Electronic supplementary information

"Synthesis and reactivity of triethylborane adduct of *N*-heterocyclic carbene: Versatile synthons for synthesis of *N*-heterocyclic carbene complexes"

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General Procedures.

All manipulations involving air and moisture-sensitive organometallic compounds were carried out under an atmosphere of dry argon or nitrogen, which was purified by SICAPENT (Merck Co., Inc.), by using a standard Schlenk tube or high-vacuum techniques. All solvents were distilled over appropriate drying agents prior to use. LiBEt₃H in a THF solution (1.0 M) was purchased from Aldrich, and used as received. BH₃·THF complex in a THF solution (1.0 M), BF₃·OEt₂, and Mo(CO)₆ were purchased form Kanto Kagaku, and used as received. Other reagents employed in this research were used without further purification. 1,3-Diisopropylimidazolium chloride (I¹Pr•HCl. $1a)^{1}$ 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes•HCl. $1b)^{2}$ 3-methyl-1-{2-[(3-methyl-1H-imidazolium-1-yl)-methyl]benzyl}-1H-imidazolium dibromide (7a),³ and 3-methyl-1-{3-[(3-methyl-1H-imidazolium-1-yl)-methyl]benzyl}-1H-imidazolium dibromide $(7b)^3$ were prepared according to literature methods.

IR spectra were recorded on a HORIBA FT-730 spectrometer. ¹H and ¹³C{¹H} NMR spectra were recorded on a JEOL EX-270 spectrometer at ambient temperature, unless otherwise mentioned. ¹¹B{¹H} and ¹¹B NMR spectra were recorded on a JEOL Lambda-500 and an EX-270 spectrometers at ambient temperature. ¹H and ¹³C{¹H} NMR chemical shifts were reported in ppm relative to internal Me₄Si. ¹¹B{¹H} and ¹¹B NMR chemical shifts were recorded in ppm relative to external BF₃·OEt₂. All coupling constants were recorded in Hz. The splitting patterns are indicated as s, singlet; d, doublet; t, triplet; quint, quintet; sept, septet.

Preparation of IⁱPr·BEt₃ (2a).

1a (577 mg, 3.06 mmol) was put in a Schlenk tube, which was attached to a high-vacuum line. THF (ca. 15 mL) was added by a trap-to-trap-transfer technique at -78 °C. At this temperature, LiBEt₃H (3.1 mL of its 1.0 M THF solution, 3.1 mmol) was added by syringe. Then the reaction mixture was allowed to warm to room temperature. After removing the volatiles under reduced pressure, the residual solid was extracted with hexane (3 x 20 mL). The light brown powder, thus, formed was washed with pentane (3 x 3 mL) and dried in vacuo to yield **2a** (610 mg, 2.44 mmol,

80%). Anal. Calcd for $C_{15}H_{31}BN_2$: C; 72.00, H; 12.49, N; 11.20%. Found: C; 71.63, H; 12.50, N; 11.13%. ¹H NMR (in CDCl₃) δ 0.46 (quint, J = 7.3Hz, 6H, BCH₂CH₃), 0.63 (t, J = 7.3 Hz, 9H, BCH₂CH₃), 1.37 (d, J = 6.6 Hz, 12H, ⁱPr-CH₃), 5.43 (sept, J = 6.6 Hz, 2H, ⁱPr-CH), 6.92 (s, 2H, CH=CH). ¹³C{¹H} NMR (in CDCl₃) δ 11.4 (BCH₂CH₃), 14.3 (br, BCH₂CH₃), 23.8 (ⁱPr-CH₃), 48.3 (ⁱPr-CH), 116.0 (CH=CH), 173.5 (br, NCN); (in C₆D₆) δ 12.3 (BCH₂CH₃), 15.2 (br, BCH₂CH₃), 23.7 (ⁱPr-CH₃), 48.6 (ⁱPr-CH), 116.7 (CH=CH), 174.0 (br, NCN). ¹¹B{¹H} NMR (in CDCl₃) δ -12.6 (BEt₃).

