

## Spectroscopic Study of the Metallation Reactions of Bis(dialkylamino)-4-methyl-and 2,4-dimethyl-2,4-pentadienylboranes

Jawad K. Shneine

Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq.

E-mail: shneine@yahoo.com.

### Abstract

Metalation Reactions of 2,4-dimethyl-and 4-methyl-2,4-pentadienylboranes, prepared from the reaction of potassium-2-methyl- and 2,4-dimethyl-1,3-pentadienide with chlorobis (dialkylamino) borane (R=Me, Et), were investigated. Lithiumdiethylamide LiNEt<sub>2</sub> in THF was used as base to achieve metalation. Li(TMEDA\*)-1-dimethylamino-3-methylboratabenzene and bora-2,4- and bora-2,5-cyclohexadiene were obtained from bis(dialkylamino)-4-methyl-2,4-pentadienylborane in moderate and good yields. Mass, <sup>11</sup>B, <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy were used to characterize the intermediates and products. Steric effects found to have dominating and controlling role on the results.

Keywords: Borabenzene, Boratabenzene, Boracyclohexadiene, Boron Heterocycles.

### Introduction

Formerly, borabenzene and boratabenzene derivatives are mainly obtainable via the cobaltocene route [1] and via the tincene route [2]. These routes, however, are accompanied with difficulties. Therefore, it was essential to find other improved routes to synthesize these compounds. In this respect, Herberich and coworkers were successful to find new improved route and able to synthesize boratabenzene and Boracyclohexadienes based on 2,4-pentadienylboranes in good and moderate yields [3, 4]. Recently, boratabenzene six ring heterocycle anion gained an enormous attention due to its ability to form various stable organometallic complexes with suitable transition metal cations [5, 6, 7, 8, 9, 10]. In this work, metalation reactions of bis (dialkylamino)-4-methyl- and -2,4-dimethyl-2,4-pentadienylboranes (Alkyl = Me, Et) were intensively studied to see in how far this novel route found by Herberich would be applicable to synthesize another Boratabenzene and Boracyclohexadienes derivatives that could be used as ligands in organometallic chemistry.

\*TMEDA=N,N,N,N-tetramethylethylenediamine,  
LiNEt<sub>2</sub>=Lithiumdiethylamide,  
THF=Tetrahydrofuran,  
LDA=Lithiumdiisopropylamide,  
LiTMP=Lithium-2,2,6,6-

tetramethylpiperidide, TMS=Tetramethylsilan,  
BuLi=n-Butyllithium

### Experimental

All materials were at least 99 % pure and supplied from Aldrich. The following apparatus were used in this work: NMR spectrometer: Varian VXR 500 MHz (<sup>1</sup>H 500 MHz, <sup>13</sup>C 126 MHz); Bruker WP 80 (<sup>1</sup>H: 80 MHz); Joel JNM PS 100(<sup>11</sup>B 32 MHz); Bruker WH 270 (<sup>13</sup>C 68 MHz); Mass spectrometer: Varian MAT CH5 (70 eV electron energy). All used procedures were achieved under nitrogen atmosphere and used dried glass ware liberated of oxygen and moisture. Liquid nitrogen was used, when very low temperatures (-78 °C) were required.

#### 1) Preparation of Bis(dialkylamino) chloroborane [11]:

In a 4 L three-necked round bottom flask, fitted with mechanical stirrer, 623 mL (6.0 mol)dialkylamine dissolved in 1 L pentane were introduced and cooled to -78 °C. To this solution 164 mL (2.0 mol) Borontrichloride, cooled at -78 °C, carefully added and the reaction mixture was stirred for 12h. The resulting solid material (hydrochloride) was filtered. After removing the solvent the product was obtained by fractional distillation. ClB(NEt<sub>2</sub>)<sub>2</sub>: B.p 86 °C /31 mbar, yield 44.5 %. As side product BCl<sub>2</sub>(NEt<sub>2</sub>) was isolated at 73 °C /33 mbar.

## 2) Preparation of 2,4-dimethyl-1,3-pentadiene and 2-methyl-1,3-pentadiene [12]:

In a 2 L three-necked round bottom flask 24.3 g (1.0 mol) Mg-span and 100 mL diethylether were introduced. To this content a solution of 62 mL (1.0 mol) methyl iodide in 100 mL diethylether, was added and refluxed for 1 h with stirring. To the content 0.8 mol (4-methylpent-3-en-2-one or 3-Penten-2-one) in 100 mL diethylether was then added under cooling and stirring. After 2 hours ice/water was slowly added at 0 °C. The resulting salt was dissolved in diluted acetic acid. The organic phase was separated and the aqueous layer was extracted with diethylether. The collected organic phases were washed with sodium carbonate and dried with sodium sulfate anhydrous. The resulting alcohol was refluxed with potassiumhydrogensulfate at 160 °C for 2 h. The resulting diene was separated from water, washed with sodiumcarbonate solution and dried from calcium chloride.

