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Doubly hydrogen-bridged 1,2-diphenylenediboranes derived from 9-chloro-9-borafluorene and ligand exchange reactions

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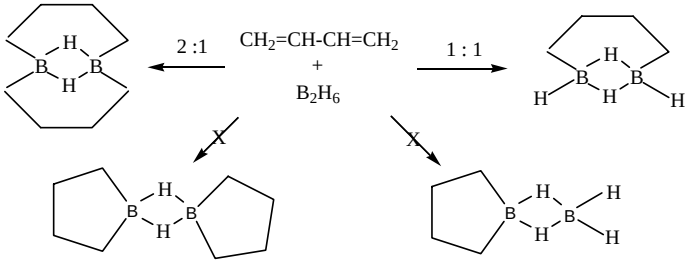
Abstract

Cyclic 1,2-diphenylenediboranes containing a doubly hydrogen-bridged structure, including 1,2-(2,2′biphenylylene)diborane(I) and 1,2-(2,2′biphenylylene)-1,2-diethyldiborane (II), are conveniently prepared by treating 9-chloro-9-borafluorene with $NaBH_4$ and $Na(Et)_3BH$, respectively. The reaction mechanism involves an initial Cl–H exchange to form 9-borafluorene containing a reactive 5-member ring diarylborane moiety, which subsequently engages in a facile ring expansion with the in situ formed B–H containing residue (BH_3 or $HBEt_2$) to result in cyclic 1,2-diphenylenediboranes compounds. The doubly hydrogen-bridged structure shows good thermal stability up to 50 °C. Upon thermal cleavage at higher temperature, all free B–H groups become very reactive involving hydroboration with α-olefin. The complexization study also reveals that this intradiborane moiety forms a 1:2 complex with a strong base, such as pyridine.

Keywords: Arylborane; 9-Ethyl-9-borafluorene; 1,2-(2,2′Biphenylylene)diborane; 1,2-(2,2′Biphenylylene)-1,2-diethyldiborane

1. Introduction

Cyclic organodiboranes with a unique stable intramolecular doubly hydrogen-bridged structure, such as 1,2-tetramethylenediborane and 1,2: 1,2-bis(tetramethylene)diborane, have been the subject of some debate [1–5]. These compounds were prepared by hydroboration reaction of butadiene with diborane (Eq. (1)) under some specific conditions. The early suggestion that an intermolecular hydrogen-bridged structure was formed was replaced by the concept of an intramolecular doubly hydrogen-bridged structure after careful structure analysis by Young and Shore [4] and after the high ring opening reactivity of borolane with borane was shown by Brown et al. [5].



(1)

It is very interesting to examine this unusual borolane (5-member ring) instability phenomenon in the corresponding cyclic arylborane system, such as 9-borafluorene that has two stronger B–C bonds with π-electron delocalization,

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which may discourage the ring-expansion from intermolecular to intramolecular diborane structure. On the other hand, it is also very desirable to study an effective synthesis route to prepare asymmetric diarylborane compounds containing a relatively stable B–H moiety that is inert to ethylene and 1-propene monomers but reactive with the M–C catalytic site (M: transition metals) during the transition metal coordination polymerization. Such a compound would be a suitable chain transfer agent [6] in metallocene-mediated olefin polymerization to prepare borane group terminated polyolefin, and the resulting arylborane terminal group would offer good oxidative selectivity to form B–O–O–C (polymer chain) species for the subsequent control radical polymerization [7] to prepare functional polyolefin diblock copolymers with well-control molecular structure.

2. Experimental

2.1. General

All manipulations were carried out under inert atmosphere or by using standard Schlenk technique. All ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker AM 300 instrument. Atmospheric pressure chemical ionization mass (APCI-MS) was examined in a Perseptive Mariner LC/MS instrument (with corona needle at −5200 V).

