. The fourth column in Table 2 illustrates conversions of the reduction performed in 0.1 M *iso*-PrOH solution containing [$LBPh_2$], **2**, or [LBF_2], **3**, and KOH (ketone–catalyst–KOH = 100 : 1 : 5).

As already stated, electronic properties (the nature and position) of the substituents on the phenyl ring of the ketone caused the 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 4, 5, 9 and 10).[19] In addition, the introduction of electron-withdrawing substituents, such as F, 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 rise to easier hydrogenation.[20,21]

Conclusion

In this study, two new boron complexes containing substituted phenyl or fluorine moiety were synthesized. These boron complexes have been characterized and their spectroscopic properties were investigated. The results are agreed with the proposed structure. We found that these complexes are efficient homogeneous catalytic systems that can be readily implemented and lead to secondary alcohols from good to excellent yields. Furthermore, the influence of phenyl and fluorine groups in the catalytic transfer hydrogenation of aromatic ketones was investigated and their catalytic activities were very similar. The procedure is simple and efficient towards various aryl ketones.

Acknowledgment

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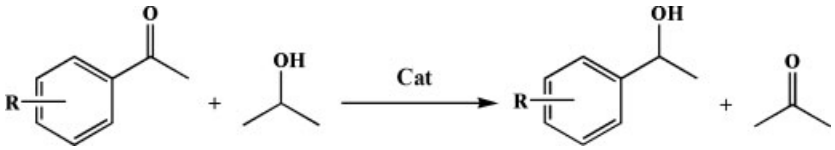
Table 2. Transfer hydrogenation results for substituted acetophenones with the catalyst systems prepared from LH and BPh_3 and $BF_3{\bullet}OEt_2$[a]



Catalyst	Entry	R	Time	Conversion (%)[b]	TON (h^{-1})[c]
[$LBPh_2$], **2**	1	4-F	9 h	99	99
	2	4-Cl	9 h	98	98
	3	4-Br	9 h	95	95
	4	2-MeO	9 h	90	90
	5	4-MeO	9 h	83	83
[LBF_2], **3**	6	4-F	9 h	99	99
	7	4-Cl	9 h	97	97
	8	4-Br	9 h	94	94
	9	2-MeO	9 h	91	91
	10	4-MeO	9 h	80	80

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 ml), KOH (0.025 mmol%), 82 °C, 9 h for **2** and **3**, respectively; the concentration of acetophenone derivatives is 0.1 M.
[b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments); yields are based on methyl aryl ketone.
[c] TON (mol product mol^{-1} catalyst).