## 3) Preparation of Potassium 2,4-dimethyl- and 2-methyl-1,3-pentadienide [12]:

To a suspension of 5.0 g (44.5 mol) potassium-*tert*-butanate in hexane a 17.8 mL of 2.5 molar solution of Butyllithium in hexane was added slowly and stirred for 2 h at room temperature. Then (44.5 mol) 2,4-dimethyl- or 2-methyl-1,3-pentadiene in 16 mL pentane was added slowly. The content was stirred for 16 h at room temperature. The resulting suspended product was placed into the next step.

## 4) Preparation of bis(dialkylamino)-2,4-dimethyl-or4-methyl-2,4-pentadienylboranes [13]:

To a solution of 0.7 equivalent of bis(dialkylamino)chloroborane in 200 mL pentane, with regard to the potassium-2,4-dimethyl- or 2-methyl-1,3-pentadienide prepared above, 16 mL THF were added. Then the potassium pentadienide was added slowly with stirring for 1 h. The solution color turned from brown into yellow. The stirring was continued overnight. After filtration, removal the solvents and vacuum distillation the product was obtained. D1=Bis(dimethylamino)-4-methyl-2,4-pentadienylborane: yield 70%, Bp. 80 °C/10 mbar, D2=Bis(diethylamino)-4-methyl-

2,4-pentadienylborane,

D3=Bis(dimethylamino)-2,4-dimethyl-2,4-pentadien-ylborane, D4=Bis(diethyl-amino)-2,4-dimethyl-2,4-pentadienylborane. <sup>1</sup>H NMR δ/ppm; <sup>3</sup>J (Hz): isomer 4b-me-E-1: 6.06 d (15.56) 1H CH<sub>3</sub>CH=CH-CH<sub>2</sub>B, 5.72 d/t, 15.56/7.30 1H CH<sub>3</sub>CH=CH-CH<sub>2</sub>B, 4.77, s (br), 1H (cis-H)CH=CHCH<sub>3</sub>; 4.75, s (br) 1H (trans-H)CH=CHCH<sub>3</sub>; 2.66, s, 12H 2[N(CH<sub>3</sub>)<sub>2</sub>]; 1.81, s(br) 3H (cis-H)CH=CHCH<sub>3</sub>; 1.75, d (7.30) 2H -CH<sub>2</sub>B; <sup>13</sup>C NMR δ/ppm, <sup>1</sup>J (Hz): 143.8, s CH=CH-CH<sub>3</sub>-CH, 131.3 d(140.4) CH<sub>3</sub>CH=CH-CH<sub>2</sub>B, 129.6, d(140.6) CH<sub>3</sub>CH=CH-CH<sub>2</sub>B, 112.6 t(145.6) CH<sub>2</sub>=CHCH<sub>3</sub>; 40.0, q(126,5) 2[N(CH<sub>3</sub>)<sub>2</sub>]; 19.0 br CH<sub>2</sub>B; 18.7 s CH=CHCH<sub>3</sub>-CH; Mass m/z: 180 25% M<sup>+</sup>; 99 100% B(NMe<sub>2</sub>)<sup>+</sup>; 56 85% HBNMe<sub>2</sub><sup>+</sup>; δ <sup>11</sup>B NMR = 34 ppm

