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Synthesis, structure, and reactivity of β-diketiminate boron(III) complexes

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Abstract

The chemistry of boron supported by the β-diketiminate ligand, tolylnacnac (tolylnacnacH=2-*N*-*p*-tolylamino-4-*N*-*p*-tolylimino-2-pentene), has been investigated. (tolylnacnac)Li reacted with one equivalent of $BF_3{\cdot}OEt_2$ to afford (tolylnacnac)BF_2 (**1**) in 46% yield. The structure of compound **1** was solved indicating that the diketiminate ligand is η^2-bound to B to form a six-membered heterocycle. While alkylation of compound **1** can be effected with alkyl lithium or Grignard reagents, nucleophilic addition to the diketiminate ligand occurred in the reaction between compound **1** and MeLi to afford [η^2-$(Me)_2$C(Ntolyl)CH=C(Ntolyl)Me]BMe (**2**). For Me_3SiCH_2Li, deprotonation of the diketiminate ligand afforded [η^2-CH_2=C(Ntolyl)CH=C(Ntolyl)Me]BCH_2SiMe_3 (**3**). Conversely, alkyl Grignard reagents selectively delivered two alkyl groups to the boron center, and several pseudo-tetrahedral (tolylnacnac)BR_2 (**4a**–**d**; **a**, R=Me, **b**, R=^{n}Pr, **c**, R=vinyl, **d**, R=allyl) complexes have been prepared. The structures of compounds **2**, **3**, and **4a** were solved, and variations in B–N and B–C metrical data for compounds **2** and **4a** were correlated to bond order, inductive effects of the co-ligands, and hybridization of the boron center. The reaction between compound **4a** and tris(pentafluorophenyl)boron gave [(tolylnacnac)BMe]$^+$[$MeB(C_6F_5)_3$]$^-$ (**5**). Compound **5** reacted with pyridine to give an adduct, [(tolylnacnac)B(py)Me]$^+$[$MeB(C_6F_5)_3$]$^-$ (**6**).

Keywords: Three-coordinate boron; Four-coordinate boron; X-ray structure; β-Diketiminate ligand; Abstraction reaction

1. Introduction

Recently, several research groups have examined nitrogen-based ligands as complements to cyclopentadienyl ligands. Popular chelating ligands that contain two nitrogen coordination sites include bis(amide) [1], bis(amidinate) [2], α- and β-iminoamine [3,4], and aminotroponiminate [5] ligands. β-Diketiminates have been known for many years, and were initially employed in spectroscopic studies of coordination compounds [6,7]. In synthetic applications, the chemistry of this ligand class is dominated by dianionic tetraazamacrocyclic analogs [8], with examples of monoanionic diketiminate complexes having been described more recently. The facile synthesis of acyclic β-iminoamines from 2,4-pentanedione and primary aryl amines [9] makes β-diketiminate ligands attractive candidates in stoichiometric and catalytic applications since steric and electronic requirements of the ligand can be fine tuned by varying the amine source [4,10–15].

We have begun to explore chemistry of the main-group and transition metal complexes supported by the tolylnacnac ligands (tolylnacnacH=2-*N*-*p*-tolylamino-4-*N*-*p*-tolylimino-2-pentene) [16–18]. We recently reported that the tolylnacnac ligand stabilizes aluminum alkyl complexes [19]. Remarkably, (tolylnacnac)$AlMe_2$ does not react with moisture at room temperature and can be stored in the air without decomposition for months, illustrating the kinetic stability imparted by diketiminate ligands. Herein, we want to describe chemistry and structures of related boron complexes.

2. Experimental

2.1. General considerations

All manipulations were carried out using standard Schlenk techniques. Solvents were freshly distilled over sodium/benzophenone ketyl and were saturated with dinitrogen before use. Elemental analyses (C, H, N) were performed by Desert Analytics, Tucson, Arizona or Atlantic Microlabs, Inc. Varian VXR-300 NMR spectrometer was used to record ^{1}H (299.96 MHz), ^{11}B (96.23 MHz), ^{13}C (75.43 MHz) and ^{19}F (282.203 MHz) NMR spectra

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unless noted otherwise. ^{1}H and ^{13}C chemical shifts were referenced to the residual solvent peaks. ^{11}B chemical shifts were referenced to a neat $BF_3{\cdot}OEt_2$ (0 ppm) external standard. ^{19}F NMR spectra were referenced to a neat $CFCl_3$ (0 ppm) external standard. $CDCl_3$ was dried over activated 4-Å molecule sieves, and vacuum transferred to an air-free flask. C_6D_6 was dried over activated 4-Å molecule sieves, and vacuum transferred to a sodium-mirrored air-free flask. Uncorrected melting points of crystalline samples in sealed capillaries (under an argon atmosphere) were reported as ranges. Low resolution mass spectra were obtained on a portable Trio-1 VG Masslab Ltd. mass spectrometer and were reported in the form (M, %I), where M was the highest mass observed for a molecular ion or fragment peak, and %I was the intensity of the peak relative to the most intense peak in the spectrum. A YSI model 31A conductivity bridge with an Orion conductivity cell 01801A was used to measure conductivities at room temperature.

$^{n}BuLi$ and BCl_3 were purchased from the Aldrich Chemical Co. and were used as received. $BF_3{\cdot}OEt_2$ was distilled over calcium hydride under reduced pressure before use. 2-*p*-tolylamino-4-*p*-tolylimino-2-pentene (tolylnacnacH) was prepared by straightforward modification of the literature method [6]. $B(C_6F_5)_3$ was prepared from BCl_3 and C_6F_5Li [38]. MeLi was prepared from Li and $ClCH_3$ and was stored as a 1.4 M solution in ether. $LiCH_2(SiMe_3)$ was prepared from Li and $ClCH_2SiMe_3$. Grignard reagents were prepared from magnesium turnings and corresponding organic halides in ether. Concentrations of the ethereal solutions were determined by titration before use.

2.2. Syntheses of compounds

2.2.1. (Tolylnacnac)BF_2 (**1**)

A 10-ml toluene solution of Li(tolylnacnac) (7.0 g, 25 mmol) was added to a stirred 20-ml toluene solution of freshly distilled $BF_3{\cdot}OEt_2$ (3.5 g, 25 mmol) at 0°C. Upon warming to room temperature, a precipitate formed. After stirring for 12 h, the mixture was filtered and the filtrate was concentrated to afford compound **1** as yellow crystals (3.7 g, 46%). mp 189–190°C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.87 (s, 6H), 2.33 (s, 6H), 5.16 (s, 1H), 7.08–7.17 (m, 8H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 21.03, 21.31, 95.15, 127.2, 129.4, 136.8, 138.5, 163.5; ^{11}B (96 MHz, $CDCl_3$) δ 2.0 (t, 1:2:1 J=29.1 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −128.9 (q, 1:1:1:1, J=29.8 Hz). LRMS 326.2 (M^+, 45). Anal. Calcd. for $C_{19}H_{21}BF_2N_2$: C, 69.96; H, 6.49; N, 8.58. Found C, 69.74; H, 6.45; N, 8.44.

