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Supporting Information

Catalyst Design Based on Agostic Interaction: Synthesis, Characterization, and Catalytic Activity of Bis(pyrazolyl)borate Copper Complexes

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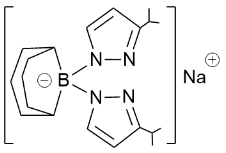
General Methods

All manipulations were carried out under nitrogenusing standard Schlenk techniques or in a glove box, unless otherwise stated. Solvents were dried and degassed using standard procedures prior to use. Sodium hydride (60 wt% dispersion in mineral oil) was purchased from Sigma Aldrich and was washed with hexane prior to use. Na[BBN(pz^{x})$_2$] (**1** and **2**, x = H and Me) were prepared by literature methods and Na[BBN(pz^{iPr})$_2$], **3**, was prepared as described below.[1] Column chromatography was performed on neutral alumina. All NMR spectra were recorded on a Bruker AV400 (^{1}H 400.1 MHz; ^{13}C 100.6 MHz; ^{31}P 162.0 MHz; ^{11}B 128.0 MHz) or a Bruker AV600 (^{1}H 600 MHz; ^{13}C 151 MHz; ^{11}B 193.0 MHz) spectrometer. ^{1}H and ^{13}C NMR chemical shifts are referenced to residual solvent protons or TMS, ^{11}B NMR spectra are externally referenced to $BF_3{\cdot}OEt_2$ in C_6D_6 (δ = 0.00 ppm), and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. Elemental analyses data were obtained on a Thermo Quest Italia SPA EA 1110 instrument.

1. Preparation and Characterization of Complexes 3, 4, 5 and 6

Complex **3**. To a stirred mixture of 9-BBN dimer (1.22 g, 5 mmol) and NaH (0.24 g, 10 mmol) in toluene (10 mL) was slowly added into a toluene solution of

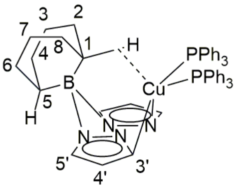
3-isopropyl-1H-pyrazole (Hpz^{iPr}, 2.20 g, 20 mmol) (10 mL) using a syringe. Hydrogen evolution was immediately observed. The reaction mixture was refluxed for 1-2 h until no more gas was released. During reaction a white precipitate was formed. The mixture was cooled to room temperature, and the solvent was removed to produce a white solid which was washed with hexane and dried under vacuum. Yield: 3.55 g, 98%.



^{1}H NMR (400 MHz, CD_3CN): δ 7.42 (d, 2H), 5.85 (d, *J* = 2.0 Hz, 2H), 2.94 (hept, *J* = 6.9 Hz, 2H), 1.86 (m, 2H), 1.73 (tt, *J*= 12.3, 5.6 Hz, 4H), 1.67–1.57 (m, 4H), 1.41–1.32 (m, 2H), 1.21 (m, 2H), 1.16 (d, *J* = 7.0 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN): δ 159.22, 132.81, 99.13, 32.21, 28.64, 25.27, 24.15, 22.98. ^{11}B NMR (128 MHz, CD_3CN): δ -1.77. ESI-MS: Na[(BBN)Bp^{iPr}]$^{-}$ calcd. m/z: 339.3, found: 339.0.

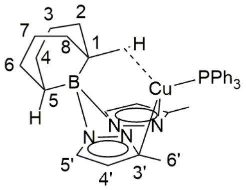
Complexes **4** and **5**. A slurry of compound Na[BBN(pz^{x})$_2$] (**1**, x = H; **2**, x = Me) (0.5 mmol) and $(PPh_3)_2Cu(I)NO_3$ (0.33 g, 0.5 mmol) in toluene (60 mL) was stirred vigorously at room temperature for 8 h. Then the mixture was filtered to remove the generated nitrate. After concentration of the filtrate to saturation, addition of hexane, and cooling to –30 °C, colorless crystals were obtained after a few days, which were collected by filtration, washed with hexane, and dried under vacuum.

