Supplementary Material (ESI) for Chemical Communications

Supplementary Information

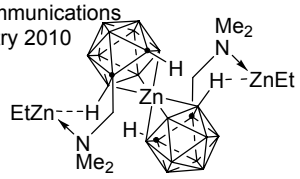
Charge-compensated Zn metallocenes with σ-/π-chelating carboranyl ligands for the formation of constrained geometry Ru(II) and Ni(II) complexes

Jong-Dae Lee, Won-Sik Han, Tae-Jin Kim, Sang Hern Kim, and Sang Ook Kang

Experimental Section

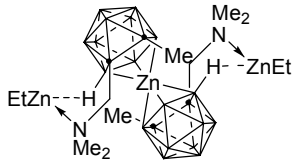
General Procedures All manipulations were performed under a dry, oxygen-free nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere HE-493 drybox. Toluene, hexane, and pentane were distilled under nitrogen from sodium/benzophenone. Dichloromethane was dried with CaH_2. Pyridine-d_5 was distilled under nitrogen from sodium and stored in a Schlenk storage flask until needed. $CDCl_3$ was predried under CaH_2 and vacuum-transferred. Et_2Zn were used as received from Strem Chemical. *o*-Carborane was purchased from KatChem and used after sublimation. The dicarbollylamine ligands **1**−**4** were synthesized according to literature procedure.[1] All ^1H (300.1 MHz), ^{11}B (96.3 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded on a Varian Mercury-300BB spectrometer unless otherwise stated. ^1H and ^{13}C NMR chemical shifts were measured relative to internal residual peaks from the lock solvent (99.5% $(CD_3)_2SO$, 99.9% $CDCl_3$, 99.5% NC_5D_5) and then referenced to Me_4Si (0.00 ppm). All ^{11}B NMR chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. Elemental analyses were performed using a Carlo Erba Instruments CHNS-O EA1108 analyzer. All melting points were uncorrected.

1. (a) Kim D. –H; Won, J. H.; Kim, S. –J.; Ko, J.; Kim, S. –H.; Cho, S.; Kang, S. O. *Organometallics* **2001**, *20*, 4298. (b) Lee, Y. –J.; Lee, J. –D.; Jeong, H. –J.; Son, K. –C.; Ko, J.; Cheong, M.; Kang, S. O. *Organometallics* **2005**, *24*, 3008. (c) Lee, J. –D.; Lee, Y. –J.; Son, K. –C.; Cheong, M.; Ko, J.; Kang, S. O. *Organometallics* **2007**, *26*, 3374.



$[(\eta^3\text{-}C_2B_9H_9)_2Zn][(\eta^1\text{-}NMe_2)ZnEt]_2$ **5**

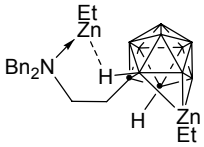
10 mL of a toluene solution of $ZnEt_2$ (0.72 g, 6.0 mmol) was added to a stirred solution of 20 mL of toluene containing compound **1** (0.38 g, 2.0 mmol) by cannula at –78 ºC. Subsequently, the dry-ice/acetone bath was removed, and the solution was heated under reflux in N_2 for 12 h. The volatiles were removed under vacuum. Compound **5** was purified by recrystallization from toluene in 87% yield (0.62 g, 0.87 mmol). Mp: 178 °C (dec.). HRMS: calcd for $[^{12}C_{12}{}^{11}B_{18}{}^{1}H_{40}{}^{14}N_2{}^{65}Zn_3]^+$ 711.4083. Found: 711.4114. IR spectrum (KBr pellet, cm^{-1}) ν(B–H) 2540, ν(C–H) 2876, 2910. ^{1}H NMR (300.1 MHz, Pyridine–d_5) δ 0.80 (q, 2H, $^3J_{HH}$ = 7.5 Hz, Zn–CH_2CH$_3$), 0.97 (q, 2H, $^3J_{HH}$ = 7.5 Hz, Zn–CH_2CH$_3$), 1.53 (t, 3H, $^3J_{HH}$ = 8.1 Hz, Zn–CH$_2$CH_3), 1.84 (t, 3H, $^3J_{HH}$ = 8.1 Hz, Zn–CH$_2$CH_3), 2.14 (s, 6H, NMe_2), 2.17 (d, 1H, $^2J_{HH}$ = 13.2 Hz, CH_2N), 2.28 (d, 1H, $^2J_{HH}$ = 13.2 Hz, CH_2N), 2.35 (s, 1H, C_{cab}–H), 2.45 (s, 6H, NMe_2), 2.53 (d, 1H, $^2J_{HH}$ = 13.2 Hz, CH_2N), 2.78 (d, 1H, $^2J_{HH}$ = 13.2 Hz, CH_2N). ^{13}C NMR (75.4 MHz, Pyridine–d_5) δ –3.83 (ZnEt), 2.79 (ZnEt), 12.98 (ZnEt), 13.15 (ZnEt), 47.15 (NMe_2), 47.62 (NMe_2), 66.81 (CH$_2$N), 67.72 (CH$_2$N). ^{11}B NMR (96.3 MHz, Pyridine–d_5) δ –21.07 (1B), –22.96 (2B), –26.43 (1B), –27.45 (1B), –28.73 (1B), –38.84 (1B), –42.71 (1B), –44.68 (1B).