CP grade toluene, hexane, tetrahydrofuran (THF), and ether were deoxygenated by argon purge before refluxing for 48 h and then distilled over sodium benzophenone right before their use. 1-octene was purified by distillation over CaH_2. Butyllithium (2.5 M in hexane), BCl_3 (1.0 M in heptane), $NaBH_4$ and $NaBHEt_3$ (1.0 M in THF) were used as received.

2.2. Synthesis of 9-Cl-9-borafluorene

In a 500 ml flask equipped with a magnetic stirrer, 6.24 g (20 mmol) *O*, *O*′-dibromobipheny was dissolved in 200 ml of Et_2O. To the solution at 0 °C was added dropwise 40 mmol of *n*-butyllithium (2.5 M) in 16 ml of hexane. The addition was complete in 30 min. The solution was stirred for 2 h before vacuum distillation at ambient temperature to remove all the volatiles. The residues was then washed with 30 ml of hexane twice, and suspended in 200 ml of hexane. To the suspension at 0 °C under vigorously stirring was added dropwise 20 mmol of BCl_3 (1.0 M) in 20 ml of heptane. The addition was complete in 30 min. After stirring overnight, the reaction mixture was filtered to obtain a yellow clear filtrate. After removing the volatiles by vacuum at ambient temperature, 1.4 g of 9-Cl-9-boraflurene (36% yield), a yellow oil that turned to yellow crystal after cooling, was distilled out under vacuum (50 mTorr) at 130 °C. Its structure was confirmed by ^{1}H, ^{13}C, and ^{11}B NMR spectra: ^{1}H NMR ($CDCl_3$) δ 7.63 ppm (d 1H), δ 7.42 ppm (m 2H), δ 7.24 ppm (t, 1H); ^{13}C NMR ($CDCl_3$) δ 153.42, 136.91 132.99,129.31,120.57 ppm; ^{11}B NMR ($CDCl_3$) δ 62.46 ppm (s).

2.3. Synthesis 1,2-(2,2′-diphenylylene)diborane

To a suspension of $NaBH_4$ (0.4 g, 10.5 mmol) in 20 ml of THF was added a solution of 9-Cl-9-borafluorene (2.0 g, 10.1 mmol) in 30 ml of THF at ambient temperature. The mixture was stirred for 30 minutes before filtering out the solid. After vacuum-removal of solvent from the solution at ambient temperature, the residue was added with 20 ml of hexane and warmed to 50 °C to assure clear solution before crystallization at 0 °C for 3 h to form colorless crystal. 1.7 g of 1,2-(2,2′-diphenylylene)diborane (91% yield), a colorless needle-liked crystal was isolated by filtration and dried under vacuum. Its structure was confirmed by APCI-MS and multiple nuclei NMR techniques. ^{11}B NMR ($CDCl_3$) δ 13.92 ppm (d $J_{B,H} = 134$ Hz); ^{1}H NMR ($CDCl_3$) δ 8.38 ppm (d, 1H), δ 7.79 ppm (d, 1H), δ 7.54 ppm (t, 1H), δ 7.32 ppm (t, 1H), δ 4.44 ppm (b, dd, 1H), δ 0.94 ppm (b, s, 1H); ^{13}C NMR (in $CDCl_3$) δ 141.32, 138.48, 130.87, 126.57, 124.42 ppm.

2.4. Synthesis of 9-ethyl-borafluorene and 1,2-(2,2′-diphenylylene)-1,2-diethyldiborane

To a solution of 9-Cl-9-borafluorene (2.0 g, 10 mmol) in 30 ml of THF at −78 °C was added 10 ml of $NaBHEt_3$ solution (1.0 M in THF). After stirring the solution for 30 min, the mixture was slowly warmed up to ambient temperature over 4 h. The volatiles were removed by vacuum at room temperature, and the residue was added with 50 ml of toluene and filtered. After vacuum removal of the solvent from the filtrate, a mixture of 9-ethyl-9-borafluorene and 2,2′-diphenyl-1,2-diethyl-1,2-diborane with about 1/1 mole ratio, a faint green oil, was distilled out under vacuum (50 mTorr) at 140 °C. Crystallization was carried out to separate the two compounds. The mixture was dissolved in 20

