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Synthesis and Crystal Structure of *N*-[3,5-*Bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-*N*-ethylnitrous amide and *N*-[3,5-*Bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-*N*-isopropylnitrous amide

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The title compound *N*-[3,5-*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-*N*-ethylnitrous amide (**2**, m.f. $C_{20}H_{32}N_2O_5B_2$) and *N*-[3,5-*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl]phenyl)-*N*-isopropylnitrous amide (**4**, m.f. $C_{21}H_{34}N_2O_5B_2$) have been synthesized and characterized by elemental analysis, MS, IR, ^1H, ^{13}C, ^{11}B NMR spectroscopies. In addition, their crystal structures were determined by single-crystal X-ray diffraction. The crystal of **2** belongs to monoclinic, space group $P2_1/n$ with a = 6.3220(13), b = 28.910(6), c = 12.827(3) Å, β = 102.61(3)°, Z = 4, V = 2287.8(8) Å^3, D_c = 1.167 g/cm^3, μ(MoK_α) = 0.081 mm^{-1}, F(000) = 864, the final R = 0.0737 and wR = 0.1548 for 4209 observed reflections with I > 2σ(I), while the compound **4** crystallizes in triclinic, space group $P\bar{1}$ with a = 6.8730(14), b = 10.827(2), c = 17.000(3) Å, α = 101.30(3), β = 92.07(3), γ = 92.11(3)°, Z = 2, V = 1238.5(4) Å^3, D_c = 1.116 g/cm^3, μ(MoK_α) = 0.077 mm^{-1}, F(000) = 448, the final R = 0.0934 and wR = 0.1628 for 4546 observed reflections with I > 2σ(I).

Keywords: Synthesis, Crystal structure, Nitroso group.

INTRODUCTION

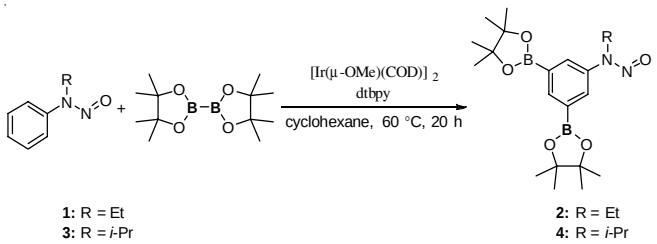
Transition metal catalyzed C-H borylation reaction has received significant attention in recent years for the synthetic utility of boronate esters and this method can avoid the need of pre-installed of halogen which make the synthetic route more straight forward[1-4]. While the high selectivity of arene C-H borylation can be obtained by appropriate choice of 1,2- or 1,3-disubstituted arene substrate, a mixture of borylation products is often obtained with iridium catalyst when using mono-substituted arene[5-7]. We recently launched a program on C-H functionalization with the *N*-nitroso as the directing group[8,9]. It is thus anticipated that the *N*-nitroso can act as a steric tool to synthesized *meta*- pinacol boronate esters through Ir-catalyzed C-H borylation. Herein we report the synthesis and crystal structure of *N*-[3,5-*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-*N*-ethylnitrous amide (**2**) and *N*-[3,5-*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-*N*-isopropylnitrous amide (**4**) using $[Ir(\mu\text{-OMe})(COD)]_2$ (COD = cyclooctadiene) with 4,4'-di-*tert*-butylbipyridine (dtbpy) as the ligand.

EXPERIMENTAL

$[Ir(\mu\text{-OMe})(COD)]_2$, *bis*(pinacolato) diboron, 4,4'-di-*tert*-butyl bipyridine were purchased and employed without purification. Cyclohexane was distilled over Na/benzophenone before use. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ (with tetramethylsilane as an internal reference) solution on a Bruker AVANCE 400 MHz. The carbon directly attached to the boron atom was not seen by ^{13}C NMR spectroscopy[10]. ^{11}B NMR spectra were referenced to an external $BF_3{\cdot}Et_2O$ sample in $CDCl_3$ (0.0 ppm). High-resolution MS (HRMS) spectra were obtained on a Thermo Fisher Scientific LTQ FT Ultra facility. Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wave number (cm^{-1}). Arene substrate **1** and **3** were prepared according to previous manuscripts[8,9].