2.2.2. [η^2-$(Me)_2C$(Ntolyl)CH=C(Ntolyl)Me]BMe (**2**)

A stirred suspension of **1** (0.88 g, 2.7 mmol) in 20 ml diethyl ether was treated with LiMe (1.4 M, 3.8 ml, 5.4 mmol) ether solution at 0°C and the reaction mixture was warmed to room temperature. After stirring for 12 h, the mixture was filtered and the solvent was removed from the filtrate to give a yellow oil. The oil was extracted with pentane and the solvent volume was reduced to ~2 ml. Compound **2** crystallized upon standing overnight at −78°C as pale yellow crystals (0.52 g, 61%). mp 87–90°C (dec); ^{1}H NMR (500 MHz, C_6D_6) δ −0.009 (s, 3H), 1.33 (s, 6H), 1.58 (d, J=1.0 Hz, 3H), 2.07 (s, 3H), 2.12 (s, 3H), 4.45 (q, J=1.0 Hz, 1H), 6.82 (d, J=8.3 Hz, 2H), 6.90 (m, 4H), 7.05 (d, J=8.3 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) δ 1.7 ($\upsilon_{1/2}$=50 Hz), 20.87, 20.91, 21.23, 31.87, 54.94, 109.0, 129.1, 129.4, 130.1, 132.0, 135.1, 135.2, 143.0, 143.2; ^{11}B (96 MHz, $CDCl_3$) δ 30.7 ($\upsilon_{1/2}$=283 Hz). Anal. Calcd. for $C_{21}H_{37}BN_2$: C, 79.25; H, 8.55; N, 8.80. Found C, 79.03; H, 8.52; N, 8.78.

2.2.3. [η^2-CH_2=C(Ntolyl)CH=C(Ntolyl)Me]BCH_2SiMe_3 (**3**)

A 100-ml Schlenk tube was charged with **1** (0.46 g, 1.4 mmol) and $LiCH_2SiMe_3$ (0.26 g, 2.8 mmol) in a glovebox. Diethyl ether (20 ml) was added to the mixture at 0°C with stirring. After 30 min, the mixture was filtered and the solvent was removed under vacuum. The resultant orange oil was taken into pentane, and compound **3** crystallized as a pale yellow solid (0.25 g, 47%) upon standing at −80°C overnight. mp 78–80°C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.44 (s, 9H), −0.13 (s, 2H), 1.57 (s, 3H), 2.34 (m, 6H), 2.83 (s, 1H), 3.51 (s, 1H), 5.40 (s, 1H), 6.98 (d, J=8.1 Hz, 2H), 7.05 (d, J=8.1 Hz, 2H), 7.16 (d, J=8.1 Hz, 2H), 7.20 (d, J=8.1 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 1.07, 5.06 ($\upsilon_{1/2}$=43 Hz), 20.90, 20.97, 21.10, 79.34, 104.7, 129.3, 129.6, 130.0, 135.8, 136.0, 140.4, 141.4, 142.1, 149.4; ^{11}B NMR (96 MHz, $CDCl_3$) δ 33 ($\upsilon_{1/2}$=475 Hz). LRMS 373 (M^+–H, 55). Anal. Calcd. for $C_{23}H_{31}BN_2Si$: C, 73.78; H, 8.55; N, 7.48. Found C, 73.52; H, 8.29; N, 7.45.

2.2.4. (Tolylnacnac)BMe_2 (**4a**)

A stirred suspension of **1** (0.48 g, 1.5 mmol) in 15 ml diethyl ether was treated with an ethereal solution of MeMgI (1.2 M, 2.4 ml, 2.9 mmol) at 0°C. After 5 min, the mixture was filtered and the solvent was removed under vacuum. The crude product was extracted with pentane, and compound was isolated as yellow crystals (0.31 g, 66%) upon standing at −80°C overnight. mp 115–118°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.44 (s, 6H), 1.66 (s, 6H), 2.31 (s, 6H), 4.82 (s, 1H), 6.90 (d, J=8.1 Hz, 4H), 7.09 (d, J=8.1 Hz, 4H); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) δ 8.22 (br, s, $\upsilon_{1/2}$=64 Hz), 20.92, 21.77, 95.18, 127.54, 129.46, 135.5, 143.36, 162.23; ^{11}B NMR (96 MHz, C_6D_6) δ 1.07 (s, $\upsilon_{1/2}$=259 Hz). LRMS 318 (M^+ 1), 303 (M^+–Me, 100). Anal. Calcd. for $C_{21}H_{27}BN_2$: C, 79.25; H, 8.55; N, 8.80. Found C, 79.32; H, 8.61; N, 8.76.

2.2.5. (Tolylnacnac)B^nPr_2 (**4b**)

Compound **4b** was prepared in a similar fashion to

compound **4a** from **1** and ^{n}PrMgBr in 56% yield as bright yellow crystals. mp 98–102°C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.11 (m, 4H), 0.73 (t, J=6.9 Hz, 6 H), 1.20 (m, 4H), 1.63 (s, 6H), 2.34 (s, 6H), 4.59 (s, 1H), 6.97 (d, J=8.1 Hz, 4H), 7.10 (d, J=8.1 Hz, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 18.52, 19.35, 20.98, 22.03, 27.8 ($\upsilon_{1/2}$=34 Hz), 93.56, 127.47, 128.8, 135.4, 142.5, 163.8; ^{11}B NMR (96 MHz, $CDCl_3$) δ 4.3 ($\upsilon_{1/2}$=377 Hz). Anal. Calcd. for $C_{25}H_{35}BN_2$: C, 80.21; H, 9.42; N, 7.48. Found C, 80.44; H, 9.54; N, 7.34.

2.2.6. (Tolylnacnac)B(C_2H_3)$_2$ (4c)

Compound **4c** was prepared in a similar fashion to compound **4a** from compound **1** and (C_2H_3)MgBr in 50% yield as yellow solid. mp 85–88°C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.79 (s, 6H), 2.29 (s, 6H), 5.03 (s, 1H), 5.02 (dd, J=4.5, 13.2 Hz, 2H), 5.28 (dd, J=4.5, 13.2 Hz, 2H), 5.87 (dd, J=4.5, 13.2 Hz, 2H), 6.93 (d, J=8.1 Hz, 4H), 7.04 (d, J=8.1 Hz, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 21.04, 21.88, 96.70, 121.4, 127.4, 128.8, 135.4, 142.4, 148.1 ($\upsilon_{1/2}$=30 Hz), 162.1; ^{11}B NMR (96 MHz, $CDCl_3$) δ −1.2 ($\upsilon_{1/2}$=240 Hz). Anal. Calcd. for $C_{23}H_{27}BN_2$: C, 80.52; H, 8.16; N, 8.17. Found C, 80.44; H, 8.04; N, 8.07.