## 5) Lithium(TMEDA)-1-Dimethylamino-3-methylboratabenzene [3, 4]:

A solution of 0.6 mL (6.0 mmol) diethylamine in 15 mL THF was prepared. To this a solution of 2.4 mL of 2.5 molar butyllithium in 5 mL THF was added slowly at 0 °C. The content was then cooled down to -78 °C using liquid nitrogen. The resulting lithium diethylamide was added to one equivalent of TMEDA and 5 mL THF. Then a solution of 1.0 g (6.0 mmol) of Bis(dimethylamino)-4-methyl-2,4-pentadienylborane in THF was added under stirring. The content was then stirred at room temperature for 20 h. Following THF was removed and the resulting dark red oil is treated with pentane and cooled. A white crystalline product was obtained. yield 65 %, m.p 72 °C. <sup>1</sup>H NMR δ/ppm; <sup>3</sup>J (Hz): 6.95 dd(10.4/6.7) 1H; 5.45 d, (10.4) 1H at C2, 4.46 s, 1H at C6; 5.37 d(6.7) 1H at C4; 2.68 s, 6H, N(CH<sub>3</sub>)<sub>2</sub>; 2.21 s, 4H, CH<sub>2</sub>(TMEDA); 2.12 s, 3H meta-BC<sub>5</sub>H<sub>4</sub>-CH<sub>3</sub>, 2.8 s, 12H CH<sub>3</sub>(TMEDA); <sup>13</sup>C NMR δ/ppm, <sup>1</sup>J (Hz): 142.7, s -CH=C5(CH<sub>3</sub>)-CH=B; 134.5 d (126.4) -C3H=; 100.8 d(151.7) C4H=; 57.8, t(126.4) CH<sub>2</sub>(TMEDA); 45.7 q(126.4) CH<sub>3</sub>(TMEDA); 39.5 q, (126.4) N(CH<sub>3</sub>); 16.4 q(126.4) -CH=C5(CH<sub>3</sub>)-CH=B, δ <sup>11</sup>B NMR=30 ppm.

## 6) 4,4,5,5-tetramethyl-2-(4-methylpenta-2,4-dienyl)-[1, 2, 3]dioxaborolane [3,4]:

In a one neck round bottom flask 5.5 g (46.6 mmol) pinacol, dissolved in 16 mL

THF, was placed, and a solution of 9.2 g (46.6 mmol) bis(diethylamino)-4-methyl-2,4-pentadienylborane in THF was added slowly under stirring in a period of 30 min at room temperature. Stirring was continued for 16 h. Then the solvent was removed and product was distilled under vacuum. Yield 75 %, B.p. 83 °C / 10 mbar.  $^1\text{H}$  NMR  $\delta$ /ppm;  $^3\text{J}$  (Hz): 6.08, d(15.56) 1H,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}-\text{CH}_2\text{B}<$ ; 5.68, d/tr (15.56/7.63) 1H,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}-\text{CH}_2\text{B}<$ ; 4.77, s 2H,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}-\text{CH}_2\text{B}<$ ; 1.79 s. 3H,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}-\text{CH}_2\text{B}$ ; 1.72, d(7.63) 2H  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}-\text{CH}_2\text{B}$ ; 1.21, s 12H  $-\text{O}-\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}_3)_2-\text{O}-$ ;  $^{13}\text{C}$  NMR  $\delta$ /ppm,  $^1\text{J}$  (Hz): 142.8 s,  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}-$ ; 133.3, d(142.9)  $-\text{CH}=\text{CH}-\text{CH}_2-\text{B}<$ ; 125.8 d(142.9)  $-\text{CH}=\text{CH}-\text{CH}_2-\text{B}<$ ; 113.2 t(131.0)  $\text{CH}_2=\text{C}(\text{CH}_3)-$ ; 83.0 s  $-\text{O}-\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}_3)_2-\text{O}-$ ; 24.6 q (119.0)  $-\text{O}-\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}_3)_2-\text{O}-$ ; 18.6 q (J is not determinable)  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}=\text{C}$ ; 16.5 br.  $-\text{CH}_2-\text{B}<$ ;  $\delta$   $^{11}\text{B}$  NMR = 34 ppm; Mass m/z: 198 (42%)  $\text{M}^+$ ; 151 (39%)  $[(\text{CH}_3)_2\text{CH}-\text{CH}=\text{CH}-\text{CH}_2-\text{B}-\text{O}-\text{CH}_2\text{CH}_3]^+$ ; 108 (100%),  $\text{CH}_2=\text{CMe}-\text{CH}=\text{CH}-\text{CH}_2-\text{BO}^+$ ,

#### 7) Lithium(THF)[2,2,3,3-tetramethyl-1,4-dioxo-spiro[4,5]-5-boratadeca-6,8-diene]

- With Lithiumdiisopropylamide (LDA),
- With Lithium-2,2,6,6-tetramethylpiperidide (LiTMP); on every occasion procedure number 4 was applied for the metalation of Dioxaborolane.