Synthetic procedure: The synthesis route of title compounds **2** and **4** is outlined in **Scheme-I**. $[Ir(\mu\text{-OMe})(COD)]_2$ (8 mg, 0.012 mmol,), dtbpy (6.4 mg, 0.024 mmol), B_2pin_2 (203 mg, 0.8 mmol)[11], arene substrate (0.4 mmol) and cyclohexane (2 mL) were added into a dry vial with a magnetic stir bar in a glove box. The vial was sealed and the reaction mixture was stirred at 60 °C for 20 h. Then the volatiles were removed *in vacuo* and the residue was subjected to column chromatography provided the corresponding boronate ester.

***N*-[3,5-*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-*N*-ethylnitrous amide (2):** The title compound was obtained as pale white solid in 76 % yield. R_f = 0.2



Scheme-1: Synthesis of compound **2** and **4**

(Et_2O:Hexane, 1:5). IR (neat) ν = 2979, 1603, 1410, 1319, 1261, 1139, 1113, 859,707 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.00 (d, *J* = 0.9 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 1.35 (s, 24H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.44, 140.24, 129.01, 84.16, 39.38, 24.88, 11.74. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.08. HRMS (DART) Calcd. for $C_{20}H_{33}N_2O_5B_2$: $[M + H]^+$, 401.2643; found: *m/z* 401.2638.

***N*-[3,5-*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-*N*-isopropylnitrous amide (4):** The title compound was obtained as a pale white solid in 78 % yield of inseparable mixture of *syn* and *anti* isomers in 78 % yield[8,9]. By ^1H NMR, the *syn*:*anti* ratio was determined to be approximately 1:0.66. R_f = 0.18 (Et_2O:Hexane, 1:5). IR (neat) ν = 2973, 1601, 1382, 1353, 1317, 1139, 1111, 848,715 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 8.32 (d, *J* = 9.1 Hz, 1H), 8.31 (s, 1H × 0.66), 7.84 (d, *J* = 1.0 Hz, 2H), 7.46 (d, *J* = 1.0 Hz, 2H × 0.66), 5.18 (hept, *J* = 6.8 Hz, 1H), 4.97 (hept, *J* = 6.8 Hz, 1H × 0.66), 1.51 (d, *J* = 6.8 Hz, 3H × 0.66), 1.35 (s, 24H), 1.32 (s, 24H × 0.66), 1.22 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 142.05, 141.48, 138.68, 136.28, 136.04, 134.73, 84.15, 84.08, 56.33, 46.69, 24.87, 22.23, 19.85. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.10. HRMS (DART) Calcd. for $C_{21}H_{35}N_2O_5B_2$: $[M + H]^+$, 415.2799; found: *m/z* 415.2794.

Crystal structure determination: Crystal of the title compound **2** for X-ray structure determination was obtained by slow evaporation in ether/hexane solution at 0 °C. A pale yellow single crystal with dimensions of 0.30 mm × 0.20 mm × 0.10 mm was selected for X-ray diffraction analysis at 293(2) K. The data was collected on CAD4/PC with MoK_α radiation (λ = 0.71073 Å). A total of 4602 reflections were bollected in the range of 1.41 < θ < 25.38° at room temperature and 4209 independent reflections (R_{int} = 0.0668) with I > 2σ(I) were used in the structure determination and refinements. The structure was solved by direct methods with SHELXS-97 program and reined on F^2 with SHELXL-97 program. The non-hydrogen atoms were refined anisotropically and the hydrogen atom were determined with theoretical calculation. A full-matrix least-squares refinement gave final R = 0.0737, wR = 0.1548 (w = $1/[\sigma^2(F_0^2) + (0.0700P)^2 + 0.0000P]$, where $P = (F_0^2 + 2F_c^2)/3$), R = 0.1690 and wR = 0.1914 for all data. The largest parameter shift $(\Delta/\sigma)_{max}$ is 0.000. The goodness-of-fit indicator is 1.001. the maximum and minimum peaks in the final difference Fourier map are 0.353 and -0.222 e/Å^3, respectively. All calculation were performed on a PC with SHELXTL program[12].