2.2.7. (Tolylnacnac)B(C_3H_5)$_2$ (4d)

Compound **4d** was prepared from compound **1** and freshly prepared (C_3H_5)MgBr in 69% as a pale yellow solid. mp 53–58°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (d, J=7.5 Hz, 4H), 1.64 (s, 6H), 2.32 (s, 6H), 4.59 (m, 4H), 4.73 (s, 1H), 5.78 (m, 1H), 7.02 (d, J=8.1 Hz, 4H), 7.09 (d, J=8.1 Hz, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 20.80, 21.99, 30.98 ($\upsilon_{1/2}$=32 Hz), 95.27, 110.6, 127.9, 129.0, 135.8, 142.0, 142.4, 163.9; ^{11}B NMR (96 MHz, $CDCl_3$) δ 0 ($\upsilon_{1/2}$=31 Hz). Anal. Calcd. for $C_{25}H_{31}BN_2$: C, 81.08; H, 8.44; N, 7.56. Found C, 80.77; H, 8.40; N, 7.50.

2.2.8. [(Tolylnacnac)BMe]$^{+}$[MeB(C_6F_5)$_3$]$^{-}$ (5)

Toluene solutions of B(C_6F_5)$_3$ (0.54 g, 1.0 mmol) and **4a** (0.34 g, 1.0 mmol) were combined at 0°C with stirring. After 10 min, the reaction mixture was concentrated to ~2 ml and layered with pentane. After cooling to −30°C overnight, an oily solid deposited at the bottom of the Schlenk flask. The mother liquor was decanted and the solid was washed with pentane. After drying under high vacuum, compound **5** was collected as colorless solid (0.61 g, 70%). mp 83–87°C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27 (s, 3H), 0.41 (s, br, 3H), 2.25 (s, 6H), 2.42 (s, 6H), 6.73 (s, 1H), 6.94 (d, J=8.1 Hz, 4H), 7.34 (d, J=8.1 Hz, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 1.43 (br, $\upsilon_{1/2}$=30 Hz, 10.7 (br, $\upsilon_{1/2}$=113 Hz), 21.03, 22.67, 111.62, 124.95, 128.0 (B–C, $\upsilon_{1/2}$=120 Hz), 131.4, 136.5, (d, $^{1}J_{C-F}$=246 Hz), 137.3, 137.4 (d, $^{1}J_{C-F}$=242 Hz), 140.5, 148.2 (d, $^{1}J_{C-F}$=236 Hz), 170.6; ^{11}B NMR (96 MHz, $CDCl_3$) δ −14.8 ($\upsilon_{1/2}$=30 Hz), 37.1 ($\upsilon_{1/2}$=1200 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −167.2 (m), −164.5 (m), −132.9 (m). Anal. Calcd. for $C_{39}H_{27}B_2F_{15}N_2$: C, 56.42; H, 3.28; N, 3.37. Found C, 56.10; H, 3.24; N, 3.33. For conductivity measurements, solutions were prepared in the glovebox. The molar conductivity of a methylene chloride solution of [(tolylnacnac)BMe]$^{+}$[MeB(CF_5)$_3$]$^{-}$ (4.7×10^{-3} M) was 1.6×10^{-2} Sm^{2} mol^{-1}. The molar conductivity of [^{n}Bu_4N]$^{+}$$Br^{-}$ solution at the same concentration was $\Lambda_M=1.2\times10^{-2}$ Sm^{2} mol^{-1}.

2.2.9. [(Tolylnacnac)B(py)Me]$^{+}$[MeB(C_6F_5)$_3$]$^{-}$ (6)

A stirred suspension of compound **5** (0.30 g, 0.36 mmol) in 5 ml toluene was treated with an excess of pyridine (0.5 ml, 6.2 mmol) at 0°C. Upon addition, the mixture turned yellow. The volatile materials were removed under vacuum, and the resulting yellow oil was triturated with pentane to give compound **6** as yellow solid (0.25 g, 76%). mp 107–109°C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.073 (s, 3H), 0.48 (s, br, $\upsilon_{1/2}$=10 Hz, 3H), 1.97 (s, 6H), 2.32 (s, 6H), 5.76 (s, 1H), 6.53 (d, J=8.1 Hz, 4H), 7.13 (d, J=8.1 Hz, 4H), 7.63 (dd, J=5.1, 7.5 Hz, 2H), 8.11 (t, J=7.5 Hz, 1H), 8.49 (d, J=5.1 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 5.26 ($\upsilon_{1/2}$=47 Hz), 10.2 ($\upsilon_{1/2}$= 141 Hz), 20.88, 22.30, 101.8, 125.8, 126.1, 129.0 ($\upsilon_{1/2}$= 150 Hz), 130.6, 136.1 (d, $^{1}J_{C-F}$=247 Hz), 137.4 (d, $^{1}J_{C-F}$= 240 Hz), 138.5, 139.0, 141.8, 145.7, 148.2 (d, $^{1}J_{C-F}$=227 Hz), 168.4; ^{11}B NMR (96 MHz, $CDCl_3$) δ −15.23 (s, $\upsilon_{1/2}$=65 Hz), −4.19 (s, $\upsilon_{1/2}$=80 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −167.2 (m), −164.6 (m), −132.7 (m). Anal. Calcd. for $C_{44}H_{32}B_2F_{15}N_3$: C, 58.11; H, 3.55; N, 4.62. Found C, 58.22; H, 3.63; N, 4.54.

2.3. X-ray analysis

X-ray quality crystals of **1** were grown from a concentrated toluene solution at −30°C. X-ray quality crystals of **2**, **3**, and **4** were grown from concentrated pentane solutions at −30°C.