#### 8) 5-Methyl-1-[2-trimethylsilyloxy-1,1,2-trimethylpropoxy]bora-2,4- and bora-2,5-cyclo-hexadiene [3, 4]:

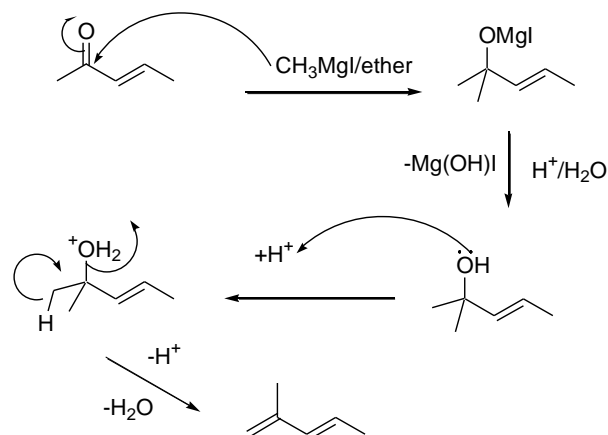
A double equivalent of chlorotrimethylsilane, dissolved in THF, was slowly added to the resulting salt from preparation step 7 at  $-78$  °C and stirred overnight. After removal of the solvent and distillation, dark brown oil was obtained.  $^1\text{H}$  NMR  $\delta$ /ppm;  $^3\text{J}$  (Hz): 1) 2, 5-isomer: 7.07 d(12.51) 2H<sub>2</sub>, H<sub>6</sub>; 6.23, dt(12.51/1.84) 2H<sub>3</sub>, H<sub>5</sub>; 3.00, tt (3.05/1.84) 2H<sub>3</sub>; 1.73 s 3H,  $\text{CH}_3$  at C5, ring; 1.39 s 6H, 2B-O-C(CH<sub>3</sub>)<sub>2</sub>, 0.10 s 9H, OSiMe<sub>3</sub>, 2) 2, 4-isomer: 6.45 dd(12.48/5.48) 1H<sub>3</sub>; 5.76 d(12.48) 1H<sub>4</sub>; 5.30 d(12.48) 1H<sub>2</sub>; 2.20 s 2H<sub>6</sub>; 1.85 s CH<sub>3</sub> at C5 ring, 1.37 s 6H BO-CMe<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-OSiMe<sub>3</sub>; 1.26 6H BO-C(CH<sub>3</sub>)<sub>2</sub>-C Me<sub>2</sub>-OSiMe<sub>3</sub>, 0.08 s

9H -OSiMe<sub>3</sub>; Mass m/z: 280 ( $\text{M}^+$ , 5%), 173 ( $\text{CMe}_2\text{CMe}_2\text{OSiMe}_3^+$ , 15%), 131 ( $\text{CMe}_2\text{OSiMe}_3^+$ , 60%), 107 ( $\text{C}_5\text{H}_5\text{MeBO}^+$ , 90%) 73 ( $\text{SiMe}_3^+$ , 100%);  $\delta$   $^{11}\text{B}$  NMR of 2,5-isomer = 37 ppm; of 2,4-isomer = 45 ppm.

## Results and Discussion

### Experiments with 2,4-Dimethyl-1,3-pentadiene:

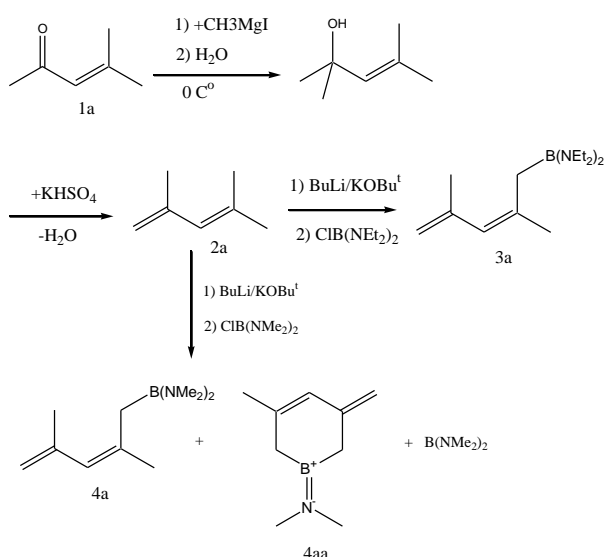
The starting materials 2-methyl-1,3-pentadiene and 2,4-dimethyl-1,3-pentadiene were obtained by converting  $\alpha,\beta$ -unsaturated carbonyls (4-methylpent-3-en-2-one (mesityl oxide) or 3-Penten-2-one) into dienes via alcohols. The Nucleophilic attack of Grignard reagent ( $\text{CH}_3\text{MgI}$ ) on the carbonyl carbon of mesityl oxide or 3-Penten-2-one gave an alkoxide tetrahedral intermediate, which is subsequently protonated by adding aqueous acid to yield the corresponding alcohols. Acid catalyzed dehydration of alcohols gave the desired dienes (Fig.(1)) [14].