$[(\eta^3\text{-}8\text{-}CH_3\text{-}C_2B_9H_9)_2Zn][(\eta^1\text{-}NMe_2)ZnEt]_2$ **6**

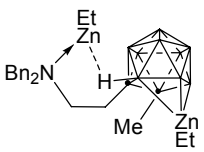
A procedure analogous to the preparation of **5** was used, but starting from **2** (0.21 g, 1.0 mmol) in toluene. Yield: 29% (0.21 g, 0.29 mmol). Mp: 192 °C (dec.). HRMS: calcd for $[^{12}C_{14}{}^{11}B_{18}{}^{1}H_{44}{}^{14}N_2{}^{65}Zn_3]^+$ 724.3836. Found: 724.3856. IR spectrum (KBr pellet, cm^{-1}) ν(B–H) 2535, ν(C–H) 2885, 2950. ^{1}H NMR (300.1 MHz, Pyridine–d_5) δ 0.72 (br, 2H, Zn–CH_2CH$_3$), 1.21 (br, 2H, Zn–CH_2CH$_3$), 1.44 (t, 3H, $^3J_{HH}$ = 7.5 Hz, Zn–CH$_2$CH_3), 1.62 (t, 3H, $^3J_{HH}$ = 7.5 Hz, Zn–CH$_2$CH_3),

1.96 (s, 3H, C_{cab}–*Me*), 2.09 (s, 6H, N*Me*$_2$), 2.10 (d, 1H, $^2J_{HH}$ = 13.2 Hz, C*H*$_2$N), 2.17 (d, 1H, $^2J_{HH}$ = 13.2 Hz, C*H*$_2$N), 2.39 (s, 6H, N*Me*$_2$), 2.52 (d, 1H, $^2J_{HH}$ = 13.2 Hz, C*H*$_2$N), 2.89 (d, 1H, $^2J_{HH}$ = 13.2 Hz, C*H*$_2$N). ^{13}C NMR (75.4 MHz, Pyridine–d_5) δ –2.72 (Zn*Et*), –0.19 (Zn*Et*), 14.10 (Zn*Et*), 14.97 (Zn*Et*), 24.76 (C_{cab}–*Me*), 46.94 (N*Me*$_2$), 47.55 (N*Me*$_2$), 66.20 (*C*H$_2$N), 66.93 (*C*H$_2$N). ^{11}B NMR (96.3 MHz, Pyridine–d_5) δ –4.25 (1B), –8.74 (1B), –14.76 (2B), –19.10 (1B), –22.26 (1B), –24.59 (1B), –39.61 (1B), –42.21 (1B).



[(η^3-$C_2B_9H_9$)ZnEt][(η^1-NBn$_2$)ZnEt] **7**

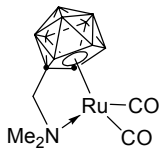
A procedure analogous to the preparation of **5** was used, but starting from **3** (0.36 g, 1.0 mmol) in THF. Yield: 34% (0.19 g, 0.34 mmol). Mp: 157 °C (dec.). HRMS: calcd for [$^{12}C_{24}{}^{11}B_9{}^1H_{38}{}^{14}N^{65}Zn_2$]$^+$ 557.2581 Found: 557.2552. IR spectrum (KBr pellet, cm^{-1}) ν(B–H) 2514, ν(C–H) 2877, 2955. ^{1}H NMR (300.1 MHz, Pyridine–d_5) δ 0.74 (br, 2H, Zn–C*H*$_2$CH$_3$), 0.91 (br, 2H, Zn–C*H*$_2$CH$_3$), 1.33 (br, 3H, Zn–CH$_2$C*H*$_3$), 1.54 (br, 3H, Zn–CH$_2$C*H*$_3$), 2.40 (s, 1H, C_{cab}–*H*), 2.65 (m, 1H, C*H*$_2$CH$_2$N), 2.74 (m, 1H, CH$_2$C*H*$_2$N), 3.05 (m, 1H, C*H*$_2$CH$_2$N), 3.17 (m, 1H, CH$_2$C*H*$_2$N), 3.30 (d, 1H, $^2J_{HH}$ = 13.5 Hz, PhC*H*$_2$N), 3.47 (d, 1H, $^2J_{HH}$ = 13.5 Hz, PhC*H*$_2$N), 3.60 (d, 1H, $^2J_{HH}$ = 4.2 Hz, PhC*H*$_2$N), 3.69 (d, 1H, $^2J_{HH}$ = 4.2 Hz, PhC*H*$_2$N), 7.29–7.65 (m, 10H, *Ph*CH$_2$N). ^{13}C NMR (75.4 MHz, Pyridine–d_5) δ –2.99 (Zn*Et*), –2.51 (Zn*Et*), 13.56 (Zn*Et*), 14.25 (Zn*Et*), 33.97 (*C*H$_2$CH$_2$N), 52.01 (CH$_2$*C*H$_2$N), 58.18 (Ph*C*H$_2$N), 126.92–129.22 (*Ph*CH$_2$N). ^{11}B NMR (96.3 MHz, Pyridine–d_5) δ –8.19 (1B), –9.78 (1B), –15.01 (2B), –16.56 (2B), –18.27 (2B), –44.04 (1B).



[(η^3-8-CH_3-$C_2B_9H_9$)ZnEt][(η^1-NBn$_2$)ZnEt] **8**

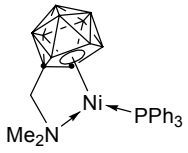
A procedure analogous to the preparation of **5** was used, but starting from **4** (0.37 g, 1.0 mmol) in