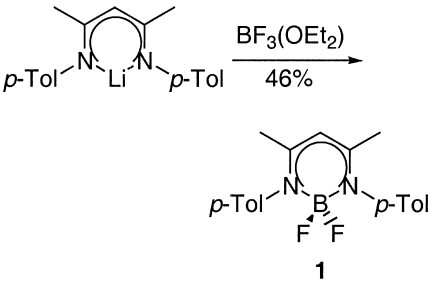
Crystals of **1**, **2, 3** and **4a** were coated with Paratone-*N* oil and suitable single crystals were selected under a microscope and mounted on a glass fiber. The crystals were then transferred to the goniometer of a Siemens SMART CCD diffractometer using Mo Kα radiation (λ= 0.71073 Å). Data were collected as 30 s per frame at 173 K. initial cells were calculated by the Smart from three sets of 15 frames. All data sets were collected over a hemisphere of reciprocal space. SAINT was used to integrate 1025 frames and to generate the *raw* file [39]. Final unit cell parameters were obtained by least-squares refinement of strong reflections obtained. Absorption correction and time decay were applied to the data by SADABS. In all structures, the non-hydrogen atoms were found using SHELXS-86. Atomic coordinates and thermal parameters were refined using the full-matrix least-squares program,

SHELXL-97, and calculations were based on F^2 data. All non-hydrogen atoms were refined using anisotropic thermal parameters. All hydrogen atoms were placed in calculated positions using HFIX. All crystallographic computations were performed on Silicon Graphics Indigo computers.

3. Results and discussion

When $BF_3{\cdot}OEt_2$ was treated with Li(tolylnacnac) in toluene, the β-diketiminate boron difluoride complex, (tolylnacnac)BF_2 (**1**) was isolated in 46% yield (Eq. (1)). Compound **1** was characterized by conventional spectroscopic methods. Variable temperature (VT) ^{1}H NMR data (toluene-d_8, −50 to 50°C) are consistent with the presence of a C_2 axis containing B and the methine carbon of the diketiminate ligand in compound **1**. The ^{11}B NMR spectrum of compound **1** exhibits a 1:2:1 triplet ($^1J_{B-F}$=29.1 Hz) at δ 2.0, and the ^{19}F NMR spectrum reveals a 1:1:1:1 quartet at δ −128.9 with a similar value of $^1J_{B-F}$. The solution NMR data are consistent with a monomeric boron species [20].

Eq. (1)



1

The solid state structure of compound **1** was solved (Fig. 1). Cell parameters and refinement details for compound **1** are listed in Table 1, which contains data for all structures in this paper. The structure contains a pseudo-tetrahedral boron center and the diketiminate ligand is η^2-bound to boron through the nitrogen atoms. The atoms in the diketiminate backbone (C(2), C(3), C(4), N(1) and N(2)) and B are essentially coplanar. The similar bond distances for N(1)–B (1.550(3) Å) and N(2)–B (1.553(3) Å) the C–C and N–C pairs (C(2)–C(3)=1.384(3) Å, C(3)–C(4)=1.401(3) Å; N(1)–C(2)=1.339(3) Å, N(2)–C(4)=1.347(3) Å) suggest that the C_3N_2 backbone is delocalized [21]. Delocalization is confirmed by chemical equivalence of symmetry related protons between −50 and +50°C. The average B–F bond distances of 1.404(4) Å in compound **1** (B–F(1), 1.411(3) Å; B–F(2), 1.396(3) Å) are very close to those of 2,2-difluoro-1,3,4,6-tetramethyl-3-aza-1-azonia-2-bora-4,6-cyclohexadiene (Chart 1 **A**) (B–F 1.403(2) Å) [21] and 4,4-difluoro-1,3,5,7,8-pentamethyl-3a,4a-diaza-4-bora-*s*-indacene (Chart 1 **B**) (B–F 1.394(3) Å) [22,23].

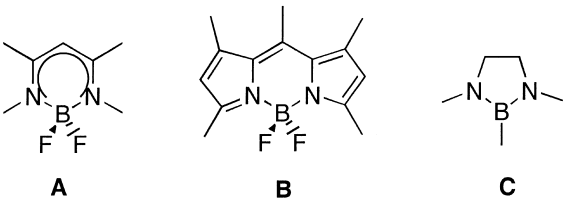


Chart 1.

3.1. Alkylation chemistry

Related difluoride compounds related to compound **1** have been described in the literature. For example, Vinamidine boron difluoride (**A**) has been used as a ligand, binding in η^5-fashion, to stabilize the tricarbonylchromium fragment [10]. Since our interests centered on the reactivity at boron, alkylation of compound **1** with various lithium and magnesium reagents was examined (Scheme 1).

When compound **1** was treated with two equivalents of MeLi in ether, [η^2-$(Me)_2$C(Ntolyl)CH=C(Ntolyl)Me]BMe (**2**) was isolated in 61% yield. The desired dimethyl boron compound could not be detected in the crude reaction mixture. The inequivalent methyl resonances for the ligand backbone in the ^{1}H NMR spectrum for compound **2** initially suggested a structure where the tolylnacnac ligand was η^1-bound to the BMe_2 moiety. However, spectroscopic data did not support the 'arm-off' structure since the

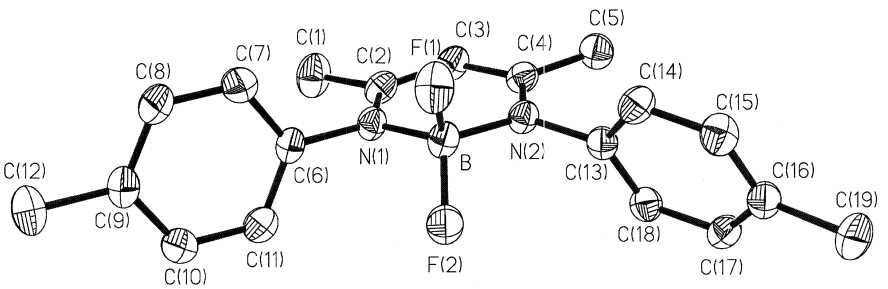
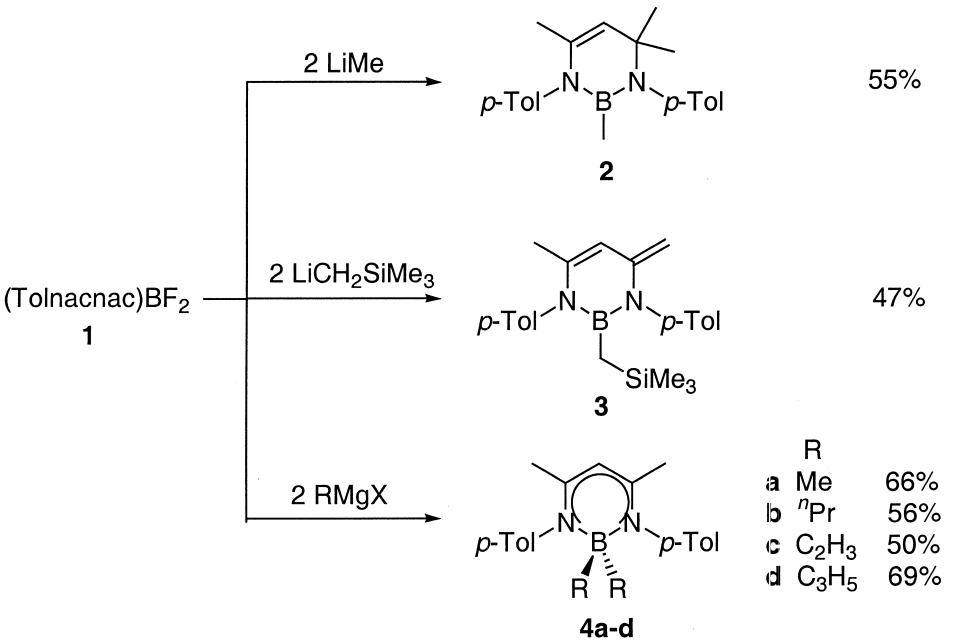