Preparation of IMes·BEt₃ (2b)

This compound was prepared from **1b** (745 mg, 2.19 mmol) and LiBEt₃H (2.2 mL of its 1.0 M THF solution, 2.2 mmol) in the same manner as that for **2a**. Adduct **2b** was isolated as a light brown solid (yield, 405 mg, 1.00 mmol, 46%). Anal. Calcd for $C_{27}H_{39}BN_2$: C; 80.58, H; 9.77, N; 6.96%. Found: C; 80.45, H; 9.53, N; 6.92%. ¹H NMR (in CDCl₃) δ -0.13 (quint, J = 7.9 Hz, 6H, BCH₂CH₃), 0.55 (t, J = 7.9 Hz, 9H, BCH₂CH₃), 2.15 (s, 12H, Mes-*o*-CH₃), 2.36 (s, 6H, Mes-*p*-CH₃), 6.78 (s, 2H, CH=CH), 6.96 (s, 4H, Mes-*m*-H). ¹³C{¹H} NMR (in CDCl₃) δ 12.2 (BCH₂CH₃), 13.6 (br, BCH₂CH₃), 18.1 (Mes-*o*-CH₃), 21.0 (Mes-*p*-CH₃), 122.8 (CH=CH), 128.6, 135.5, 136.4, 138.4 (Mes-Ph), 180.4 (br, NCN). ¹¹B{¹H} NMR (in CDCl₃) δ -13.3 (BEt₃).

Preparation of IⁱPr·BH₃ (3a).

To a solution of **2a** (75 mg, 0.30 mmol) in THF (10 mL) was added BH₃·THF complex (0.3 mL of its 1.07 M THF solution, 0.32 mmol) at -78 °C. The reaction mixture was allowed to warm to room temperature. After being stirred for several hours at ambient temperature, the volatiles were removed under reduced pressure. The white solid, thus, formed, was washed with pentane (2 x 5 mL) and dried in vacuo to yield **3a** (19 mg, 0.11 mmol, 37%). ¹H NMR (in C₆D₆) δ 0.93 (d, J = 7.3 Hz, 12H, ⁱPr-CH₃), 2.11 (quint, J = 87.7 Hz, 3H, BH₃) 5.26 (sept, J = 6.6 Hz, 2H, ⁱPr-CH), 6.17 (s, 2H, CH=CH). ¹³C{¹H} NMR (in C₆D₆) δ 22.2 (ⁱPr-CH₃), 49.1 (ⁱPr-CH), 114.5 (CH=CH). A signal being assignable to the carbene carbon in **3a** was not detected. ¹¹B NMR (in C₆D₆) δ -36.4 (quint, J = 88.0 Hz, BH₃).

Preparation of IMes·BH₃ (3b).

This compound was prepared from **2b** (30 mg, 75 μ mol), BH₃·THF complex (70 μ L of its 1.07 M THF solution, 75 μ mol), and THF (10 mL) in the same manner as that for **3a**. Adduct **3b** was isolated as a white solid (yield, 20 mg, 63 μ mol, 84 %). ¹H NMR (in C₆D₆) δ 2.05 (s, 12H,

Mes-*o*-CH₃), 2.09 (s, 6H, Mes-*p*-CH₃), 5.99 (s, 2H, CH=CH), 6.74 (s, 4H, Mes-*m*-H). A signal being assignable to BH₃ was not detected in ¹H NMR spectrum. ¹¹B NMR (in C₆D₆) δ -36.8 (q, J = 88.0 Hz, BH₃). This compound **3b** has been prepared by Jennings and Clyberne et al. in a different route.⁴

Preparation of IMes·BF₃ (4b).

To a solution of **2b** (118 mg, 0.29 mmol) in CH_2Cl_2 (7 mL) was added $BF_3 \cdot OEt_2$ (five drops, ca. 50 mg, 0.35 mmol) at ambient temperature. After being stirred for several hours, the volatiles were removed under reduced pressure. The white solid, thus formed, was washed with THF (2 x 3 mL) and dried in vacuo to yield **4b** (61 mg, 0.16 mmol, 55%).

¹H NMR (in CDCl₃) δ 2.12 (s, 12H, Mes-*o*-CH₃), 2.35 (s, 6H, Mes-*p*-CH₃), 7.01 (s, 4H, Mes-*m*-H), 7.08 (s, 2H, CH=CH). ¹¹B{¹H} NMR (in CDCl₃) δ -0.78 (q, J = 34.1 Hz, BF₃). This compound **4b** has been prepared by Arduengo et al. in a different route.⁵

Preparation of [Mo(CO)₅(IⁱPr)] (5a).