THF. Yield: 53% (0.53 g, 0.51 mmol). Mp. 159 °C (dec.). HRMS: calcd for $[^{12}C_{24}{}^{11}B_9{}^{1}H_{40}{}^{14}N^{65}Zn_2]^+$ 571.2738. Found: 571.2760. IR spectrum (KBr pellet, cm^{-1}) ν(B–H) 2484, 2541, ν(C–H) 2887, 2964. ^{1}H NMR (300.1 MHz, Pyridine–d_5) δ 0.77 (br, 2H, Zn–CH_2CH$_3$), 0.93 (br, 2H, Zn–CH_2CH$_3$), 1.55 (t, 3H, $^2J_{HH}$ = 8.4 Hz, Zn–CH$_2$CH_3), 1.69 (t, 3H, $^2J_{HH}$ = 8.4 Hz, Zn–CH$_2$CH_3), 1.98 (s, 3H, C_{cab}–*Me*), 2.55 (m, 1H, CH_2CH$_2$N), 2.76 (m, 1H, CH$_2$CH_2N), 2.93 (m, 1H, CH_2CH$_2$N), 3.06 (m, 1H, CH$_2$CH_2N), 3.25 (d, 1H, $^2J_{HH}$ = 13.8 Hz, PhCH_2N), 3.44 (d, 1H, $^2J_{HH}$ = 13.8 Hz, PhCH_2N), 3.50 (d, 1H, $^2J_{HH}$ = 13.8 Hz, PhCH_2N), 3.61 (d, 1H, $^2J_{HH}$ = 13.8 Hz, PhCH_2N), 7.10–7.43 (m, 10H, *Ph*CH$_2$N). ^{13}C NMR (75.4 MHz, Pyridine–d_5) δ –2.57 (Zn*Et*), –2.02 (Zn*Et*), 12.53 (Zn*Et*), 14.00 (Zn*Et*), 32.89 (*C*H$_2$CH$_2$N), 40.58 (CH$_2$*C*H$_2$N), 58.44 (Ph*C*H$_2$N), 126.86–128.97 (*Ph*CH$_2$N). ^{11}B NMR (96.3 MHz, Pyridine–d_5) δ –9.20 (1B), –12.01 (1B), –15.88 (1B), –16.79 (1B), –23.87 (2B), –32.47 (1B), –43.52 (2B).



[(η^5:η^1-7-Me_2NCH_2-7,8-$C_2B_9H_9$)$Ru(CO)_2$ **9**

Over a period of 30 min, a $[(CO)_3RuCl_2]_2$ (0.05 g, 0.1 mmol) was added to a stirred solution of **5** (0.06 g, 0.1 mmol) in toluene (20 mL) at room temperature. After addition was complete, the solution was stirred at room temperature for 6 h. The solution was filtered in air, and the solvent was removed under reduced pressure. The remaining solid was passed through a short column of silica gel with CH_2Cl_2 as the eluent. The orange band was collected and purified by recrystallization with CH_2Cl_2. **9**: Yield: 58% (0.02 g, 0.06 mmol). Anal. Found: C 24.33, H 5.32, N 4.10. Calcd: C 24.26, H 5.23, N 4.04. Mp: 176 °C (dec). IR spectrum (KBr pellet, cm^{-1}) ν(C–H) 3046, ν(B–H) 2579, 2542, ν(C=O) 2043, 1990. ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 2.81 (s, 3H, N*Me*$_2$), 2.95 (s, 3H, N*Me*$_2$), 3.53 (br, 1H, Ccab–*H*), 3.84 (d, 1H, NC*H*$_2$, $^2J_{HH}$ = 14 Hz), 3.99 (d, 1H, NC*H*$_2$, $^2J_{HH}$ = 14 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 57.67 (N*Me*$_2$), 58.04 (N*Me*$_2$), 77.46 (N*C*H$_2$), 222.68 (Ru–*C*O). ^{11}B NMR (96.3 MHz, $CDCl_3$) δ 2.19 (1B), –1.90 (1B), –3.41 (1B), –6.10 (1B), –14.16 (2B), –16.01 (1B), –22.11 (2B).



[(η^5:η^1-7-Me_2NCH_2-7,8-$C_2B_9H_9$)$Ni(PPh_3)$ **10**

Over a period of 30 min, a $(PPh_3)_2NiCl_2$ (0.13 g, 0.2 mmol) was added to a stirred solution of **5** (0.06 g, 0.1 mmol) in toluene (20 mL) at room temperature. After the addition was complete, the the solution was stirred at room temperature for 6 h. The dark residue after removal of the solvents was flash chromatographed on silica gel using 10% CH_2Cl_2 in hexane to remove some organics, followed by 50% CH_2Cl_2 in hexane. The red band was collected and purified by recrystallization with CH_2Cl_2. **10**: Yield: 67% (0.07 g, 0.14 mmol). Anal. Found: C 54.30, H 6.68, N 2.90. Calcd: C 54.12, H 6.52,

N 2.74, Mp. 178 °C (decomp.). IR (KBr pellet, cm^{-1}) ν(C–H) 3057, 2929, ν(B–H) 2536, ν(C=C) 1436, ν(C–P) 1095. ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 1.80 (s, 3H, N*Me*$_2$), 1.99 (s, 3H, N*Me*$_2$), 3.03 (d, 1H, NC*H*$_2$, $^{2}J_{HH}$ = 14 Hz), 3.20 (d, 1H, NC*H*$_2$, $^{2}J_{HH}$ = 14 Hz), 3.75 (br, 1H, Ccab–*H*), 7.62–7.91 (m, 15H, P*Ph*$_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 42.44 (N*Me*$_2$), 60.56 (N*C*H$_2$), 128.83, 130.88, 134.59 (P*Ph*$_3$). ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –3.31 (1B), –10.20 (3B), –16.21 (1B), –20.13 (3B), –24.76 (1B).

Table 1. Crystal data and structure refinement for **5**·C_6H_6.