Fig. 1. ORTEP of **1** (ellipsoids drawn at 50% probability level) and atom-labeling scheme. Selected bond length (Å) and bond angles (°): F(1)–B, 1.411(3); F(2)–B, 1.396(3); N(1)–B, 1.550(3); N(2)–B, 1.553(3); N(1)–C(2), 1.339(3); N(2)–C(4), 1.347(3); C(4)–C(3), 1.401(3) C(3)–C(2), 1.384(3). F(2)–B–F(1), 107.8(2); F(2)–B–N(1), 110.6(2); F(1)–B–N(1), 109.4(2); F(2)–B–N(2), 110.4(2); F(1)–B–N(2), 110.0(2).

Table 1
Data collection parameters for compounds **1**, **2**, **3**, and **4a**

Compound	**1**	**2**	**3**	**4a**
Formula	$C_{19}H_{21}BF_2N_2$	$C_{21}H_{27}BN_2$	$C_{23}H_{31}BN_2Si$	$C_{21}H_{27}BN_2$
Formula weight	326.19	318.26	374.40	318.26
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/c$	$P\bar{1}$
Unit cell				
a (Å)	13.133(3)	40.617(8)	6.2891(13)	7.679(2)
b (Å)	7.312(2)	6.1689(12)	25.017(5)	7.899(2)
c (Å)	18.537(4)	15.096(3)	14.543(3)	17.726(4)
α (°)				99.83(3)
β (°)	103.14(3)	97.77(3)	95.73(3)	92.59(3)
γ (°)				115.42(3)
V (Å^3)	1733.4(6)	3747.7(13)	2276.7(8)	948.3(3)
Z	4	8	4	2
d_{cal} (mg/m^3)	1.250	1.128	1.092	1.115
Abs. coeff. (mm^{-1})	0.088	0.065	0.112	0.064
F(000)	688	1376	808	344
Size (mm)	0.20×0.18×0.18	0.30×0.22×0.20	0.28×0.26×0.26	030×0.25×0.25
θ range (°)	1.73–28.20	2.02–28.31	1.63–28.23	2.35–28.21
Index ranges	$-16\le h\le 16$	$-50\le h\le 45$	$-8\le h\le 8$	$-9\le h\le 10$
	$-4\le k\le 9$	$-5\le k\le 8$	$-33\le k\le 33$	$-10\le k\le 10$
	$-23\le l\le 23$	$-14\le l\le 20$	$-19\le l\le 19$	$-23\le l\le 23$
Reflections collected	10 162	6635	26 000	10 662
Independent reflections	3993 [R(int)=0.0261]	3797 [R(int)=0.0848]	5489 [R(int)=0.0374]	4366 [R(int)=0.0313]
Data/restraints/parameters	3993/0/217	3797/0/217	5489/0/244	4366/0/217
GOF/F^2	1.444	1.022	1.437	1.420
R [$I>2\sigma(I)$]	$R_1=0.0662$, $wR_2=0.2070$	$R_1=0.0997$, $wR_2=0.2060$	$R_1=0.0636$, $wR_2=0.1962$	$R_1=0.0722$, $wR_2=0.2176$
R (all data)	$R_1=0.0959$, $wR_2=0.2215$	$R_1=0.2401$, $wR_2=0.2595$	$R_1=0.0873$, $wR_2=0.2082$	$R_1=0.1108$, $wR_2=0.2349$
Lgst. dif. pk. & hole (e Å^{-3})	0.440 and −0.400	0.288 and −0.327	0.468 and −0.473	0.443 and −0.432

high field peak (δ −0.01, C_6D_6) assigned to the boron methyl groups integrated as three hydrogen atoms instead of the expected six. Methylation at the imine-carbon was confirmed by a quaternary carbon resonance in the ^{13}C NMR spectrum (δ 54.94, $CDCl_3$) [24]. Although imines are generally less electrophilic than corresponding alde-



Scheme 1.

hydes or ketones, nucleophilic addition in an imine ligand has literature precedent. For example, Jordan et al. [25] reported a similar methylation on the dibenzotetraazaannulene ligand of a zirconium complex.

The structure for compound **2** was confirmed by single crystal X-ray diffraction analysis (Fig. 2), and selected bond lengths and bond angles are listed in Table 2. The boron center in compound **2** is planar, as indicated by the sum of angles about boron (360.0(7)°). The bond distances of B–N (B–N(1), 1.431(6) Å; B–N(2), 1.425(6) Å) and B–C (B–C(21), 1.563(7) Å) **2** resemble those in 1,2,3-trimethyl-1,3,2-diazaborolidine (Chart 1 **C**) [26]. As expected, the C–C distances in the C_3N_2B ring in compound **2** (C(2)–C(3), 1.305(6) Å; C(3)–C(4), 1.488(6) Å) are no longer equivalent, since the delocalization observed in compound **1** is broken by the quaternary carbon C(4).

When a more hindered alkyl lithium reagent, $LiCH_2SiMe_3$, was used, alkylation at boron and deprotonation of the tolylnacnac group occurred, giving [η^2-CH_2=C(Ntolyl)CH=C(Ntolyl)Me]BCH_2SiMe_3 (**3**) in 47% yield (Scheme 1). Presumably since CH_2SiMe_3 is more sterically demanding than Me, deprotonation of an activated diketiminate methyl group is favored over nucleophilic attack at the imine-carbon in the reaction between compound **1** and $LiCH_2SiMe_3$. Compound **3** was characterized by spectroscopic methods and single crystal X-ray diffraction, and an ORTEP diagram for compound **3** is shown in Fig. 3. Like compound **2**, boron is three-coordinate, and B–C and B–N distances in structures for compounds **2** and **3** are similar. The biggest structural difference between **2** and **3** is apparent delocalization along the diene backbone of the chelating ligand in **3** as indicated by the C–C distances for carbons from C(1) through C(5): C(1)–C(2) = 1.413(3), C(2)–C(3) = 1.395(3), C(3)–C(4) = 1.389(3), and C(4)–C(5) = 1.427(3) Å. The ^{11}B chemical shifts for compounds **2** (δ 31) and **3** (δ 33) are similar to that for $(MeBNMe)_3$ (δ 35.9) [27].