4. Yield: 0.35 g, 83%.



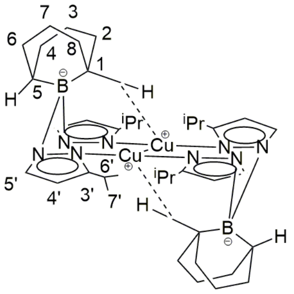
^{1}H NMR plus ^{13}C-^{1}H HSQC (600 MHz, C_6D_6): δ 7.74 (d, *J* = 2.1 Hz, 2H, H$^{5'}$), 7.47 (dt, *J* = 9.1, 3.7 Hz, 12H, Ph), 7.37 (s, 2H, H$^{3'}$), 7.08–6.97 (m, 18H, Ph), 6.04 (s, 2H, H$^{4'}$), 2.58 (s, 1H, H^{1}), 2.50 (dq, *J* = 12.3, 6.1, 5.3 Hz, 2H, H^{4}), 2.25 (qt, *J* = 13.0, 6.7 Hz, 2H, H^{3}), 2.16 (dd, *J* = 13.6, 7.0 Hz, 2H, H^{4}), 1.94 (t, *J* = 9.8 Hz, 2H, H^{2}), 1.84 (dt, *J* = 12.0, 5.2 Hz, 2H, H^{2}), 1.81–1.77 (s, 1H, H^{5}), 1.74 (dt, *J* = 14.1, 7.2 Hz, 2H, H^{3}). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 139.42 (C$^{3'}$), 134.20 (Ph), 134.08 (Ph), 133.18 (C$^{5'}$), 129.66 (Ph), 128.99 (Ph), 128.94 (Ph), 103.88 (C$^{4'}$), 32.79 (C^{4}), 31.10 (C^{2}), 31.01 (C^{1}), 25.29 (C^{3}), 21.54 (C^{5}). ^{11}B NMR (128 MHz, $CDCl_3$): *δ* -0.79. ^{31}P NMR (162 MHz, $CDCl_3$): *δ* -0.24. Elemental Analysis Calcd. (%) for $C_{50}H_{50}BCuN_4P_2$: C, 71.22; H, 5.98; N, 6.64. Found: C, 72.98; H, 6.11; N, 6.62.

5. Yield: 0.24 g, 79%.



^{1}H NMR plus ^{13}C-^{1}H HSQC (600 MHz, C_6D_6): δ 7.67 (d, *J* = 6.6 Hz, 6H, Ph), 7.66–7.63 (d, 2H, H$^{5'}$), 7.02 (d, *J* = 5.4 Hz, 9H, Ph), 5.87

(d, *J* = 1.9 Hz, 2H, $H^{4'}$), 2.62 (s, 1H, H^{5}), 2.55 (dq, *J* = 12.3, 6.3, 5.6 Hz, 2H, H^{4}), 2.28 (td, *J* = 11.7, 11.2, 4.8 Hz, 2H, H^{3}), 2.22–2.14 (m, 2H, H^{4}), 1.98 (s, 6H, $H^{6'}$), 1.97 (d, *J* = 7.6 Hz, 2H, H^{2}), 1.81 (q, *J* = 7.0 Hz, 3H, H^{1+3}). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 147.39 ($C^{3'}$), 134.18 (Ph), 134.08 (Ph), 133.89 (Ph), 133.69 (Ph), 133.45 (Ph), 130.45 ($C^{5'}$), 129.21 (Ph), 129.14 (Ph), 103.57 ($C^{4'}$), 32.82 (C^{4}), 31.95 (C^{1}), 31.15 (C^{2}), 25.43 (C^{3}), 21.51 (C^{5}), 14.44 ($C^{6'}$). ^{11}B NMR (128 MHz, $CDCl_3$): *δ* -1.43. ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 4.59. Elemental Analysis Calcd. (%) for $C_{34}H_{39}BCuN_4P$: C, 67.05; H, 6.45; N, 9.20. Found: C, 66.96; H, 6.49; N, 9.28.



Complex **6**. A slurry of compound Na[BBN(pz^{iPr})$_2$] (**3**) (0.36 g, 1.0 mmol) and Cu(I)(CH_3CN)$_4$$PF_6$ (0.33 g, 1.0 mmol) in toluene (50 mL) was stirred vigorously at room temperature for 48 h. Then the mixture was filtered to remove the generated sodium hexafluorophosphate. After concentration of the filtrate to saturation and cooling to –30 °C, colorless crystals were obtained after a few days, which were collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.16 g, 38%.