Identification code	kor591a
Empirical formula	$C_{20}H_{52}B_{18}N_2Zn_3$
Formula weight	711.33
Temperature	233(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, *P*bcn
Unit cell dimensions	a = 14.811(5) Å
	b = 19.090(7) Å
	c = 13.027(4) Å
Volume	3683(2) Å^3
Z, D_{calc}	4, 1.283 g/mm^3
μ	1.955 mm^{-1}
F(000)	1464
Crystal size	0.46 × 0.17 × 0.14 mm
θ range for data collection	2.13 to 28.33 °
Limiting indices	–19≤h≤9, –25≤k≤25, –16≤l≤17
Reflections collected / unique	25547 / 4578 [R(int) = 0.1176]
Completeness to θ = 25.96	0.7715 and 0.4667
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4578 / 0 / 204
Goodness-of-fit on F^2	1.018
Final R indices [I>2σ (I)]	R_1 = 0.0663, wR_2 = 0.1708
R indices (all data)	R_1 = 0.1591, wR_2 = 0.2504
Absolute structure parameter	0.0037(8)
Largest diff. peak and hole	1.387 and –0.645 e.Å^{-3}

[a]$R_1 = \sum||F_o|-|F_c||$ (based on reflections with $F_o^2>2\sigma F^2$), [b]$wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.095P)^2]$; , $P = [\max(F_o^2, 0)+2F_c^2]/3$(also with $F_o^2>2\sigma F^2$)

Table 2. Bond lengths [Å] for **5**·C_6H_6.

Zn(1)-B(10)	2.108(7)	B(3)-C(8)	1.692(9)
Zn(1)-B(10)#1	2.108(7)	B(3)-B(4)	1.762(1)
Zn(1)-B(9)	2.283(7)	B(3)-B(9)	1.773(1)
Zn(1)-B(9)#1	2.283(7)	B(4)-B(10)	1.749(1)
Zn(1)-B(11)#1	2.392(8)	B(4)-B(9)	1.763(1)
Zn(1)-B(11)	2.392(8)	B(4)-B(5)	1.786(1)
Zn(2)-C(15)	1.944(8)	B(5)-B(6)	1.763(1)
Zn(2)-N	2.065(6)	B(5)-B(10)	1.770(1)
Zn(2)-B(11)	2.511(7)	B(5)-B(11)	1.785(1)
Zn(2)-B(6)	2.517(7)	B(6)-C(7)	1.726(9)
Zn(2)-H(11)	1.92(5)	B(6)-B(11)	1.786(1)
N-C(14)	1.479(8)	C(7)-C(12)	1.525(8)
N-C(13)	1.487(8)	C(7)-C(8)	1.552(8)
N-C(12)	1.500(8)	C(7)-B(11)	1.620(9)
B(1)-B(6)	1.768(1)	C(8)-B(9)	1.662(1)
B(1)-B(2)	1.779(1)	B(9)-B(10)	1.804(1)
B(1)-B(3)	1.782(1)	B(10)-B(11)	1.793(1)
B(1)-B(5)	1.788(1)	B(11)-H(11)	1.11(5)
B(1)-B(4)	1.796(1)	C(15)-C(16)	1.494(1)
B(2)-C(8)	1.708(1)	C(50)-C(51)	1.345(16)
B(2)-C(7)	1.734(9)	C(50)-C(50)#2	1.47(2)
B(2)-B(6)	1.756(1)	C(51)-C(52)	1.335(2)
B(2)-B(3)	1.769(1)	C(52)-C(52)#2	1.34(2)

Table 3 Angles [deg] for Cb16.

B(10)-Zn(1)-B(10)#1	180.0(1)	B(11)-B(5)-B(1)	107.3(5)
B(10)-Zn(1)-B(9)	48.3(3)	B(4)-B(5)-B(1)	60.3(4)
B(10)#1-Zn(1)-B(9)	131.7(3)	C(7)-B(6)-B(2)	59.7(4)
B(10)-Zn(1)-B(9)#1	131.7(3)	C(7)-B(6)-B(5)	102.4(5)
B(10)#1-Zn(1)-B(9)#1	48.3(3)	B(2)-B(6)-B(5)	109.1(5)
B(9)-Zn(1)-B(9)#1	180.0(1)	C(7)-B(6)-B(1)	104.7(5)
B(10)-Zn(1)-B(11)#1	133.6(3)	B(2)-B(6)-B(1)	60.6(4)
B(10)#1-Zn(1)-B(11)#1	46.4(3)	B(5)-B(6)-B(1)	60.8(4)
B(9)-Zn(1)-B(11)#1	106.5(3)	C(7)-B(6)-B(11)	54.9(4)
B(9)#1-Zn(1)-B(11)#1	73.5(3)	B(2)-B(6)-B(11)	106.5(5)
B(10)-Zn(1)-B(11)	46.4(3)	B(5)-B(6)-B(11)	60.4(4)
B(10)#1-Zn(1)-B(11)	133.6(3)	B(1)-B(6)-B(11)	108.2(5)
B(9)-Zn(1)-B(11)	73.5(3)	C(7)-B(6)-Zn(2)	86.4(3)
B(9)#1-Zn(1)-B(11)	106.5(3)	B(2)-B(6)-Zn(2)	134.9(4)
B(11)#1-Zn(1)-B(11)	180.0(3)	B(5)-B(6)-Zn(2)	106.5(4)
C(15)-Zn(2)-N	132.1(3)	B(1)-B(6)-Zn(2)	164.4(5)
C(15)-Zn(2)-B(11)	141.0(3)	B(11)-B(6)-Zn(2)	69.0(3)
N-Zn(2)-B(11)	85.2(2)	C(12)-C(7)-C(8)	116.4(5)
C(15)-Zn(2)-B(6)	135.1(3)	C(12)-C(7)-B(11)	120.2(5)
N-Zn(2)-B(6)	84.6(2)	C(8)-C(7)-B(11)	112.4(5)
B(11)-Zn(2)-B(6)	41.6(2)	C(12)-C(7)-B(6)	122.1(5)
C(15)-Zn(2)-H(11)	125.3(1)	C(8)-C(7)-B(6)	110.9(5)
N-Zn(2)-H(11)	91.6(1)	B(11)-C(7)-B(6)	64.4(4)
B(11)-Zn(2)-H(11)	24.6(1)	C(12)-C(7)-B(2)	116.4(5)
B(6)-Zn(2)-H(11)	65.9(1)	C(8)-C(7)-B(2)	62.3(4)
C(14)-N-C(13)	107.7(6)	B(11)-C(7)-B(2)	115.6(5)
C(14)-N-C(12)	110.4(5)	B(6)-C(7)-B(2)	61.0(4)