ml of hexane, then cooled down to −20 °C for 10 h. About 0.65 g of 1,2-(2,2′-diphenylylene)-1,2-diethyldiborane (25%) colorless crystal was isolated by filtration and dried under vacuum. Its structure was confirmed by ^{1}H, ^{13}C and ^{11}B NMR spectra: ^{1}H NMR ($CDCl_3$) δ 8.10 ppm (d, 1H), δ 7.68 ppm (d, 1H), δ 7.14 ppm (t, 1H), δ 7.02 ppm (t, 1H), δ 2.20 ppm (b, s, 1H), δ 1.66 ppm (dd, 2H), δ 1.28 ppm (t, 3H); ^{13}C NMR-DEPT135 ($CDCl_3$) δ 133.50, 132.23, 126.74, 125.72, 13.08 ppm; ^{11}B NMR ($CDCl_3$) δ 19.65 ppm (s).

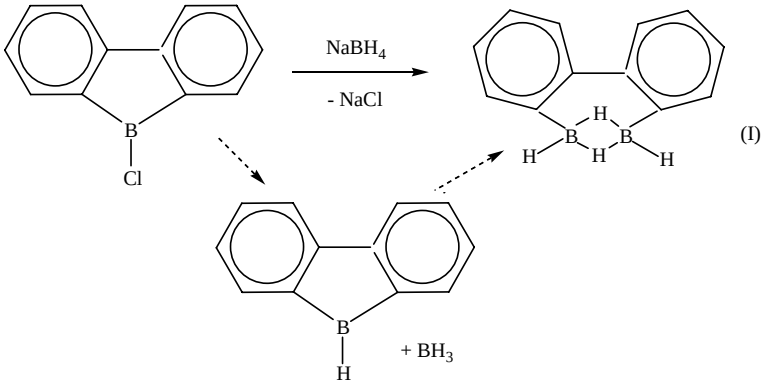
After vacuum removal of hexane in filtrate, 0.50 g of 9-ethyl-9-borafluorene (27%), a faint green oil, was distilled out under vacuum (70 mTorr) at 140 °C. Its structure was confirmed by ^{1}H and ^{11}B NMR spectra: ^{1}H NMR ($CDCl_3$) δ 7.21 ppm (d, 1H), δ 6.92 ppm (d, 1H), δ 6.84 ppm (t, 1H), δ 6.68 ppm (t, 1H), δ 1.24 ppm (dd, 1H), δ 0.88 ppm (t, 1.5H); ^{11}B NMR ($CDCl_3$) δ 73.46 ppm (s 1B).

2.5. Hydroboration of 1-octene with 1,2-(2,2′-diphenylylen)diborane

To a solution of 1,2-(2,2′-diphenylylen)diborane (0.2 g, 1.13 mmol) was added 10 ml of 1-octene. The mixture was refluxed for 4 h before removing the excess 1-octene by vacuum distillation (100 mTorr). About 0.6 g of 2,2′-biphenyl-1,1,2,2-teraoctylborane (95% yield), a colorless viscose liquid, was obtained. Its structure was confirmed by ^{1}H and ^{11}B NMR spectra: ^{1}H NMR ($CDCl_3$) δ 7.68 ppm (t, 1H), δ 7.34 ppm (m, 3H), δ 1.47 ppm (m, 4H), δ 1.02 ppm (m, 16H), δ 0.58 ppm (t, 6H); ^{11}B NMR ($CDCl_3$) δ 79.46 ppm (s).