I¹Pr·BEt₃ (**2a**) (106 mg, 0.42 mmol), Mo(CO)₆ (111 mg, 0.42 mmol), and toluene (10 mL) were put in a Schlenk tube. After being refluxed for 2h, the volatiles were removed under reduced pressure. The residual light brown solid was washed with hexane (2 x 10 mL) and dried in vacuo to give of [Mo(CO)₅(IⁱPr)] (**5a**) (110 mg, 0.28 mmol, 67%). Anal. Calcd for C₁₄H₁₆MoN₂O₅: C, 43.31; H, 4.15; N, 7.22%. Found. C, 43.34; H, 4.28; N, 7.12%. IR(KBr) vCO 1971, 1925, 1909, 1888 cm⁻¹. ¹H NMR (in CDCl₃) δ 1.44 (d, J = 6.8 Hz, 12H, ⁱPr-CH₃), 5.19 (sept, J = 6.8 Hz, 2H, ⁱPr-CH), 7.04 (s, 2H, CH=CH). ¹³C{¹H} NMR (in C₆D₆) δ 23.5 (ⁱPr-CH₃), 53.3 (ⁱPr-CH), 118.0 (CH=CH), 184.0 (br, NCN), 206.6 (cis-CO), 212.1 (trans-CO).

Preparation of [Mo(CO)₅(IMes)] (5b).

This compound was prepared from IMes·BEt₃ (**2b**) (220 mg, 0.55 mmol), Mo(CO)₆ (142 mg, 0.54 mmol), and toluene (15 mL) in the same manner as that for [Mo(CO)₅(IⁱPr)] (**5a**). Complex **5b** was isolated as a pale brown solid (yield, 194 mg, 0.36 mmol, 67 %). Anal. Calcd for $C_{26}H_{24}MoN_2O_5$: C, 57.78; H, 4.48; N, 5.18%. Found: C, 57.66; H, 4.49; N, 5.28%. IR(KBr) vCO 1972, 1915, 1877 cm⁻¹. ¹H NMR (in CDCl₃) δ 2.08 (s, 12H, Mes-*o*-CH₃), 2.36 (s, 6H, Mes-*p*-CH₃), 7.03 (s, 4H, Mes-*m*-H), 7.05 (s, 2H, CH=CH). ¹³C{¹H} NMR (in CDCl₃) δ 17.7 (Mes-*o*-CH₃), 21.2 (Mes-*p*-CH₃), 123.4 (CH=CH), 129.3, 135.4, 137.7, 139.5 (Mes-Ph), 193.2 (br, NCN), 205.0 (cis-CO), 211.1 (trans-CO).

Reaction of 3b with $Mo(CO)_6$ in toluene. Formation of 5b and $Mo(\eta$ -toluene)(CO)₃ (6).

IMes·BH₃ (**3b**) (36 mg, 0.11 mmol), Mo(CO)₆ (30 mg, 0.11 mmol), and toluene (8 mL) were put in a Schlenk tube. After being refluxed for 2h, the volatiles were removed under reduced pressure. The residual yellow solid was subjected to ¹H NMR measurement, which showed the formation of **5b** and Mo(η -toluene)(CO)₃ (**6**) in the ratio of ca. 1/1. The characterization of Mo(η -toluene)(CO)₃ was done by the comparison of the authentic sample prepared according to the literature method.⁶

Reaction of 4b with Mo(CO)₆.

IMes·BF₃ (**4b**) (38 mg, 0.094 mmol), Mo(CO)₆ (26 mg, 0.098 mmol), and toluene (8 mL) were put in a Schlenk tube. After being refluxed for 2h, the volatiles were removed under reduced pressure. The residual solid was subjected to ¹H NMR measurement, and then the solid was extracted with acetonitrile (10 mL). After removing the volatiles, compound **4b** was recovered as a white powder (31 mg, 0.077 mmol, 82%).

Preparation of [1,1'-dimethyl-3,3'-(1,2-xylylene)diimidazolin-2,2'-diylidene]·(BEt₃)₂ (8a).