C(13)-N-C(12)	109.3(5)	C(7)-C(8)-B(9)	112.3(5)
C(14)-N-Zn(2)	106.9(4)	C(7)-C(8)-B(3)	113.5(5)
C(13)-N-Zn(2)	108.8(5)	B(9)-C(8)-B(3)	63.8(4)
C(12)-N-Zn(2)	113.6(4)	C(7)-C(8)-B(2)	64.1(4)
B(6)-B(1)-B(2)	59.4(4)	B(9)-C(8)-B(2)	116.7(5)
B(6)-B(1)-B(3)	106.5(5)	B(3)-C(8)-B(2)	62.7(4)
B(2)-B(1)-B(3)	59.6(4)	C(8)-B(9)-B(4)	104.0(5)
B(6)-B(1)-B(5)	59.4(4)	C(8)-B(9)-B(3)	58.9(4)
B(2)-B(1)-B(5)	106.9(5)	B(4)-B(9)-B(3)	59.8(4)
B(3)-B(1)-B(5)	106.8(5)	C(8)-B(9)-B(10)	105.5(5)
B(6)-B(1)-B(4)	106.6(5)	B(4)-B(9)-B(10)	58.7(4)
B(2)-B(1)-B(4)	106.6(6)	B(3)-B(9)-B(10)	107.9(5)
B(3)-B(1)-B(4)	59.0(4)	C(8)-B(9)-Zn(1)	84.4(4)
B(5)-B(1)-B(4)	59.8(4)	B(4)-B(9)-Zn(1)	118.9(5)
C(8)-B(2)-C(7)	53.6(4)	B(3)-B(9)-Zn(1)	138.4(5)
C(8)-B(2)-B(6)	102.5(5)	B(10)-B(9)-Zn(1)	60.8(3)
C(7)-B(2)-B(6)	59.3(4)	B(4)-B(10)-B(5)	61.0(4)
C(8)-B(2)-B(3)	58.2(4)	B(4)-B(10)-B(11)	106.4(5)
C(7)-B(2)-B(3)	101.5(5)	B(5)-B(10)-B(11)	60.1(4)
B(6)-B(2)-B(3)	107.5(5)	B(4)-B(10)-B(9)	59.5(4)
C(8)-B(2)-B(1)	103.7(5)	B(5)-B(10)-B(9)	106.9(5)
C(7)-B(2)-B(1)	103.9(5)	B(11)-B(10)-B(9)	102.2(5)
B(6)-B(2)-B(1)	60.0(4)	B(4)-B(10)-Zn(1)	129.7(5)
B(3)-B(2)-B(1)	60.3(4)	B(5)-B(10)-Zn(1)	134.0(5)
C(8)-B(3)-B(4)	102.7(5)	B(11)-B(10)-Zn(1)	75.2(3)
C(8)-B(3)-B(2)	59.1(4)	B(9)-B(10)-Zn(1)	70.9(3)
B(4)-B(3)-B(2)	108.5(5)	C(7)-B(11)-B(5)	105.9(5)
C(8)-B(3)-B(9)	57.2(4)	C(7)-B(11)-B(6)	60.7(4)

B(4)-B(3)-B(9)	59.8(5)	B(5)-B(11)-B(6)	59.2(4)
B(2)-B(3)-B(9)	108.2(5)	C(7)-B(11)-B(10)	107.4(5)
C(8)-B(3)-B(1)	104.3(5)	B(5)-B(11)-B(10)	59.3(4)
B(4)-B(3)-B(1)	60.9(5)	B(6)-B(11)-B(10)	108.3(5)
B(2)-B(3)-B(1)	60.1(4)	C(7)-B(11)-Zn(1)	83.2(4)
B(9)-B(3)-B(1)	108.9(5)	B(5)-B(11)-Zn(1)	116.8(4)
B(10)-B(4)-B(9)	61.8(4)	B(6)-B(11)-Zn(1)	136.9(4)
B(10)-B(4)-B(3)	110.9(5)	B(10)-B(11)-Zn(1)	58.4(3)
B(9)-B(4)-B(3)	60.4(4)	C(7)-B(11)-Zn(2)	88.9(4)
B(10)-B(4)-B(5)	60.1(4)	B(5)-B(11)-Zn(2)	106.0(4)
B(9)-B(4)-B(5)	108.0(5)	B(6)-B(11)-Zn(2)	69.4(3)
B(3)-B(4)-B(5)	107.7(5)	B(10)-B(11)-Zn(2)	160.2(5)
B(10)-B(4)-B(1)	110.0(5)	Zn(1)-B(11)-Zn(2)	137.0(3)
B(9)-B(4)-B(1)	108.7(5)	C(7)-B(11)-H(11)	119(2)
B(3)-B(4)-B(1)	60.1(4)	B(5)-B(11)-H(11)	123(3)
B(5)-B(4)-B(1)	59.9(4)	B(6)-B(11)-H(11)	115(3)
B(6)-B(5)-B(10)	110.4(5)	B(10)-B(11)-H(11)	128(3)
B(6)-B(5)-B(11)	60.4(4)	Zn(1)-B(11)-H(11)	102(3)
B(10)-B(5)-B(11)	60.6(4)	Zn(2)-B(11)-H(11)	46(3)
B(6)-B(5)-B(4)	107.2(5)	N-C(12)-C(7)	112.3(5)
B(10)-B(5)-B(4)	58.9(4)	C(16)-C(15)-Zn(2)	117.3(6)
B(11)-B(5)-B(4)	105.2(5)	C(51)-C(50)-C(50)#2	117.6(7)
B(6)-B(5)-B(1)	59.7(4)	C(52)-C(51)-C(50)	121.2(1)
B(10)-B(5)-B(1)	109.4(5)	C(51)-C(52)-C(52)#2	121.1(7)