3. Results and discussion

In this paper, we report a convenient route (one-pot reaction) to prepare two cyclic aryldiborane compounds, including 1,2-(2,2′biphenylylene)diborane(I) and 1,2-(2,2′biphenylylene)-1,2-diethyldiborane (II), containing a double intramolecular hydrogen bridge structure. The chemistry involves a consecutive ligand exchange reaction, including 5-member ring expansion, between 9-chloro-9-borafluorene (9-CBF) [8] and $NaBH_4$ and $NaBH(Et)_3$, respectively. Although both compounds were previously reported by Koster and Willemsen [9] using a multiple-step high temperature reaction process, the experimental results were difficult to reproduce in our laboratory. The complicated reaction mechanism may involve several steps, including ligand exchange, elimination, and coupling cyclization. In addition, the reactivity of aryldiborane compounds was not reported.



(2)

Treatment of 9-CBF with an equimolar quantity of $NaBH_4$/THF solution (Eq. (2)) at 25 °C results in immediate precipitation of NaCl and essentially pure 1,2-(2,2′biphenylylene)diborane (I) within 30 min, which is evidenced by the combination of APCI-MS and multiple nuclei NMR techniques. This product forms colorless, needle-liked crystals after recrystallization in hexane.

As shown in Fig. 1, both experimental and theoretical mass spectral patterns for 1,2-(2,2′biphenylylene)diborane (I) ($m/e = 179$ for diborane (I)/H^+) are in excellent agreement. The ^{11}B NMR spectra in Fig. 2 show a clean chemical shift change from a singlet at 62.46 ppm (vs. etherated BF_3) for 9-CBF to a doublet at 13.4 and 14.6 ppm (singlet at 14.2 ppm in the ^{1}H-decoupled spectrum) for 1,2-(2,2′biphenylylene)diborane (I). Both bridged and terminal hydrogens in 1,2-(2,2′biphenylylene)diborane (I) were further revealed in the ^{1}H NMR spectrum shown in Fig. 3. In addition to four pairs of symmetric aromatic protons, there are two broad chemical shifts that become clear in ^{11}B-decoupled spectra showing a triplet at around 1.17–1.27 ppm, corresponding to two bridged hydrogens, and a singlet at 4.73 ppm, corresponding to two terminal hydrogens.