Crystal of the title compound **4** for X-ray structure determination was obtained by slow evaporation in ether/hexane solution at 0 °C. A colourless single crystal with dimensions of 0.20 mm × 0.10 mm × 0.10 mm was selected for X-ray diffraction analysis at 293(2) K. The data was collected on CAD4/PC with MoK_α radiation (λ = 0.71073 Å). A total of 4956 reflections were bollected in the range of 1.22 < θ < 25.37° at room temperature and 4546 independent reflections (R_{int} = 0.0478) with I > 2σ(I) were used in the structure determination and refinements. The structure was solved by direct methods with SHELXS-97 program and reined on F^2 with SHELXL-97 program. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were determined with theoretical calculation. A full-matrix least-squares refinement gave final R = 0.0934, wR = 0.1628 (w = $1/[\sigma^2(F_0^2) + (0.0400P)^2 + 0.9000P]$, where $P = (F_0^2 + 2F_c^2)/3$), R = 0.1998 and wR = 0.1999 for all data. The largest parameter shift $(\Delta/\sigma)_{max}$ is 0.000. The goodness-of-fit indicator is 1.005. The maximum and minimum peaks in the final difference Fourier map are 0.231 and -0.216 e/Å^3, respectively. All calculation was performed on a PC with SHELXTL program[12].

RESULTS AND DISCUSSION

The single crystal of the title compounds (**2** and **4**) were obtained by slow evaporation in ether/hexane solution. The HRMS, IR and NMR spectra are in good agreement with the formulae proposed by the X-ray crystallography.

The view of the crystal structure of the title compound **2** and **4** are shown in Figs. 1 and 2, respectively. And the packing diagrams for them were shown in Figs. 3 and 4. The selected bond lengths and bond angels are listed in Tables 1 and 2, respectively. In the structure of **2**, B(1), O(1), C(7), C(8) and O(2) atoms form a five-membered ring, as well as B(2), O(3), C(13), C(14) and O(4). The bong length of B(1)-C(6) is 1.564(5) Å, close to the typical B-Cary bond (1.556 Å)[13]. The bond length of N(2) = O(5) in **2** is 1.237(4) Å and N(2)=O(5) in **4** is 1.213(5) Å, which consistent with the bond length of double bond of N=O (1.218 Å). However, the bond length of N(1)-N(2) in **2** is 1.306(4) Å and N(1)-N(2) in **4** is 1.379(6) Å, both of which are shorter than the usual N-N bond (1.425 Å) and longer than N=N bond (1.240 Å)[13]. It is because of the partial double bond character of the bonds due to partial electron delocalization of N(2)=O(5) bond.