To a solution of **7a** (533 mg, 1.24 mmol) in THF (ca. 10 mL) was added LiBEt₃H (2.5 mL of its 1.0 M THF solution, 2.5 mmol) at -78 °C. The reaction mixture was allowed to warm to room temperature. After being stirred for 24h at room temperature, the volatiles were removed under reduced pressure. The residual solid was extracted with toluene (20 mL), the solvent was removed under reduced pressure. The white solid, thus, formed was washed with pentane (3 x 10 mL) and dried in vacuo to yield **8a** (476 mg, 1.03 mmol, 83%). Anal. Calcd for C₂₈H₄₈B₂N₄: C, 72.74; H, 10.46; N, 12.12%. Found: C, 72.34; H, 10.30; N, 11.88%. ¹H NMR (in C₆D₆) δ 0.91 (quint, J = 7.3 Hz, 12H, CH₂CH₃), 1.14 (t, J = 7.3 Hz, 18H, CH₂CH₃), 3.26 (s, 6H, NCH₃), 5.25 (s, 4H, NCH₂), 5.69 (d, J = 2.0 Hz, 2H, CH=CH), 5.79 (d, J = 2.0 Hz, 2H, CH=CH₃), 6.62 (m, 2H, C₆H₄), 6.95 (m, 2H, C₆H₄). ¹³C{¹H} NMR (in C₆D₆) δ 12.3 (BCH₂CH₃), 14.8 (br, BCH₂CH₃), 37.5 (NCH₃), 50.5 (NCH₂Ph), 119.5 (CH=CH, overlapped), 122.4, 128.1, 134.6 (CH=CH, Ph), 177.3 (br, NCN). ¹¹B{¹H} NMR (in CDCl₃) δ -12.9 (BEt₃).

Preparation of [1,1'-dimethyl-3,3'-(1,3-xylylene)diimidazolin-2,2'-diylidene]·(BEt₃)₂ (8b).

This compound was prepared from **7b** (755 mg, 1.81 mmol) and LiBEt₃H (3.6 mL of its 1.0 M THF solution, 3.6 mmol) in the same manner as that for **8a**. Compound **8b** was isolated as a white solid (yield, 765 mg, 1.65 mmol, 91%). Anal. Calcd for $C_{28}H_{48}B_2N_4$: C, 72.74; H, 10.46; N, 12.12%. Found: C, 72.45; H, 10.34; N, 11.85%. ¹H NMR (in C₆D₆) δ 0.95 (quint, J = 6.6 Hz, 12H, CH₂CH₃), 1.11 (t, J = 6.6 Hz, 18H, CH₂CH₃), 3.23 (s, 6H, NCH₃), 5.13 (s, 4H, NCH₂), 5.64 (d, J = 2.0

Hz, 2H, CH=CH), 5.76 (d, J = 2.0 Hz, 2H, CH=CH), 6.54 (s, 1H, C₆H₄), 6.71 (d, J = 7.9 Hz, 2H, C₆H₄), 6.97 (t, J = 7.9 Hz, 1H, C₆H₄). ¹³C{¹H} NMR (in C₆D₆) δ 12.3 (BCH₂CH₃), 15.2 (br, BCH₂CH₃), 37.5 (NCH₃), 52.2 (NCH₂Ph), 119.7, 122.3 (CH=CH), 126.0, 126.9, 129.1, 138.1 (Ph), 176.8 (br, NCN). ¹¹B{¹H} NMR (in C₆D₆) δ -12.2 (BEt₃).

X-ray Crystallographic Analysis of 2a

Single crystals were obtained by recrystallization from a hexane solution at -30 °C. A colorless crystal was mounted on a glass fiber. Data were collected on a Rigaku AFC-7R automated four-circle diffractometer by using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) at -50 °C using the ω -2 θ scan technique to a maximum 2 θ value of 60.0°. Cell constants and an orientation matrix for data collection were determined from 24 reflections with 2 θ angles in the range 25.68 – 29.70°. The structure were solved by direct methods (SIR 92)⁷ and expanded using Fourier techniques.⁸ The refinement were carried out by a least-squares method on F^2 . A part of hydrogen atoms (H1 – H3, H7, and H11-H18) were found by the difference Fourier syntheses and refined isotropically, and the others were placed at the calculated positions and not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.⁹ Crystal data are summarized in Table 1. See the CIF data for detail.