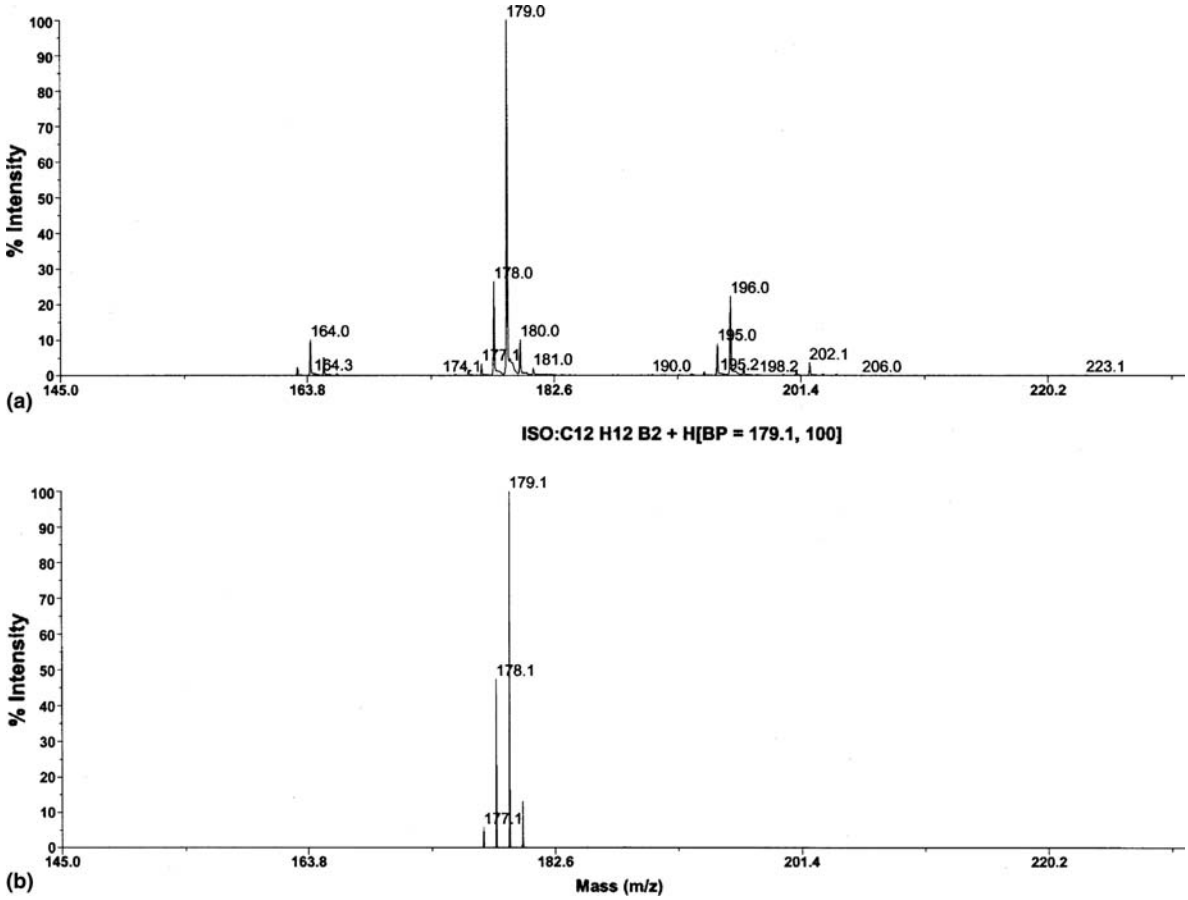


Fig. 1. (a) Experimental and (b) theoretical (parent peak) mass spectral patterns for 1,2-(2,2′biphenylylene)diborane (I).

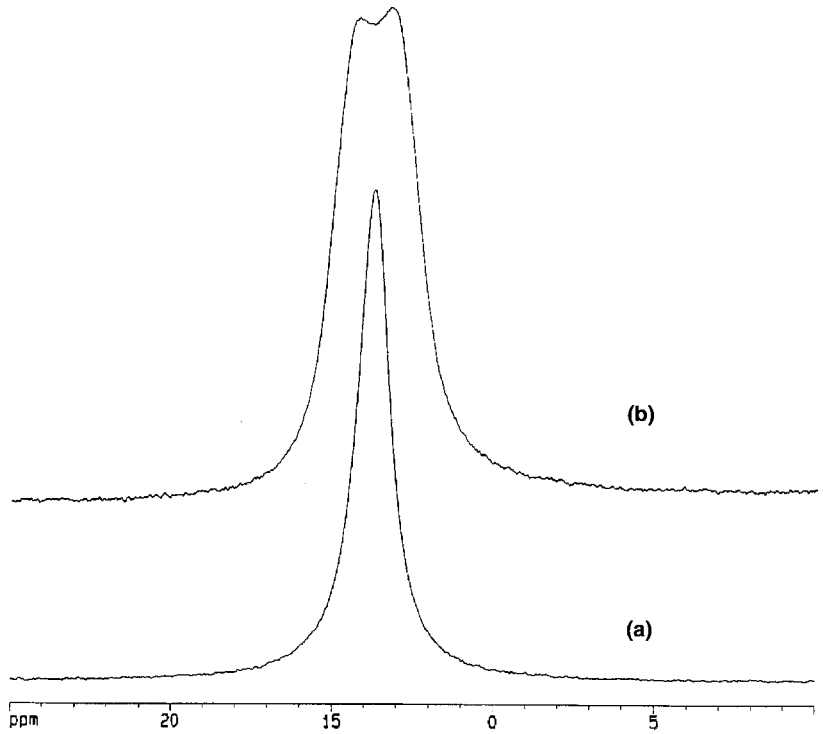


Fig. 2. ^{11}B NMR spectra of 1,2-(2,2′-diphenylylene)diborane (a) with and (b) without ^{1}H-decoupling.