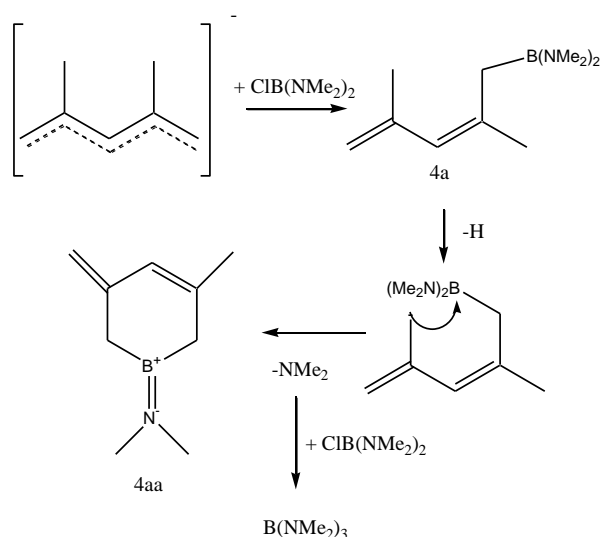
**Fig.(1) Mechanism for the nucleophilic addition of Grignard reagent to 3-Penten-2-one and the following dehydration reaction [14].**

$^{11}\text{B}$  NMR spectrum showed that the reaction of potassium-2,4-dimethyl-1,3-pentadienide with bis(dimethylamino)chloroborane yielded only the isomer *Z*-Bis(dimethylamino)-2,4-dimethyl-2,4-pentadienylborane 4a, however, with two side products with the ratio 1,15:1 4a:4aa (Fig.(2)). According to the suggested mechanism and  $^{11}\text{B}$  NMR spectrum the compound 4a could have been undergo abstraction of a proton yielding a carbanion that rearrange to form the side product 4aa (Fig.(3)). The next metalation reaction with Lithiumdiethylamide  $\text{LiNEt}_2$  did not accomplish due to the slightly product. The

$^{11}\text{B}$  chemical shifts for 4a, 4aa, and for  $\text{B}(\text{NMe}_2)_3$  are 44, 34, and 27 respectively.

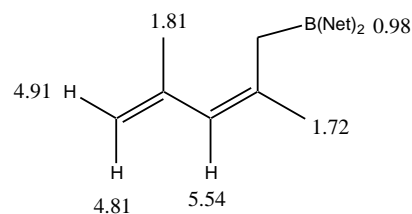


**Fig.(2) Reaction route to the formation of Bis(dialkylamino)-2,4-dimethyl-2,4-pentadienyl-borane 3a and 4a.**



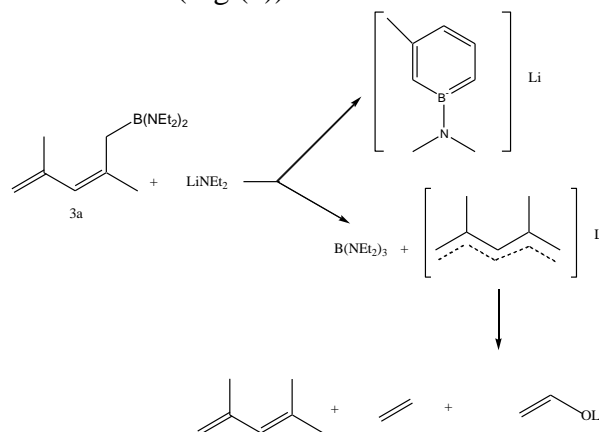
**Fig.(3) Suggested mechanism for the formation of 4a and 4aa.**

The Reaction of potassium-2,4-dimethyl-1,3-pentadienide with bis (diethylamino) chloroborane led to only the isomer *Z*-Bis (diethylamino)-2,4-dimethyl-2,4-pentadienylborane 3a which was characterized by  $^1\text{H}$  NMR (Fig.(4)). The reached regioselectivity here was attributed to the steric effect resulting from displacement of the methyl through ethyl group in the reagent bis(dialkylamino)chloroborane. The more demanding Ethyl group would prevent the attack leading to the side reactions (Fig.(3)).