Table 2
Selected bond distances (Å) and angles (°) for compounds **1**, **2**, **3** and **4a**

	1	2	3	4a
B–C		1.563(7)	1.567(3)	1.619(4)
B–C				1.626(3)
N1–B	1.550(3)	1.431(6)	1.438(3)	1.610(3)
N2–B	1.553(3)	1.425(6)	1.445(3)	1.615(3)
N1–B–N2	108.6(2)	118.5(4)	116.9(2)	105.0(2)
N1–B–C		119.6(4)	121.9(2)	109.9(2)
N2–B–C		121.9(4)	121.1(2)	110.2(2)
N1–B–C				109.6(2)
N2–B–C				109.6(2)

Three potential reaction pathways could account for the formation of compound **2** (Scheme 2). The first involves alkylation at boron followed by nucleophilic addition to the imine-carbon and subsequent LiF elimination (pathway i). Conversely, nucleophilic addition to carbon could precede alkylation at boron (pathway ii). Lastly, compound **2** could result from methyl migration in the dimethyl complex, (tolylnacnac)BMe_2 (**4a**) (pathway iii). This possibility can be excluded since compound **4a** can be independently prepared and is stable under the reaction conditions (vide infra). To distinguish between pathways i and ii, compound **1** and MeLi were reacted in a 1:1 molar ratio at −78°C. Under these conditions, a mixture of **2** and unreacted **1** formed. Thus, we cannot determine whether the initial methylation occurs at the boron or the ligand backbone.

When compound **1** was treated with two equivalents of freshly prepared MeMgI in Et_2O, the desired dimethyl product, (tolylnacnac)BMe_2 (**4a**), was isolated (Scheme 1). In this case, methylation occurred exclusively at boron,

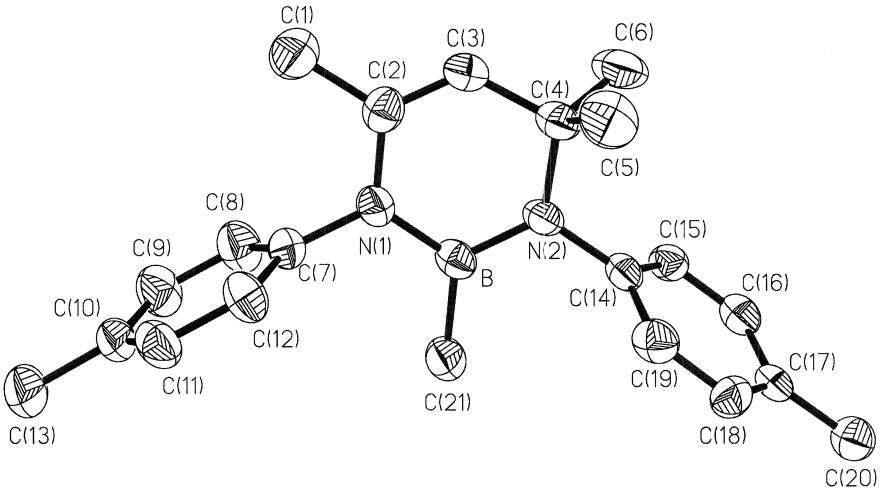


Fig. 2. ORTEP of **2** (ellipsoids drawn at 50% probability level) and atom-labeling scheme. Selected bond length (Å) and bond angles (°): C(21)–B, 1.563(7); N(1)–B, 1.431(6); N(2)–B, 1.425(6); N(1)–C(2), 1.423(6); N(2)–C(4), 1.491(5); C(3)–C(2), 1.305(6); C(3)–C(4), 1.488(6). N(2)–B–N(1), 118.5(4); N(2)–B–C(21), 121.9(4); N(1)–B–C(21), 119.6(4).

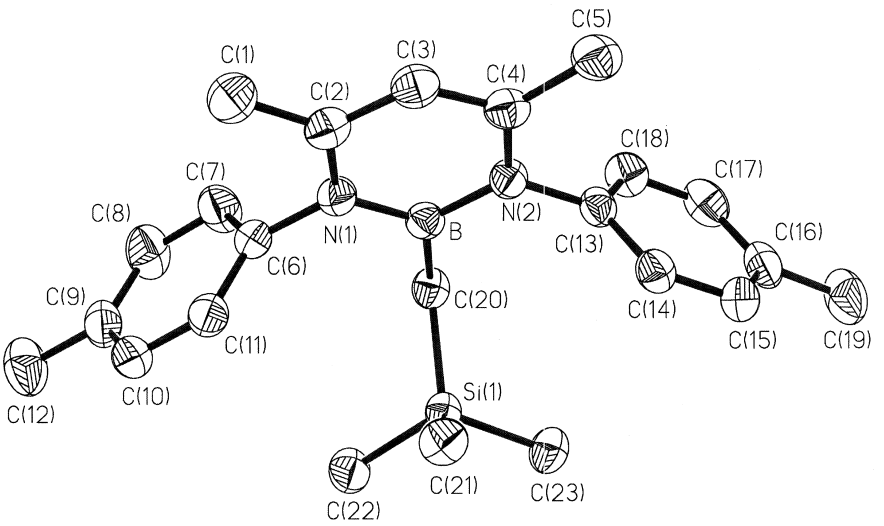
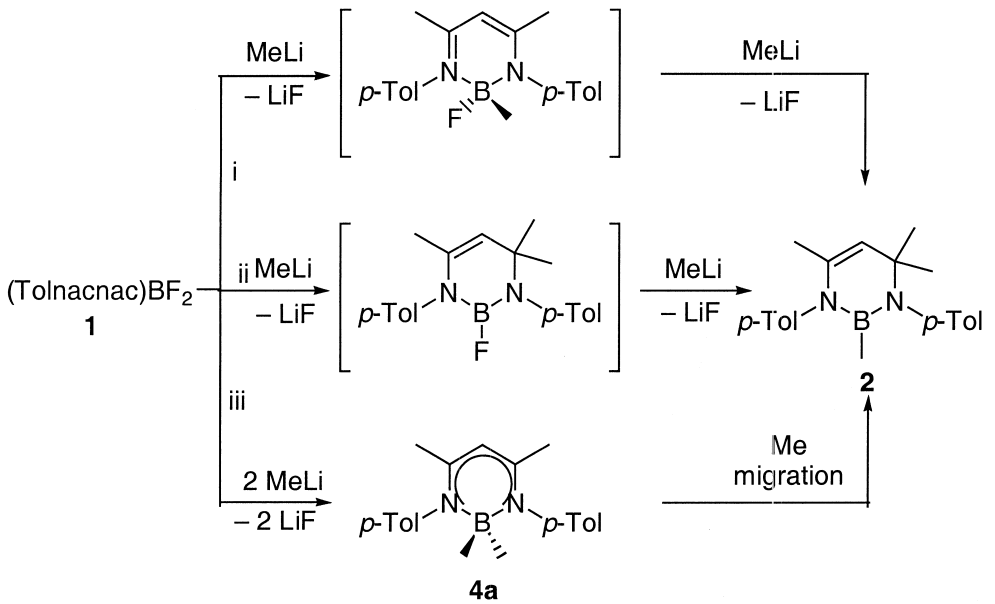