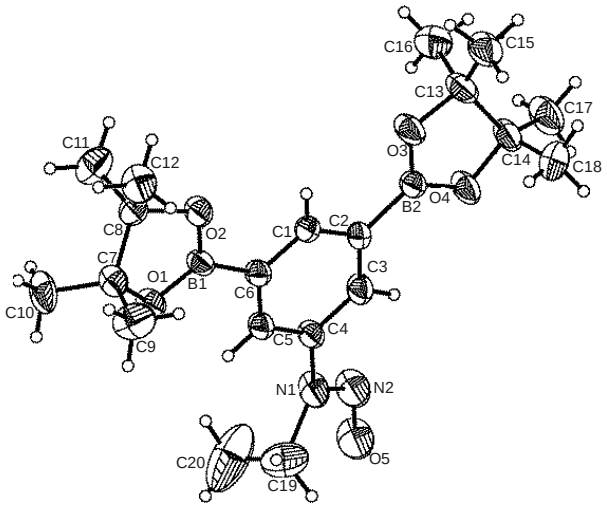


Fig. 1. Molecular structure of the title compound **2**

TABLE-1
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR COMPOUND **2**

Bond	Dist.	Bond	Dist.	Bond	Dist.
O(1)-B(1)	1.350(4)	N(1)-C(4)	1.423(4)	B(2)-O(3)	1.348(4)
B(1)-C(6)	1.564(5)	N(1)-C(19)	1.688(6)	C(1)-C(2)	1.398(4)
N(1)-N(2)	1.306(4)	N(2)-O(5)	1.237(4)	-	-
Angle	(°)	Angle	(°)	Angle	(°)
N(2)-N(1)-C(4)	117.7(3)	O(2)-B(1)-C(6)	121.1(3)	C(10)-C(7)-C(8)	115.4(3)
N(2)-N(1)-C(19)	119.9(3)	B(1)-O(2)-C(8)	106.3(3)	O(2)-C(8)-C(11)	106.6(3)
C(4)-N(1)-C(19)	120.0(3)	B(1)-O(1)-C(7)	106.7(3)	O(2)-C(8)-C(12)	107.4(3)
O(5)-N(2)-N(1)	115.0(4)	O(1)-C(7)-C(10)	108.2(3)	C(11)-C(8)-C(12)	109.6(3)
C(20)-C(19)-N(1)	95.9(6)	O(1)-C(7)-C(9)	106.7(3)	O(2)-C(8)-C(7)	101.8(3)
O(1)-B(1)-O(2)	114.5(3)	O(1)-C(7)-C(8)	110.2(3)	C(11)-C(8)-C(7)	113.7(3)
O(1)-B(1)-C(6)	124.4(3)	O(1)-C(7)-C(8)	103.0(3)	C(12)-C(8)-C(7)	116.8(3)

Symmetry transformation: a: x, y + 1, z; b: -x, y, -z +1/2; c: -x, -y + 1, -z

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR COMPOUND **4**

Bond	Dist.	Bond	Dist.	Bond	Dist.
O(1)-B(1)	1.370(5)	N(1)-C(13)	1.471(6)	B(2)-O(3)	1.357(6)
B(1)-C(16)	1.543(6)	N(1)-C(20)	1.453(5)	C(16)-C(17)	1.396(5)
N(1)-N(2)	1.379(6)	N(2)-O(5)	1.213(5)	-	-
Angle	(°)	Angle	(°)	Angle	(°)
N(2)-N(1)-C(20)	110.5(4)	O(2)-B(1)-O(1)	112.5(4)	O(1)-C(1)-C(3)	102.9(4)
N(2)-N(1)-C(13)	127.4(4)	O(2)-B(1)-C(16)	121.7(4)	C(4)-C(1)-C(3)	108.1(5)
C(20)-N(1)-C(13)	121.5(4)	O(1)-B(1)-C(16)	125.8(4)	C(2)-C(1)-C(3)	111.9(5)
O(5)-N(2)-N(1)	109.4(6)	B(1)-O(1)-C(1)	107.9(3)	O(2)-C(2)-C(5)	108.5(4)
N(1)-C(13)-C(15)	112.8(5)	B(1)-O(2)-C(2)	107.5(4)	O(2)-C(2)-C(1)	105.1(4)
N(1)-C(13)-C(14)	108.6(5)	O(1)-C(1)-C(4)	110.5(4)	C(5)-C(2)-C(1)	118.1(5)
C(15)-C(13)-C(14)	114.3(6)	O(1)-C(1)-C(2)	103.0(3)	O(2)-C(2)-C(6)	103.2(4)
O(2)-B(1)-O(1)	112.5(4)	C(4)-C(1)-C(2)	119.2(5)	C(5)-C(2)-C(6)	109.3(5)