Symmetry transformations used to generate equivalent atoms:

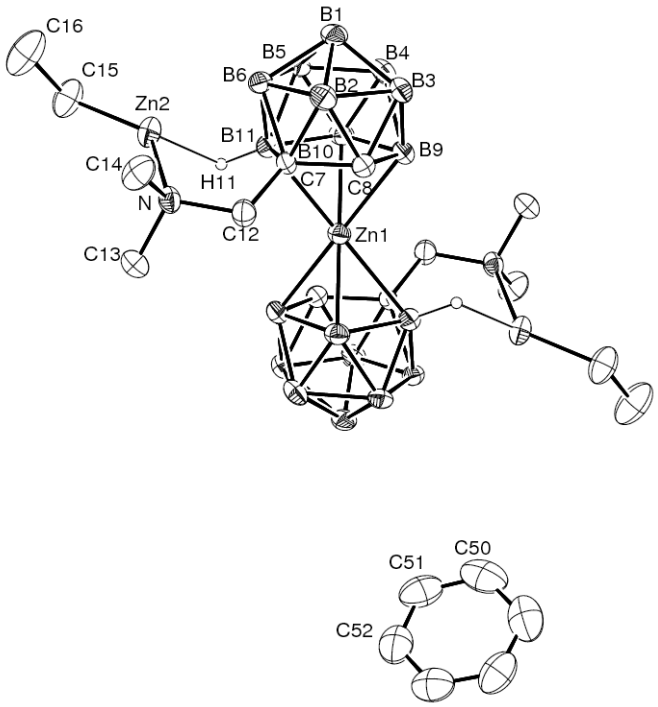


Figure 1. Molecular structure of **5**·C_6H_6 with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity, except for H11 atom.

Table 1. Crystal data and structure refinement for **8**.

Identification code	kor598
Empirical formula	$C_{23}H_{40}B_9NZn_2$
Formula weight	558.59
Temperature	233(2) K
Wavelength	0.7107 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 9.739(5) Å α = 98.253(10)°
	b = 10.464(5) Å β = 101.615(10)°
	c = 16.253(8) Å γ = 116.492(11)°
Volume	1399.6(12) Å^3
Z, D_{calc}	2, 1.325 g/mm^3
μ	1.727 mm^{-1}
F(000)	580
Crystal size	0.32 × 0.12 × 0.11 mm
θ range for data collection	1.33 to 28.41°
Limiting indices	–13≤h≤12, –13≤k≤13, –21≤l≤21
Reflections collected / unique	19321 / 6943 [R(int) = 0.2039]
Completeness to θ = 25.96	0.8327 and 0.6079
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6943 / 0 / 328
Goodness-of-fit on F^2	0.879
Final R indices [I>2σ (I)]	R_1 = 0.0828, wR_2 = 0.1973
R indices (all data)	R_1 = 0.3056, wR_2 = 0.3267
Absolute structure parameter	0.033(5)
Largest diff. peak and hole	0.617 and –0.797 e.Å^{-3}

[a]$R_1 = \sum||F_o|-|F_c||$ (based on reflections with $F_o^2>2\sigma F^2$), [b]$wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.095P)^2]$; , $P = [\max(F_o^2, 0)+2F_c^2]/3$(also with $F_o^2>2\sigma F^2$)

Table 2. Bond lengths [Å] for **8**

Zn(1)-C(29)	1.852(2)	B(5)-B(11)	1.813(2)
Zn(1)-B(10)	2.158(1)	B(6)-C(7)	1.682(2)
Zn(1)-B(9)	2.268(1)	B(6)-B(11)	1.779(2)
Zn(1)-B(11)	2.316(1)	C(7)-C(13)	1.542(1)
Zn(2)-C(31)	1.950(1)	C(7)-C(8)	1.549(1)
Zn(2)-N	2.053(7)	C(7)-B(11)	1.631(1)
Zn(2)-B(6)	2.497(2)	C(8)-C(12)	1.525(2)
Zn(2)-B(11)	2.530(1)	C(8)-B(9)	1.642(1)
Zn(2)-H(11)	1.80(6)	B(9)-B(10)	1.772(4)
N-C(14)	1.487(9)	B(10)-B(11)	1.772(2)
N-C(22)	1.512(1)	B(11)-H(11)	1.13(6)
N-C(15)	1.529(9)	C(13)-C(14)	1.509(1)
B(1)-B(6)	1.73(2)	C(15)-C(16)	1.497(1)
B(1)-B(4)	1.74(3)	C(16)-C(17)	1.361(1)
B(1)-B(5)	1.75(2)	C(16)-C(21)	1.407(1)
B(1)-B(3)	1.76(3)	C(17)-C(18)	1.408(1)
B(1)-B(2)	1.77(2)	C(18)-C(19)	1.343(2)
B(2)-C(8)	1.70(2)	C(19)-C(20)	1.343(2)
B(2)-C(7)	1.705(2)	C(20)-C(21)	1.370(1)
B(2)-B(6)	1.714(2)	C(22)-C(23)	1.501(1)
B(2)-B(3)	1.76(2)	C(23)-C(24)	1.360(1)
B(3)-B(4)	1.68(3)	C(23)-C(28)	1.376(1)
B(3)-C(8)	1.75(3)	C(24)-C(25)	1.383(1)
B(3)-B(9)	1.77(3)	C(25)-C(26)	1.314(2)
B(4)-B(9)	1.75(3)	C(26)-C(27)	1.333(2)
B(4)-B(10)	1.76(2)	C(27)-C(28)	1.382(2)
B(4)-B(5)	1.77(3)	C(29)-C(30)	1.51(2)

B(5)-B(10)	1.772(2)	C(31)-C(32)	1.466(1)
B(5)-B(6)	1.783(2)		

Table 3. Angles [deg] for 8.