X-ray Crystallographic Analysis of 2b

Single crystals were obtained by recrystallization from a hexane solution at $-30 \,^{\circ}$ C. A colorless crystal was mounted on a glass fiber. Data were collected on a Rigaku AFC-7R automated four-circle diffractometer by using graphite-monochromated Mo K α radiation ($\lambda = 0.71069 \text{ Å}$) at $-100 \,^{\circ}$ C using the ω -2 θ scan technique to a maximum 2 θ value of 60.0°. Cell constants and an orientation matrix for data collection were determined from 25 reflections with 2 θ angles in the range 28.12 – 30.00°. The structure were solved by direct methods (SIR 92)⁷ and expanded using Fourier techniques.⁸ The refinement were carried out by a least-squares method on F^2 . All hydrogen atoms were located at the calculated positions (C-H 0.95 Å) and not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.⁹ Crystal data are summarized in Table 2. See the CIF data for details.

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Table S1.Crystal data and structure refinement for 2a.

Empirical Formula Formula Weight Crystal Color, Habit Crystal Dimensions Crystal System Lattice Type	C ₁₅ H ₃₁ BN ₂ 250.23 colorless, prismatic 0.30 X 0.25 X 0.08 mm orthorhombic Primitive
No. of Reflections Used for Unit	
Cell Determination (20 range) Lattice Parameters	24 (25.7 - 29.7°) a = 16.033(8) Å b = 9.904(8) Å c = 10.58(1) Å $V = 1680(2) \text{ Å}^3$
Space Group	Pnma (#62)
Z value	4
D _{calc}	0.989 g/cm ³
F ₀₀₀	560.00
μ(ΜοΚα)	0.56 cm ⁻¹
Radiation	MoK α ($\lambda = 0.71069$ Å) graphite monochromated
Temperature	-50.0 °C
$2\theta_{max}$	59.90
No. of Reflections Measured	Total: 2788 Unique: 2575 (R _{int} = 0.066)
Corrections	Lorentz-polarization
No. of Reflections (All, $2\sigma < 52.50^{\circ}$)	1754
No. Variables	140
Reflection/Parameter Ratio	12.53
Residuals: R; Rw	0.156; 0.212
Residuals: RI	0.082
Goodness of Fit Indicator	1 65
Max Shift/Error in Final Cycle	0.022
Maximum peak in Final Diff Man	$0.20 e^{-/Å3}$
Minimum peak in Final Diff. Map	$-0.42 \text{ e}^{-/\text{Å}^3}$



Figure S1. Molecular Structure of 2a. Drawn with 30% probability. Hydrogen atoms are omitted in part for clarity.

Table S2. Crystal data and structure refinement for 2b.

Empirical Formula	C ₂₇ H ₃₉ BN ₂
Formula Weight	402.43
Crystal Color, Habit	colorless, prismatic
Crystal Dimensions	0.30 X 0.25 X 0.18 mm
Crystal System	orthorhombic
Lattice Type	Primitive
No. of Reflections Used for Unit	
Cell Determination (20 range)	25 (28.1 - 30.00)
Lattice Parameters	a = 16.929(10) Å
	b = 17.29(1) Å
	c = 8.511(8) Å
	$V = 2490(3) \text{ Å}^3$
Space Group	$P2_{1}2_{1}2_{1}$ (#19)
Z value	4
D _{calc}	1.073 g/cm^3
F ₀₀₀	880.00
μ(ΜοΚα)	0.61 cm ⁻¹
Radiation	MoK α ($\lambda = 0.71069$ Å)
	graphite monochromated
Temperature	-100.0 °C
20 _{max}	60.0 ⁰
No. of Reflections Measured	Total: 4085
	Unique: $4058 (R_{int} = 0.000)$
Corrections	Lorentz-polarization
No. of Reflections (All, $2\sigma < 55.00^{\circ}$)	3219
No. Variables	272
Reflection/Parameter Ratio	11.83
Residuals: R; Rw	0.133 ; 0.173
Residuals: R1	0.062
No. of Reflections to calc R1	1869
Goodness of Fit Indicator	1.46
Max Shift/Error in Final Cycle	0.017
Maximum peak in Final Diff. Map	0.26 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.27 e ⁻ /Å ³



Figure S2. Molecular Structure of 2b. Drawn with 30% probability. Hydrogen atoms are omitted in part for clarity.