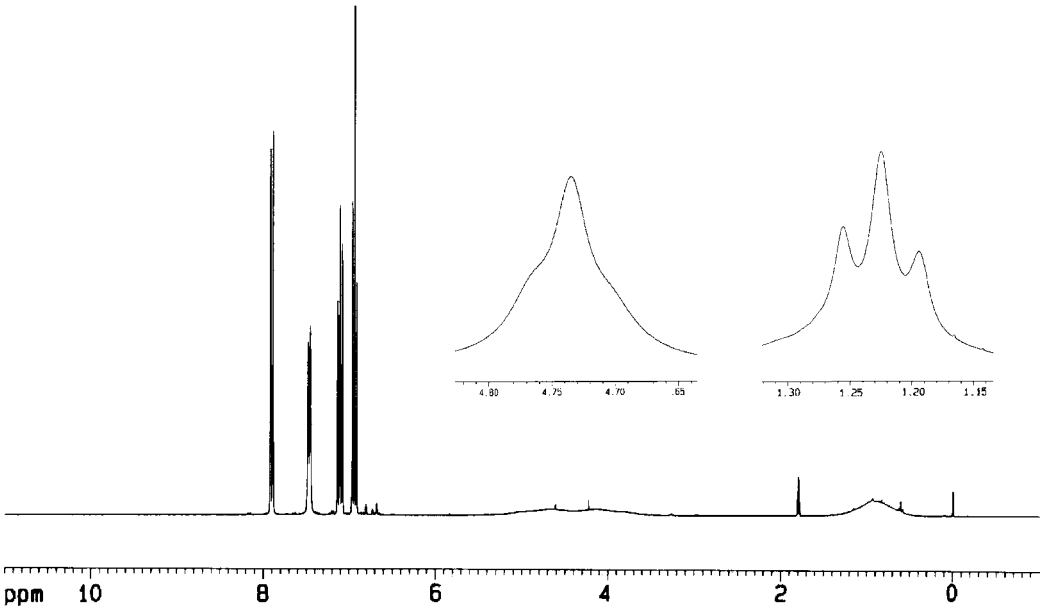
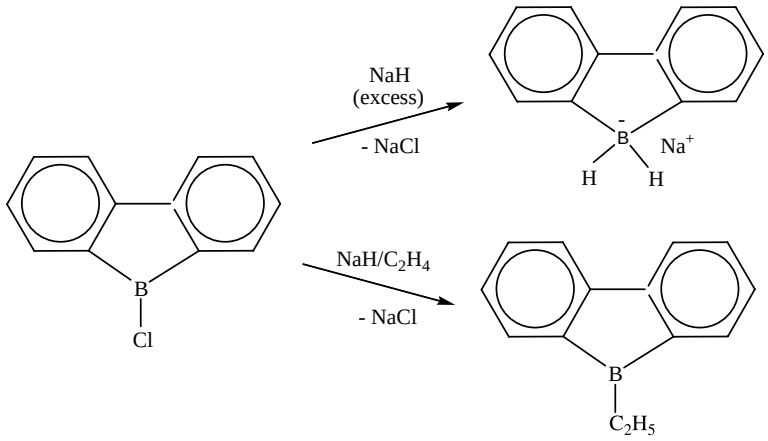
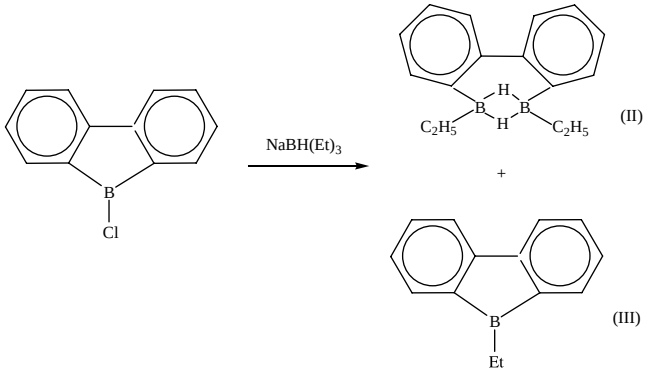


Fig. 3. ^{1}H NMR spectrum of 1,2-(2,2′biphenylylene)diborane, inserts are ^{11}B-decoupled spectra in two selected regions.