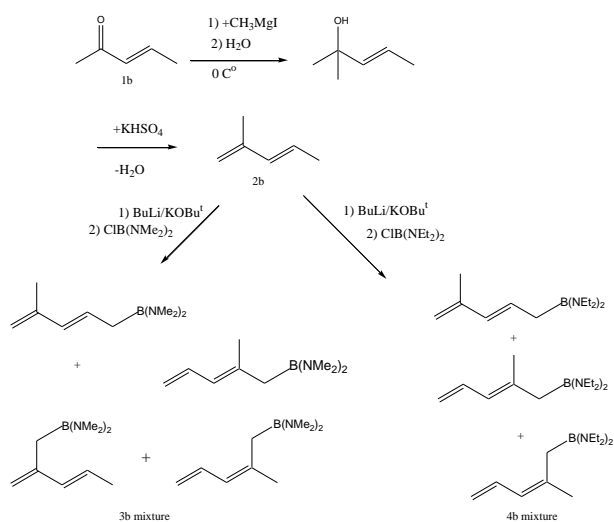
**Fig.(4) Structure of *Z*-Bis(diethylamino)-2,4-dimethyl-2,4-pentadienylborane 3a with  $^1\text{H}$  NMR data.**

Metalation of Bis(diethylamino)-2,4-dimethyl-2,4-pentadienylborane 3a with  $\text{LiNEt}_2/\text{TMEDA}$  in THF led to the target product boratabenzene, however, together with many side products. The reason was obviously the nucleophilic attack at the boron atom and reaction of the formed carbanion with the solvent THF (Fig.(5)).

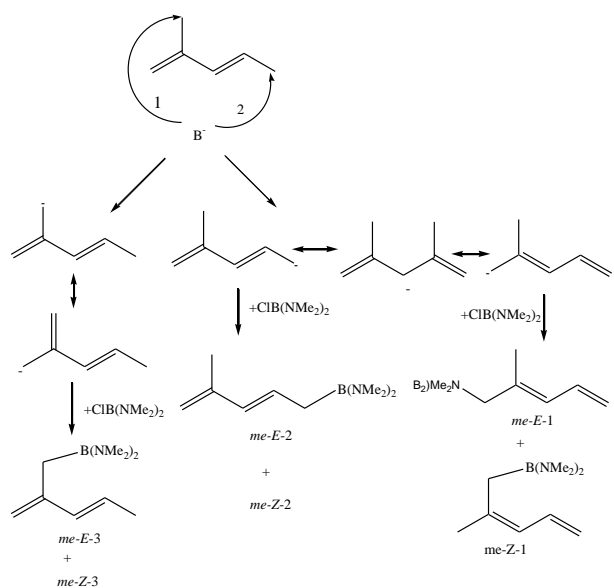


**Fig.(5) Suggested metalation reactions of Bis(diethylamino)-2,4-dimethyl-2,4-pentadienyl-borane 3a with  $\text{LiNEt}_2/\text{TMEDA}$  in THF.**

**Experiments with 2-Methyl-1,3-pentadiene**  
According to the  $^{13}\text{C}$  NMR spectrum, four geometrical isomers (me-*E*-3, me-*E*-2 and me-*E*-1+me-*Z*-1) of bis(dimethylamino)-4-methyl-2,4-pentadienylborane 3b were detected. Attack of 2-methyl-1,3-pentadiene might lead to two main carbanions of potassium-2-methyl-1,3-penta-dienide (Fig.(6)). Each Carbanion is resonance stabilized and can react with the reagent bis (dimethylamino) chloroborane. Accordingly three constitutional isomers and their other *Z* isomers of 3b could be formed which all have  $^{11}\text{B}$  chemical shift 33 ppm.



**Fig.(6) Formation of different isomers of *is*(dialkylamino)-4-methyl-2,4-pentadienylborane 3b and 4b.**

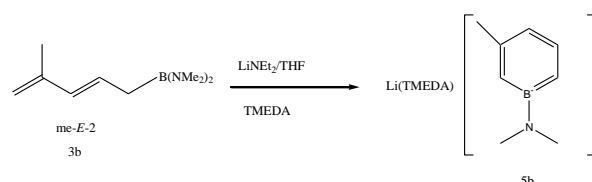


**Fig.(7) Reaction possibilities of potassium 2-methyl-1,3-pentadienide under metalation conditions.**

According to  $^{13}\text{C}$  and  $^1\text{H}$  NMR data the reaction of potassium 4-methyl-2,4-pentadienide with bis (diethylamino) chloroborane produced three geometrical isomers of bis(diethylamino)-4-methyl-2,4-pentadienylborane 4b: (et-*E*-1, et-*E*-2, and et-*Z*-1). The formation of other E/Z isomers was not easily reached due to the demanding Ethyl group in comparison with methyl group. In both cases it was established that the most stable isomer formed was the most thermodynamic stable one me-*E*/1 and et-*E*/1. Another reason for this statement was