Symmetry transformation: a: x, y+1, z; b: -x, y, -z + 1/2; c: -x, -y + 1, -z

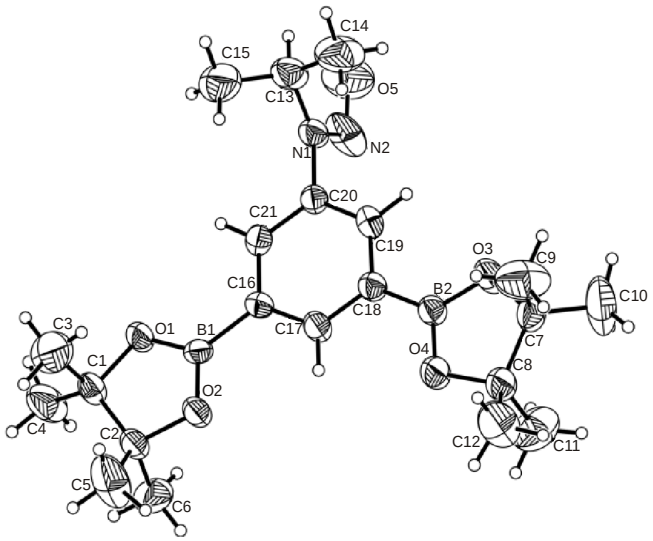


Fig. 2. Molecular structure of the title compound **4**

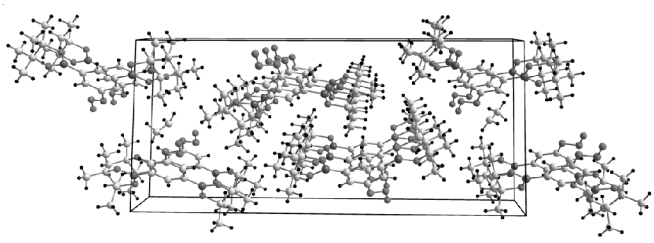


Fig. 3. Packing structure of the title compound **2**

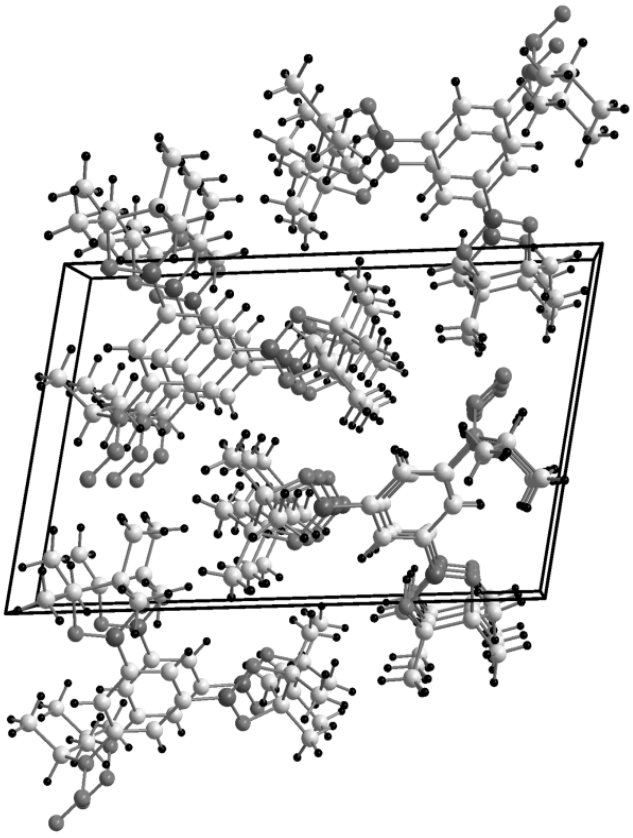


Fig. 4. Packing structure of the title compound **4**

Conclusion

In summary, *N*-[3,5-*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl]-*N*-ethylnitrous amide (**2**) and *N*-[3,5-*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]-*N*-isopropyl nitrous amide (**4**) have been synthesized and fully characterized by elemental analysis, Mass, IR, ^{1}H, ^{13}C, ^{11}B NMR spectroscopies. In addition, their crystal structure were determined by single-crystal X-ray diffraction. Particularly, compared to the traditional way, our synthesis route is found to be simple and efficient.

Supplementary data: CCDC-1006980, CCDC-1009207 and CCDC-1006981 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; or E-mail: deposit@ccdc.cam.ac.uk).

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11. When using 1 equiv. of B_2pin_2, *para*-Monosubstituted Product was Obtained in 40-50 % Besides the Disubstituted Products whose Structure was Confirmed by X-ray Diffraction Analysis (CCDC 1006981 for Substrate 3 and Monosubstitute Product of **1** is oil).
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