Fig. 3. ORTEP of **3** (ellipsoids drawn at 50% probability level) and atom-labeling scheme. Selected bond length (Å) and bond angles (°): B–C(20), 1.567(3); B–N(1), 1.438(3); B–N(2), 1.445(3); C(1)–C(2), 1.413(3); C(2)–C(3), 1.395(3); C(3)–C(4), 1.389(3); C(4)–C(5), 1.427(3); Si(1)–C(20), 1.892(2); N(1)–C(2), 1.422(3); N(2)–C(4), 1.420(3). N(1)–B–N(2), 116.9(2); N(1)–B–C(20), 121.9(2); N(2)–B–C(20), 121.1(2).

and compound **2** was not detected in the reaction mixture. In addition to diagnostic ligand peaks, the ^{1}H NMR spectrum for compound **4a** contains a high field singlet (δ −0.44, 6H) which is assigned to B*Me*$_2$ protons. The ^{11}B NMR data of **4a** (δ 1.07, $\upsilon_{1/2}$ = 259 Hz) are consistent with a tetrahedral boron center. Inter-conversion between compounds **2** and **4a** did not occur after prolonged heating of **2** or **4a** in toluene at 70°C. Attempts to make (tolylnacnac)B(F)(Me) by mixing **1** with one equivalent of MeMgI at different temperatures invariably led to **4a** and unreacted **1** [28]. Other dialkyl complexes, (tolylnacnac)BR$_2$ (**4b**–**d**, **b**, R = ^{n}Pr, **c**, R = C_2H_3, **d**, R = C_3H_5), were similarly synthesized from compound **1** and the corresponding Grignard reagents (Scheme 1).

The solid state structure of compound **4a** was determined and its ORTEP is shown in Fig. 4. Its structure contains a pseudo-tetrahedral boron center with bond angles (°): N(2)–B–N(1), 105.0(2); N(2)–B–C(21), 109.6(2); N(1)–B–C(21), 109.6(2); N(2)–B–C(20), 110.2(2); N(1)–B–C(20), 109.9(2). The average B–C bond length of 1.623(4) Å in compound **4a** is longer than that of B–C in compound **2** (1.563(7) Å) (Table 2). The elongated B–C bonds in **4a** are consistent with rehybridization from *sp*^{2} boron in compound **2** to *sp*^{3} boron in



Scheme 2.

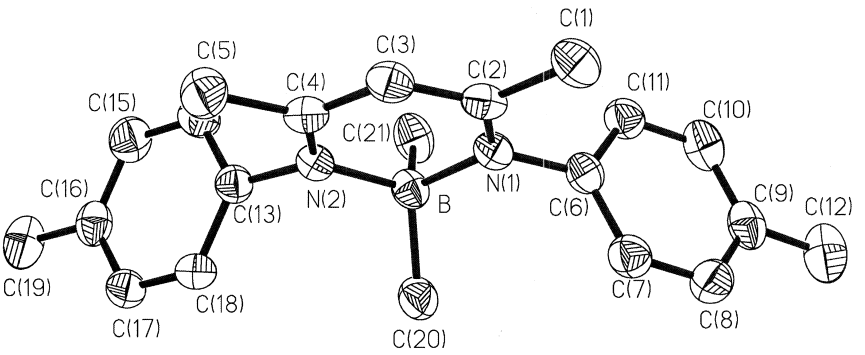


Fig. 4. ORTEP of **4a** (ellipsoids drawn at 50% probability level) and atom-labeling scheme. Selected bond length (Å) and bond angles (°): B–N(2), 1.610(3); B–N(1), 1.615(3); B–C(21), 1.626(3); B–C(20), 1.619(4); N(1)–C(2), 1.333(3); N(1)–C(6), 1.448(3); N(2)–C(4), 1.331(3); N(2)–C(13), 1.451(3); C(1)–C(2), 1.507(3); C(2)–C(3), 1.395(3); C(3)–C(4), 1.403(3); C(4)–C(5), 1.509(3). N(2)–B–N(1), 105.0(2); N(2)–B–C(21), 109.6(2); N(1)–B–C(21), 109.6(2); N(2)–B–C(20), 110.2(2); N(1)–B–C(20), 109.9(2); C(21)–B–C(20), 112.3(2); C(2)–N(1)–C(6), 120.0(2); C(2)–N(1)–B, 125.2(2); C(6)–N(1)–B, 114.7(2); C(4)–N(2)–C(13), 119.4(2).

compound **4a**. The longer B–N bond distances in compound **4a** ($B–N_{average}=1.615(3)$ Å) relative to compound **1** ($B–N_{average}=1.552(3)$ Å) are consistent with the weaker inductive effect of Me relative to F.

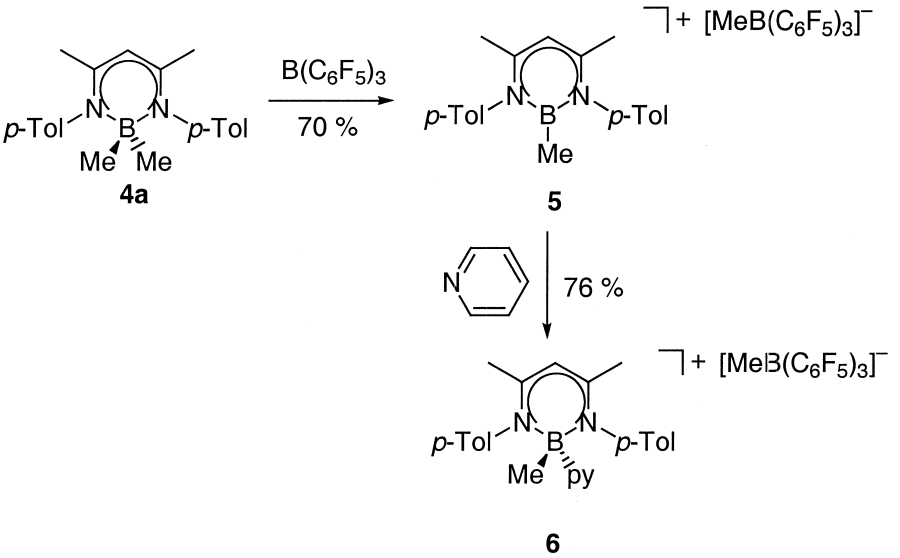
3.2. Alkyl abstraction reactions

Methyl abstraction from compound **4a** to generate a cationic boron center was examined. Unlike the aluminum analogue, (tolylnacnac)$AlMe_2$, which underwent aryl-Me exchange with $B(C_6F_5)_3$ (Eq. (2)) [19],