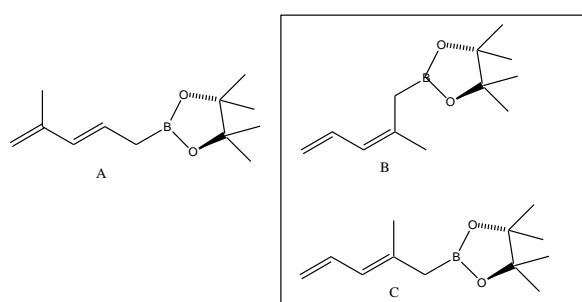
the favorable attack on the best possible position carbanion potassium pentadienide. Displacement of ethyl group through methyl group caused an increase in the concentration of formed et-*E*-2 (85 %) in comparison with me-*E*-2 (50 %).

Spectroscopic data shows that the metalation reaction of this isomer mixture 3b with  $\text{LiNEt}_2/\text{TMEDA}$  in THF yielded the aimed product lithium(TMEDA)-1-Dimethylamino-3-methyl-boratabenzene 5b with high selectivity (Fig.(8)).



**Fig.(8) Chemical Equation to the Formation of bis (dimethylamino)-4-methyl-2,4-pentadienylborane.**

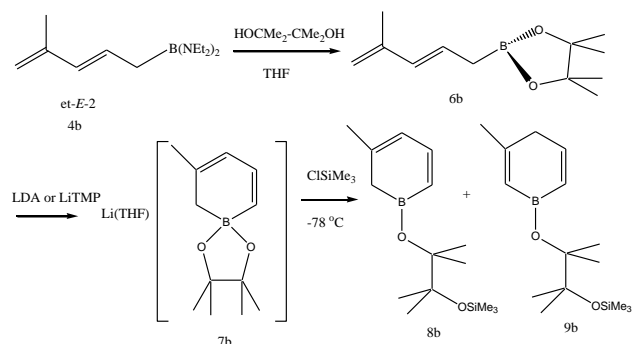
The reaction of pinacolHOCMe-CMeOH with bis(diethylamino)-4-methyl-2,4-pentadienylborane 4b in THF yielded smoothly the compound dioxaborolanes 6b as a three isomers mixture whereby the isomer A was the predominant one with the ratio 2,2:1 ; A: (B+C) (Fig.(9)).



**Fig.(9) Structure of isomer mixture of dioxaborolanes 6b.**

Metalation of 6b with LDA or with LiTMP at  $-78\text{ }^\circ\text{C}$  led to formation of white precipitate of dioxaborolane 7b that was converted into 8b and 9b with the ratio 1,5:1,0 through ring opening reaction with the electrophile  $\text{ClSiMe}_3$ . Spectroscopic characterization of the products 8b and 9b indicates indirectly the structure of 7b. In both metalation cases three  $^{11}\text{B}$  NMR signals were detected 37, 45, and 32 ppm for 8b, 9b, and for 4b respectively. Metalation with LDA proceeded with high and

improved yield in comparison with the demanding base LiTMP due to steric effect (Fig.(10)). Table (1) shows the  $^{11}\text{B}$  NMR chemical shifts for the most compound synthesized in this work.



**Fig.(10) Reaction route to spiroborate 7b and to boracyclohexadiene 8b and 9b.**

## Conclusions

In This work it was confirmed that metalation reactions using Lithiumdiethylamide in THF/TMEDA was applicable especially for 2-methyl-1,3-pentadiene and in lesser extent for 2,4-dimethyl-1,3-pentadiene. Steric effects found to have an elemental role to determine the products. Variation of Solvent, base, stoichiometricmol ratio, and bis(dialkyl)chloroborane have to be intensively studied to reach the right conditions for each substrate.