References

[1] a) A. G. Massey, *Main Group Chemistry*, 1st edn, Ellis Horwood: Chichester, **1990**, p. 487; b) S. Yadav, M. Swami, and R. V. Singh, *Phosphorus, Sulfur, and Silicon* **2010**, *185*, 394.
[2] a) S. Wang, *Coord. Chem. Rev.* **2001**, *215*, 79; b) S. Anderson, M. S. Weaver, A. J. Hudson, *Synth. Met.* **2000**, *111–112*, 459.
[3] H. Y. Chen, Y. Chi, C. S. Liu, J. K. Yu, Y. M. Cheng. K. S. Chen, P. T. Chou, S. M. Peng, G. H. Lee, A. J. Carty, S.J. Yeh C. T. Chen, *Adv. Funct. Mater.* **2005**, *15*(4), 567.
[4] a) G. Beer, J. Daub, K. Rurack, *Chem. Commun.* **2001**, 1138; b) K. Rurack, M. Kollmannsberger, J. Daub Angew, *Chem. Int. Ed.* **2001**, *40*, 385.
[5] a) V. Christou, S. E. Watkins, R. McCann, C. Redshaw, M. R. J. Elsegood, *Inorg. Chem. Acta* **2010**, *363*, 1173; b) P. Oleynik, Y. Ishihara, G. Cosa, *J. Am. Chem. Soc.* **2007**, *129*, 1842; c) D. Rohde, C. J. Yan, L. J. Wan, *Langmuir* **2006**, *22*, 4750; d) C. Risko, E. Zojer, P. Brocorens, S.R. Marder, J.L. Bredas, *Chem. Phys.* **2005**, *313*, 151.
[6] a) A. Wakamiya, T. Taniguchi, S. Yamaguchi, *Angew. Chem.* **2006**, *118*, 3242; *Angew. Chem. Int. Ed.* **2006**, *45*, 3170; b) A. Fukazawa, H. Yamada, S. Yamaguchi, *Angew. Chem.* **2008**, *120*, 5664; *Angew. Chem. Int. Ed.* **2008**, *47*, 5582; c) Q. D. Liu, M. S. Mudadu, R. Thummel, Y. Tao, S. Wang, *Adv. Funct. Mater.* **2005**, *15*, 143.
[7] a) Y. Qin, I. Kiburu, S. Shah, F. Jäckle, *Macromolecules* **2006**, *39*, 9041; b) Y. Qin, I. Kiburu, S. Shah, F. Jäckle, *Org. Lett.* **2006**, *8*, 5227; c) H. Amarne, C. Baik, S. K. Murphy S. Wang, *Chem. Eur. J.* **2010**, *16*, 4750.
[8] a) M. Elbing, G. C. Bazan, *Angew. Chem.* **2008**, *120*, 846; *Angew. Chem. Int. Ed.* **2008**, *47*, 834; b) T. W. Hudnall, C. W. Chiu, F. P. Gabbai, *Acc. Chem. Res.* **2009**, *42*, 388; c) Z. M. Hudson, S. Wang, *Acc. Chem. Res.* **2009**, *42*, 1584.
[9] E. Tas, A. Kilic, N. Konak and I. Yilmaz, *Polyhedron* **2008**, *27*(3), 1024.
[10] Q. Hou, L. Zhao, H. Zhang, Y. Wang, S. Jiang, *J. Luminescence* **2007**, *126*, 447.
[11] X. Liu, H. Xia, X. Fan, Q. Su, W. Gao, Y. Mu, *J. Phys. Chem. Solids* **2009**, *70*, 92.
[12] A. Kilic, E. Tas, B. Deveci I. Yilmaz, *Polyhedron* **2007**, *26*, 4009.
[13] O.N. Kadkin, J. An, H. Han, Y.G. Galyametdinov, *Eur. J. Inorg. Chem.* **2008**, *10*, 1682.
[14] G. Zassinovich, G. Mestroni, S. Gladiali, *Chem. Rev.* **1992**, *92*, 1051.
[15] H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, F. A. England, T. Ikariya, R. Noyori, *Angew. Chem. Int. Ed.* **1998**, *37*, 1703.
[16] H. Zhang, B. C. Yang, Y. Y. Li, Z. R. Donga, J. X. Gao, H. Nakamura, K. Murata, T. Ikariya, *J. Chem. Com., Chem. Commun.* **2003**, 142.
[17] a) M. M. Midland, S. Zderic, *J. Am. Chem. Soc.* **1982**, *104*, 525; b) J. Chandrasekharan, P. V. Ramanchadran, H.C. Brown, *J. Org. Chem.* **1985**, *50*, 5446; c) J. S. Cha, E. J. Kim, O. O. Kwon, S. Y. Kwon, W. W. Seo, S. W. Chang, *Org. Prep. Proceed. Int.* **1995**, *27*, 541.
[18] a) J. S. Cha, E. J. Kim, O. O. Kwon, J. M. Kim, *Bull. Korean Chem. Soc.* **1995**, *16*, 691; b) E. J. Corey, R. K. Bakshi, S. Shibata, *J. Am. Chem. Soc.* **1987**, *109*, 5551.
[19] R. Guo, X. Chen. C. Elphelt, D. Song, R. H. Morris, *Organic Letters* **2005**, *7*, 9.
[20] P. Pelagatti, M. Carcelli, F. Calbiani, C. Cassi, L. Elviri, C. Pelizzi, U. Rizzotti, D. Rogolino, *Organometallics* **2005**, *24*, 5836.
[21] J. W. Faller, A. R. Lavoie, *Organometallics* **2001**, *20*, 5245.