^{1}H NMR plus ^{13}C-^{1}H HSQC (600 MHz, C_6D_6): δ 7.54 (d, *J* = 2.4 Hz, 2H, $H^{5'}$), 5.91 (d, *J* = 2.4 Hz, 2H, $H^{4'}$), 3.86 (d, *J* = 4.6 Hz, 1H, H^{1}), 3.53 (hept, *J* = 6.9 Hz, 2H, $H^{6'}$), 2.55–2.43 (m, 2H, H^{4}), 2.31–2.17 (m, 4H, H^{3+4}), 2.12–2.03 (m, 2H, H^{2}), 2.03–1.94 (m, 2H, H^{2}), 1.66 (dt, *J* = 12.2, 6.9 Hz, 2H, H^{3}), 1.56 (s, *J* = 6.0 Hz, 1H, H^{5}), 1.14 (d, *J* = 6.9 Hz, 6H, $H^{7'}$), 1.10 (d, *J* = 6.8 Hz, 6H, $H^{7'}$). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 161.47 ($C^{3'}$), 135.63 ($C^{5'}$), 101.24 ($C^{4'}$), 32.13 (C^{4}), 31.52 (C^{2}), 31.50 (C^{1}), 30.70 ($C^{6'}$), 24.81 (C^{5}), 24.80 (C^{3}), 23.50 ($C^{7'}$). ^{11}B NMR (193 MHz, C_6D_6): δ -0.95. Elemental Analysis Calcd. (%) for $C_{40}H_{64}B_2Cu_2N_8$: C, 59.63; H, 8.01; N, 13.91. Found: C, 60.70; H, 8.46; N, 15.91.

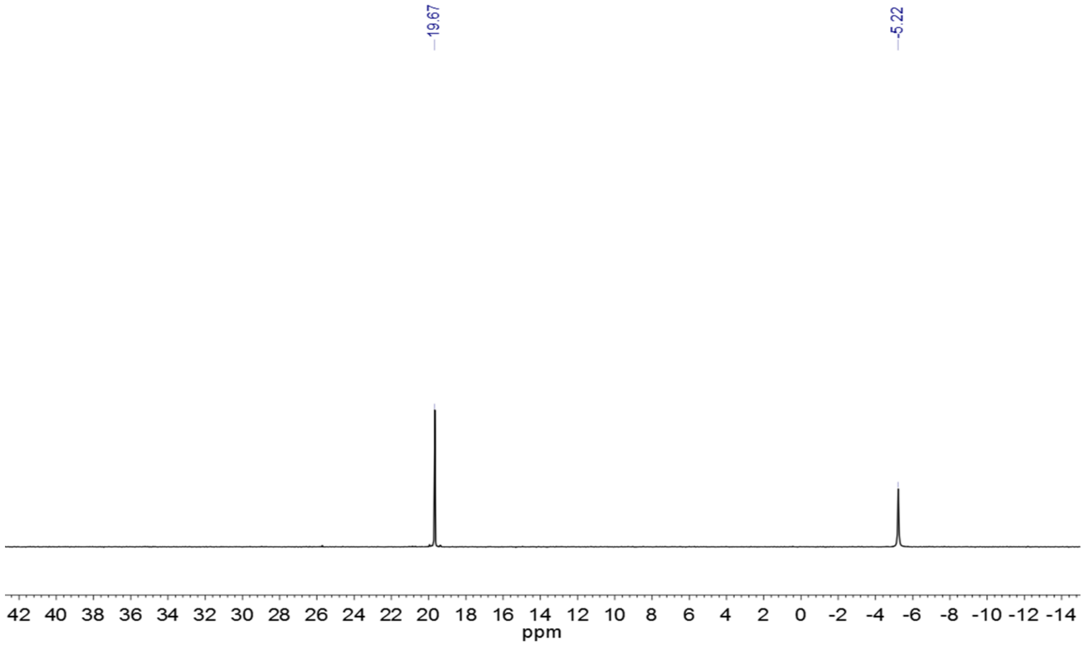
2. General Catalytic Procedure for Reactions of Carbene Insertion into N–H bonds: To a solution of the corresponding [BBN(pz^{x})$_2$]Cu(I) complex (0.025 mmol for **4** and **5**, 0.0125 mmol for **6**) in solvent (benzene or THF, 10 mL), arylamine ($PhNH_2$ or Ph_2NH, 2.5 mmol) and EDA (1 mmol) were added *via* microsyringes. The mixture was stirred at room temperature for 12 h or 24 h. The solvent was evaporated under vacuum, and the crude product was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1 for ethyl phenylglycinate, 100:1 for diethyl phenylglycinate).