Eq. (2)

$$\text{(tolylnacnac)AlMe}_2 + \text{B(C}_6\text{F}_5\text{)}_3 \rightarrow \text{(tolylnacnac)AlMe(C}_6\text{F}_5\text{)} + \text{B(C}_6\text{F}_5\text{)}_2\text{Me}$$

compound **4a** reacted with $B(C_6F_5)_3$ to give $[(tolylnacnac)BMe]^+[MeB(C_6F_5)_3]^-$ (**5**) in 70% yield (Scheme 3). Compound **5** can be formulated as an ionic compound with a discrete cation and anion, or as a methyl-bridged zwitterion [29]. The ^{11}B NMR spectrum of compound **5** contains two peaks at δ −14.8 (s, $\upsilon_{1/2}=30$ Hz) and 37.1 ($\upsilon_{1/2}=1200$ Hz), respectively. The resonance at δ −14.8 is assigned to $MeB(C_6F_5)_3$. The narrow linewidth is consistent with tetrahedral boron; however, the resonance is shifted downfield significantly from the 'free' $MeB(C_6F_5)_3$ anion. For the diketiminate boron, the ^{11}B resonance at δ 37.1 is shifted downfield substantially from the resonance for compound **4a** (δ 1.07) and appears slightly downfield from resonances for compounds **2** and **3** (~δ 32). Coupled to the observation that the line-width for the resonance at δ 37.1 is typical for three-coordinate boron, the ^{11}B data support three- and four-coordinate B centers expected for the discrete pair, $[(tolylnacnac)BMe]^+[MeB(C_6F_5)_3]^-$ [30]. The molar conductivity for a CH_2Cl_2 solution of compound **5** ($\Lambda_M=1.6\times10^{-2}$ S m^2 mol^{-1}) was similar to that for $[^nBu_4N]^+Br^-$ ($\Lambda_M=1.2\times10^{-2}$ S m^2 mol^{-1}). Thus, com-



Scheme 3.

pound **5** is largely dissociated in CH_2Cl_2. Although the resonance assigned to the $MeB(C_6F_5)_3$ protons (δ 0.41) is close the reported value for free $[MeB(C_6F_5)_3]^-$(δ 0.4) [31]; the fact that this resonance shifts to δ 0.48 when pyridine is added to solutions of **5** implies that (tolylnacnac)(Me)B$\cdots$$MeB(C_6F_5)_3$ interactions are present. Presumably, the association implied by the shift of the protons for $[MeB(C_6F_5)_3]^-$ upon pyridine addition is weak.

Inspection of the ^{1}H NMR spectra for compounds **4a** and **5** provides clues regarding the low electrophilicity of the boron center in compound **5**. Specifically, the methine proton in compound **4a** (δ 4.82) shifts downfield substantially in compound **5** (δ 6.73). This suggests enhanced aromaticity for the diketiminate ring. While the sp^3 hybridized boron center cannot participate in $p\pi$-delocalization, methyl abstraction from B provides an additional sp^2 center that completes a delocalized six-membered ring [32–34]. A possible explanation for the abcense ion-pairing in compound **5** is that stablization from increased aromaticity outweighs coulombic contributions.

We surveyed reactivity of compound **5** with olefins and Lewis bases. In contrast to some cationic aluminum alkyl compounds, compound **5** did not polymerize olefins [35,36]. More surprisingly, compound **5** did not bind diethyl ether or propylene oxide. Nonetheless, compound **5** reacted with pyridine to form $[(tolylnacnac)B(py)Me]^+[MeB(C_6F_5)_3]^-$, (**6**) (Scheme 3). The ^{1}H NMR spectrum of compound **6** contains a resonance at δ 0.48 for the $CH_3B(C_6F_5)_3$ anion. The ^{19}F NMR data for compound **6** (δ −167.2, −164.6, −132.7) are virtually identical to those for compound **5** (δ −167.2, −164.5, −132.9), and the ^{11}B NMR spectrum of compound **6** contains two peaks at δ −15.23 (s, $\upsilon_{1/2}$=65 Hz) and δ −4.19 (s, $\upsilon_{1/2}$=80 Hz). Both resonances have narrow line widths, indicating pseudotetrahedral boron centers, and the diketiminate resonance at δ −4.19 is shifted to higher field relative to compound **5**. The ^{1}H NMR spectra for mixtures of **6** and pyridine exhibit one set of pyridine resonances that differ from those of pure **6** or pyridine. Thus, exchange between the bound pyridine in **6** and free pyridine is rapid on the NMR time scale [37]. The fact that coordination occurs only with a strong Lewis base supports the notion that stabilization from aromaticity in compound **5** is significant.

4. Summary

The β-diketiminato boron (III) difluoride complex, **1**, provides a synthetic entry route to various boron alkyl complexes. While alkyllithium reagents give products that arise from ligand deprotonation or nucleophilic attack at the ligand imine carbons, magnesium alkyl halides cleanly afford the dialkyl products, (tolylnacnac)BR_2, **4a–d** (**a**, R=Me, **b**, R=^{n}Pr, **c**, R=C_2H_3, **d**, R=C_3H_5). Methyl abstraction from compound **4a** by $B(C_6F_5)_3$ gives a cationic boron diketiminate compound, **5**. Compound **5** is less Lewis acidic than $B(C_6F_5)_3$; however, a stable adduct, $[(tolylnacnac)B(py)Me^+]$ $[MeB(C_6F_5)_3^-]$ (**6**), forms upon addition of pyridine to compound **5** in toluene.

Supplementary data

Four crystal data sets were deposited at Cambridge Crystallographic Data Center. The crystallographic data center deposition codes are: 102912 for compound **1**, 102913 for compound **2**, 102914 for compound **3**, and 102915 for compound **4a**.

Acknowledgements

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