(3)

Several attempts to isolate 9-borafluorene intermediate were not successful due to the facile reaction with the in situ formed BH_3. In a similar reaction (Eq. (3)) using excess NaH (without BH_3 residue) suspended in THF, the in situ ^{11}B NMR monitoring clearly showed the initial formation of 9-borafluorene (δ: 53.85 ppm) with the presence of unreacted 9-CBF (δ: 62.46 ppm) and the corresponding sodium 9-borafluorene hydride (δ: −22.40 ppm). After 3 h, only sodium 9-borafluorenehydride remained in the solution. In the same reaction with the presence of a high concentration of ethylene (pressure = 40 psi), the 9-borafluorene intermediate reacts with ethylene to form 9-ethyl-9-borafluorene (δ: 72.30 ppm). It is clear that 9-borafluorene initially forms, however, the cyclic diarylborahydride (5-member ring) moiety is unstable despite two strong B-aryl bonds with π-electron delocalization.



(4)

The reaction between 9-CBF and $NaBH(Et)_3$ (Eq. (4)) was slightly complicated by two possible ligand exchange reactions with H and ethyl groups. In situ ^{11}B NMR spectra revealed the immediate H and Cl ligand exchange after mixing at ambient temperature to form 9-borafluorene (δ: 53.85 ppm) and BEt_3 (δ: 83.65 ppm). Both sharp peaks gradually gave away to two new peaks at 19.28 and 72.30 ppm, corresponding to 1,2-(2,2′biphenylylene)-1,2-diethyldiborane (II) and 9-ethyl-9-borafluorene (III), respectively. The (II)/(III) peak intensity ratio is proportional to the stoichiometric amount of $NaBH(Et)_3$ used. About a 1/1 peak intensity ratio was observed while an equal mole of $NaBH(Et)_3$ (vs. 9-CBF) was used. Some of the initially formed 9-borafluorene may engage in a facile ligand exchange with BEt_3 to form 9-ethyl-9-borafluorene (III) and $HBEt_2$ that then immediately reacts with another 9-borafluorene by ring-expansion to form a doubly hydrogen-bridged compound (II).

The stability of the intramolecular double B–H–B bridge in 1,2-(2,2′biphenylylene)diborane (I) was examined by hydroboration reaction and acid–base complexation with pyridine. No detectable reaction was observed between 1,2-(2,2′biphenylylene)diborane (I) and 1-octene in THF at 50 °C for 5 h. However, hydroboration reaction did take place under refluxing temperature (121 °C) with pure 1-octene. After 5 h 2,2′-biphenyl-1,1,2,2-tetraoctylborane was obtained with almost 100% yield. Apparently, the doubly hydrogen-bridged structure is stable up to 50 °C, and shows no complexation with THF (weak base). However, after thermal cleavage at higher temperatures, all four free B–H groups become very reactive to α-olefin.

It is very interesting to further examine the acid–base interaction of this intradiborane with a strong base, such as pyridine. Fig. 4 shows ^{11}B NMR spectra that were obtained by in situ monitoring the complexation between 1,2-(2,2′biphenylylene)diborane (I) and pyridine in C_6D_6 at ambient temperature. Upon the addition of pyridine, a new