$PhNHCH_2CO_2Et$: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (dtd, *J* = 27.7, 7.4, 1.9 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.65–6.57 (m, 2H), 4.29 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 171.26, 147.12, 129.42, 118.28, 113.10, 61.45, 45.96, 14.32.

$Ph_2NCH_2CO_2Et$: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.26 (m, 4H), 7.08–6.98 (m, 5H), 4.47 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 170.98, 147.51, 129.40, 121.98, 120.74, 77.48, 77.16, 76.84, 61.19, 54.19, 14.29.

3. Verification of the Catalytic Mechanism of 4: Catalytic Procedure with Excess PPh_3.

To a solution of complex **4** (0.025 mmol) in benzene (10 mL), were added aniline (2.5 mmol), EDA (1 mmol) and PPh_3 (1.5 mmol). The mixture was stirred at room temperature for 12 h. Thin-layer chromatography showed no sign of $PhNHCH_2CO_2Et$. ^{31}P NMR demonstrated resonances of the dominant product at δ = 19.67 ppm which can be assigned to $Ph_3P{=}CHCO_2Et$, and excess PPh_3 at δ = -5.22 ppm.



^{31}P NMR (162 MHz, C_6D_6)

4. X-ray Crystallography

Single-crystal X-ray diffraction data were collected on a Bruker SMART6000 CCD detector with graphite-monochromated Mo Kα radiation, λ = 0.71073 Å. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structures were solved by a combination of direct methods in SHELXTL and the difference Fourier technique and refined by full-matrix least-squares procedures. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model. The α-hydrogens of the organohydroborate rings in all complexes **4-6** were located and refined isotropically. No solvent of crystallization is present in the lattice for any of the structures. CCDC-1442819 (**4**), CCDC-1442820 (**5**), and CCDC-1442821 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif. Crystal data and refinement parameters are summarizedin Table S1.

Table S1. Crystallographic data and structure refinement results for **4**, **5** and **6**.

	4	**5**	**6**
Empirical formula	$C_{50}H_{50}BCuN_4P_2$	$C_{34}H_{39}BCuN_4P$	$C_{40}H_{64}B_2Cu_2N_8$
Mr	843.23	609.01	805.69
Temp, K	123.(2)	153.(2)	103(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$/c	$P2_1$/c	$C2$/c
a[Å]	12.0830(5)	9.1051(9)	20.5734(14)
B[Å]	23.5983(9)	22.010(2)	18.8925(14)
c[Å]	15.6640(6)	15.8051(17)	10.6494(7)
α[°]	90.00	90.00	90.00
β[°]	100.1216(15)	97.666(4)	98.618(2)

γ[°]	90.00	90.00	90.00
V[Å^3]	4396.9(3)	3139.1(6)	4092.5(5
Z	4	4	4
ρ_{calc} [g cm^{-3}]	1.274	1.289	1.308
λ [Å]	0.71073	0.71073	0.71073
μ[mm^{-1}]	0.609	0.776	1.078
F(000)	1768	1280	1712
θ range [°]	2.49 to 31.06	2.76 to 28.05	2.84 to 25.00
Reflns collected	132659	51146	35407
Independent reflns	14054	7535	7455
R_{int}	0.0625	0.1584	0.0565
GOF on F^2	1.024	1.007	1.032
R_1/wR_2[$I \geq 2\sigma(I)$]	0.0400/0.0861	0.0555/ 0.1191	0.0367/0.0819
R_1, wR_2 (all data)	0.0681/0.0992	0.1058/0.1445	0.0600/0.0899

References

[1] (a) S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Angew. Chem. Int. Ed. Engl.*, **1989**, *28*, 205; (b) M. Bortolin, U. E. Bucher, H. Ruegger, L. M. Venanzi, A. Albinati, F. Lianza and S. Trofimenko, *Organometallics*, **1992**, *11*, 2514; (c) L. Komorowski, A. Meller and K. Niedenzu, *Inorg. Chem.*, **1990**, *29*, 538; (d) M. H. Chisholm, S. S. Iyer and W. E. Streib, *New J. Chem.*, **2000**, *24*, 393.