C(29)-Zn(1)-B(10)	171.7(6)	B(5)-B(6)-Zn(2)	94.8(8)
C(29)-Zn(1)-B(9)	138.8(7)	C(13)-C(7)-C(8)	116.8(8)
B(10)-Zn(1)-B(9)	47.1(3)	C(13)-C(7)-B(11)	122.5(8)
C(29)-Zn(1)-B(11)	94.5(3)	C(8)-C(7)-B(11)	111.7(8)
B(10)-Zn(1)-B(11)	126.4(5)	C(13)-C(7)-B(6)	119.1(8)
B(9)-Zn(1)-B(11)	94.6(3)	C(8)-C(7)-B(6)	111.3(9)
C(31)-Zn(2)-N	41.4(4)	B(11)-C(7)-B(6)	64.9(7)
C(31)-Zn(2)-B(6)	126.1(2)	C(13)-C(7)-B(2)	113.0(8)
N-Zn(2)-B(6)	88.7(2)	C(8)-C(7)-B(2)	62.8(8)
C(31)-Zn(2)-B(11)	108.1(6)	B(11)-C(7)-B(2)	115.5(9)
N-Zn(2)-B(11)	109.2(6)	B(6)-C(7)-B(2)	60.8(8)
B(6)-Zn(2)-B(11)	106.0(6)	C(12)-C(8)-C(7)	120.5(9)
C(31)-Zn(2)-H(11)	113.8(5)	C(12)-C(8)-B(9)	119.1(1)
N-Zn(2)-H(11)	106.6(1)	C(7)-C(8)-B(9)	111.2(8)
C(14)-N-C(22)	57.4(1)	C(12)-C(8)-B(2)	116.7(1)
C(14)-N-C(15)	107.6(2)	C(7)-C(8)-B(2)	63.1(8)
C(22)-N-C(15)	58.7(8)	B(9)-C(8)-B(2)	114.1(1)
C(14)-N-Zn(2)	105.6(2)	C(12)-C(8)-B(3)	118.4(1)
C(22)-N-Zn(2)	108.4(1)	C(7)-C(8)-B(3)	111.4(1)
C(15)-N-Zn(2)	59.7(1)	B(9)-C(8)-B(3)	63.0(9)
B(6)-B(1)-B(4)	121.7	B(2)-C(8)-B(3)	61.3(1)
B(6)-B(1)-B(5)	122.8	C(8)-B(9)-B(4)	105.0(1)
B(4)-B(1)-B(5)	120.3	C(8)-B(9)-B(10)	107.5(6)
B(6)-B(1)-B(3)	60.7(1)	B(4)-B(9)-B(10)	60.1(8)
B(4)-B(1)-B(3)	103.9(1)	C(8)-B(9)-B(3)	61.4(8)
B(5)-B(1)-B(3)	107.5(1)	B(4)-B(9)-B(3)	57.0(1)
B(6)-B(1)-B(2)	105.3(1)	B(10)-B(9)-B(3)	107.5(9)

B(4)-B(1)-B(2)	107.3(11)	C(8)-B(9)-Zn(1)	81.9(7)
B(5)-B(1)-B(2)	59.6(9)	B(4)-B(9)-Zn(1)	122.2(9)
B(3)-B(1)-B(2)	59.9(10)	B(10)-B(9)-Zn(1)	63.2(3)
C(8)-B(2)-C(7)	125.1	B(3)-B(9)-Zn(1)	138.2(7)
C(8)-B(2)-B(6)	125.7	B(5)-B(10)-B(4)	61.2(11)
C(7)-B(2)-B(6)	122.8	B(5)-B(10)-B(11)	62.5(7)
C(8)-B(2)-B(3)	121.6	B(4)-B(10)-B(11)	107.4(11)
C(7)-B(2)-B(3)	122.7	B(5)-B(10)-B(9)	107.6(7)
B(6)-B(2)-B(3)	103.4(13)	B(4)-B(10)-B(9)	59.3(8)
C(8)-B(2)-B(1)	108.6(15)	B(11)-B(10)-B(9)	101.5(5)
C(7)-B(2)-B(1)	58.1(8)	B(5)-B(10)-Zn(1)	132.4(7)
B(6)-B(2)-B(1)	60.6(13)	B(4)-B(10)-Zn(1)	127.8(9)
B(3)-B(2)-B(1)	103.7(11)	B(11)-B(10)-Zn(1)	71.4(6)
B(4)-B(3)-C(8)	60.3(10)	B(9)-B(10)-Zn(1)	69.7(3)
B(4)-B(3)-B(2)	60.7(11)	C(7)-B(11)-B(10)	107.6(9)
C(8)-B(3)-B(2)	55.6(9)	C(7)-B(11)-B(6)	58.9(7)
B(4)-B(3)-B(1)	105.2(11)	B(10)-B(11)-B(6)	106.3(9)
C(8)-B(3)-B(1)	107.4(13)	C(7)-B(11)-B(5)	105.3(10)
B(2)-B(3)-B(1)	121.6	B(10)-B(11)-B(5)	57.4(8)
B(4)-B(3)-B(9)	126.6	B(6)-B(11)-B(5)	59.5(8)
C(8)-B(3)-B(9)	121.9	C(7)-B(11)-Zn(1)	82.0(6)
B(2)-B(3)-B(9)	122.1	B(10)-B(11)-Zn(1)	62.1(6)
B(1)-B(3)-B(9)	123.2	B(6)-B(11)-Zn(1)	134.7(8)
B(3)-B(4)-B(1)	62.0(12)	B(5)-B(11)-Zn(1)	118.4(9)
B(3)-B(4)-B(9)	62.3(12)	C(7)-B(11)-Zn(2)	99.9(6)
B(1)-B(4)-B(9)	109.7(11)	B(10)-B(11)-Zn(2)	143.6(7)
B(3)-B(4)-B(10)	112.3(12)	B(6)-B(11)-Zn(2)	68.3(6)
B(1)-B(4)-B(10)	108.4(12)	B(5)-B(11)-Zn(2)	92.9(8)