## References

- [1] Ashe, A.J.; Shu, P. "The 1-Phenylborabenzene Anion" J. Am. Chem. Soc., 93, 1804-1805, 1971.
- [2] Herberich, G. E.; Greiss, G. "Derivate des Borabenzols, I Kobalt-Komplexe des 1-Phenyl- und 1-Methylborinat-Ions1)" Chem. Ber. 105, 3413-3423, 1972.
- [3] Herberich, G. E.; Schmidt, B.; Englert, U.; Wagner, T. "Borabenzene derivatives. 2,4-Pentadienylboranes as Key Intermediates of a Novel Route to Boracyclohexadienes and Boratabenzens" Organometallics, 12, 2891-2893, 1993.
- [4] Schmidt, B. "Ein Neuer Zugang zu Derivaten des Borabenzols" Ph. D. thesis, RWTH Aachen, Germany, pp. 23, 64, 1994.
- [5] Kudinov, A. R.; Loginov, D. A.; Starikova, Z. A.; Petrovskii, P. V. "Dicationic Triple-decker Complexes with a Bridging Boratabenzene Ligand" J. Organomet. Chem. 649, 136–140, 2002.
- [6] Yuan, Y.; Wang, X.; Li, Y.; Fan, L.; Xu, X.; Chen, Y.; Li, G.; Xia, W. "Rapid Entry to Functionalized Boratabenzene Complexes through Metal-Induced Hydroboration at the Anionic 1-H-Boratabenzene Ligand" Organometallics, 30 (16), 4330–4341, 2011.
- [7] Barnes, S. S.; Légaré, M. A.; Maron, L.; Fontaine, F. G. "Reactivity of a Cl-boratabenzene Pt(II) Complex with Lewis Bases: Generation of the Kinetically Favoured Cl-Boratabenzene Anion" Dalton Trans., 40, 12439-12442, 2011.
- [8] Cui, P.; Chen, Y.; Li, G.; Xia, W. "Versatile Reactivities of ansa-Heteroborabenzene Divalent Ytterbium Amide toward Alkali-Metal Salts and the Generation of Heterometallic Ytterbium –Alkali-Metal Boratabenzene Complexes" Organometallics, 30 (7), 2012-2017, 2011.
- [9] Yuan, Y.; Chen, Y.; Li G.; Xia, W. "Synthesis and Structural Features of Boratabenzene Rare-Earth Metal Alkyl Complexes" Organometallics, 29 (17), 3722–3728, 2010.
- [10] Ashe, A. J.; Al-Ahmad, S.; Kampf, J. W. "BoratabenzeneZirconium(II) Complexes" Angew. Chem., Int. Ed. 36(18): 2014-2016, 1997.
- [11] Collective Authors, "Organikum", 17. Auflage, VEB DeutscherVerlag der Wissenschaft, Berlin, pp. 161-163, 1988.
- [12] Bahl, J. J.; Bates, R. B.; Gordon, B. "2,3-Dimethylenebutadiene Dianion; Convenient Procedure for Allylic Metalation of Conjugated Dienes" J. Org.Chem. 44, 2290-2291, 1979.
- [13] Fujitta, K.; Schlosser, M. "A Convenient and Diastereoselective Route to Homoallyl Alcohols: Addition of (z)- or (e)-Alkenyl-dimethoxyboranes to Aldehydes" Helv. Chim. Acta.65, 1258–1263, 1982.
- [14] Sarker, S. D.; Nahar, L.; "Chemistry for Pharmacy Students, General, Organic and Natural Product Chemistry", first Edition, John Wiley & Sons Ltd, England, pp. 210-211, 2007.

## الخلاصة

تمت دراسة التفاعلات الفلزية للمركبين بورينات ال-  
٢،٤- ثنائي مثيل-٢،٤- بنتادائينات وال ٢- مثيل-٢،٤-  
بنتادائينات المحضرة من تفاعل ٢- مثيل- ١،٣- بنتادائينايد  
البوتاسيوم و ٢،٤- ثنائي مثيل-١،٣- بنتادائينايد البوتاسيوم  
مع كلورو بس (ثنائي الكيل امينو) بوران حيث الكيل = مثيل  
أو أثيل. لانجاز التفاعلات المذكورة اعلاه استخدم ثنائي مثيل  
اميد الليثيوم كقاعدة مذابة في التتراهيدروفوران. نتيجة ذلك  
تم تحضير المركب بس (ثنائي مثيل امينو) -٣-مثيل بوراتا  
بنزين الليثيوم (تميدا) بناتج متوسط وكذلك المركبين بورا -  
٢،٤ - وبورا -٢،٥- سايكلوهكسداين بكمية جيدة. لغرض  
انجاز هذه الدراسة تم استخدام مطياف الكتلة وأطياف الرنين  
النووي المغناطيسي لنواة ال ١١ - بورون ، ١٣ - كربون،  
و ١- هيدروجين. أثبتت النتائج بان الاعاقة الفراغية كان لها  
تأثير مهم في تحديد نواتج التفاعلات.