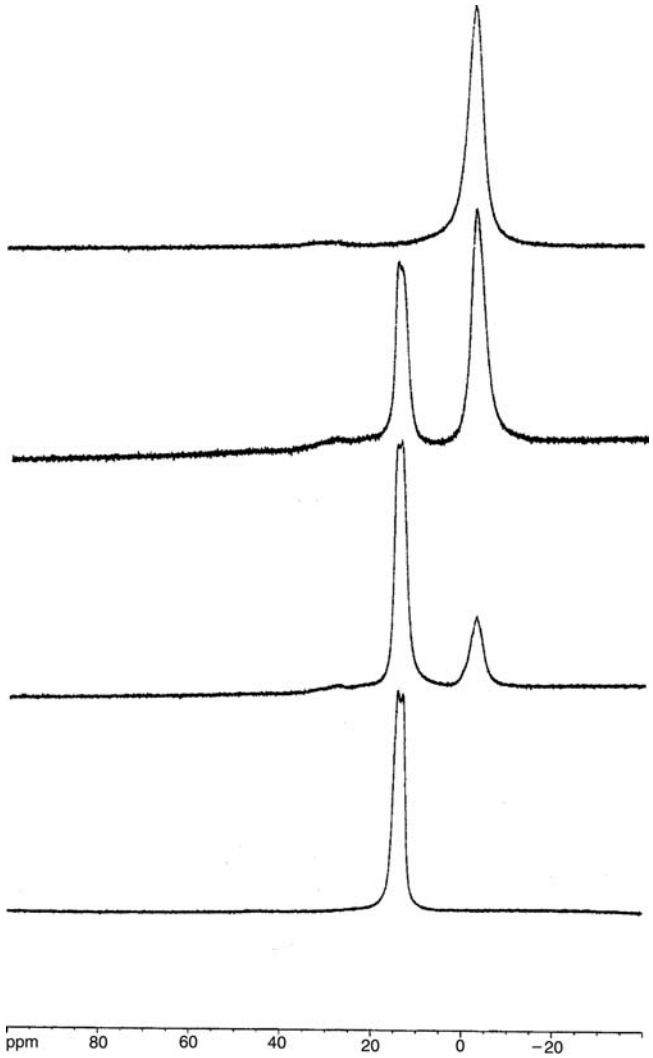


Fig. 4. ^{11}B NMR spectra of 1,2-(2,2′biphenylylene)diborane/pyridine complexes with: (a) 1:0; (b) 1:0.4; (c) 1:1; (d) 1:2 mole ratios.

peak at −2.88 ppm, corresponding to an acid–base complex, immediately appeared, and increased its concentration at the expense of 1,2-(2,2′biphenylylene)diborane (I) (a doublet at 13.4 and 14.6 ppm). At (I)/pyridine = 1/1 mole ratio, two chemical shifts showed almost equal intensities and the diborane peak completely disappeared at (I)/pyridine = 1/2 mole ratio. It is clear that this represents a fast formation of an acid–base complex with 1:2 mole ratio. In other words, after 1,2-(2,2′biphenylylene)diborane (I) complexes first with pyridine, which dissociates the hydrogen-bridge (B–H–B) structure, the remaining arylborane moiety immediately complexes with another pyridine.

4. Conclusions

In conclusion, we have developed an effective route to prepare cyclic 1,2-diphenylenediboranes, including 1,2-(2,2′biphenylylene)diborane(I) and 1,2-(2,2′biphenylylene)-1,2-diethyldiborane (II), containing a doubly hydrogen-bridged structure. The chemistry involves simple treatment (one-pot reaction) of 9-chloro-9-borafluorene with $NaBH_4$ and $Na(Et)_3BH$, respectively. Some mechanistic studies indicate an initial Cl-H ligand exchange reaction to form 9-borafluorene intermediate that contains a reactive 5-member ring diarylborahydride moiety. The subsequent ring expansion takes place with the in situ formed borane residue (BH_3 or $HBEt_2$) to result in relatively stable doubly hydrogen-bridged compounds. Upon thermal cleavage of the doubly hydrogen-bridged structure at elevated temperature (>50 °C), all free B–H groups become very reactive and wholly engage in hydroboration with α-olefin. The complexation study also reveals that this aromatic intradiborane moiety only complexes with a strong base, such as pyridine, to form a diborane/pyridine (1:2) complex.

Acknowledgements

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