B(9)-B(4)-B(10)	60.7(8)	Zn(1)-B(11)-Zn(2)	147.2(6)
B(3)-B(4)-B(5)	110.2(1)	C(7)-B(11)-H(11)	114(3)
B(1)-B(4)-B(5)	59.8(1)	B(10)-B(11)-H(11)	136(3)
B(9)-B(4)-B(5)	106.5(1)	B(6)-B(11)-H(11)	106(3)
B(10)-B(4)-B(5)	58.3(9)	B(5)-B(11)-H(11)	120(3)
B(10)-B(5)-B(1)	109.6(1)	Zn(1)-B(11)-H(11)	110(3)
B(10)-B(5)-B(4)	60.5(1)	Zn(2)-B(11)-H(11)	39(3)
B(1)-B(5)-B(4)	59.0(1)	C(14)-C(13)-C(7)	116.4(7)
B(10)-B(5)-B(6)	108.4(1)	N-C(14)-C(13)	118.1(7)
B(1)-B(5)-B(6)	58.7(8)	C(16)-C(15)-N	114.8(6)
B(4)-B(5)-B(6)	104.3(1)	C(17)-C(16)-C(21)	119.3(9)
B(10)-B(5)-B(11)	60.1(8)	C(17)-C(16)-C(15)	122.1(9)
B(1)-B(5)-B(11)	106.4(1)	C(21)-C(16)-C(15)	118.6(9)
B(4)-B(5)-B(11)	105.1(1)	C(16)-C(17)-C(18)	119.5(1)
B(6)-B(5)-B(11)	59.3(7)	C(19)-C(18)-C(17)	120.6(1)
C(7)-B(6)-B(2)	60.2(8)	C(20)-C(19)-C(18)	119.7(1)
C(7)-B(6)-B(1)	106.9(1)	C(19)-C(20)-C(21)	122.4(1)
B(2)-B(6)-B(1)	61.7(9)	C(20)-C(21)-C(16)	118.4(1)
C(7)-B(6)-B(11)	56.1(6)	C(23)-C(22)-N	114.5(7)
B(2)-B(6)-B(11)	107.7(1)	C(24)-C(23)-C(28)	116.9(9)
B(1)-B(6)-B(11)	108.8(1)	C(24)-C(23)-C(22)	121.3(8)
C(7)-B(6)-B(5)	104.5(1)	C(28)-C(23)-C(22)	121.7(9)
B(2)-B(6)-B(5)	109.3(1)	C(23)-C(24)-C(25)	122.0(9)
B(1)-B(6)-B(5)	59.7(8)	C(26)-C(25)-C(24)	120.3(1)
B(11)-B(6)-B(5)	61.2(8)	C(25)-C(26)-C(27)	119.2(1)
C(7)-B(6)-Zn(2)	99.7(6)	C(26)-C(27)-C(28)	122.5(1)
B(2)-B(6)-Zn(2)	151.4(7)	C(23)-C(28)-C(27)	119.0(1)
B(1)-B(6)-Zn(2)	146.8(1)	C(30)-C(29)-Zn(1)	120.9(1)

B(1A)-B(6)-Zn(2)	120.6(6)	C(32)-C(31)-Zn(2)	119.7(9)

Symmetry transformations used to generate equivalent atoms:

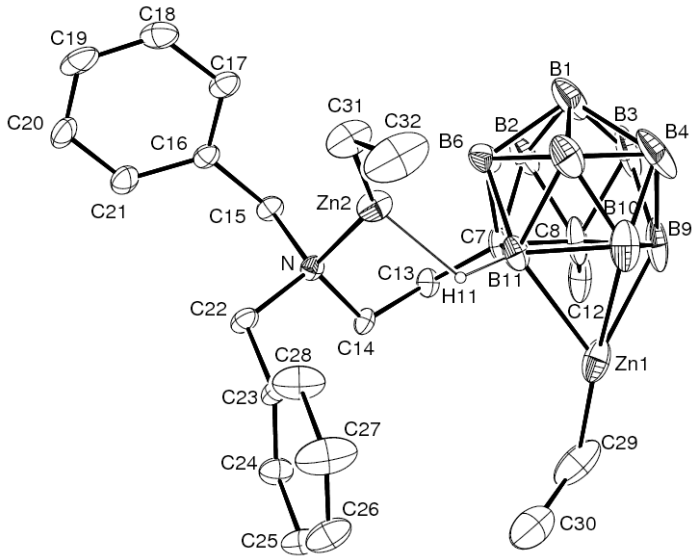


Figure 2. Molecular structure of **8** with thermal ellipsoids drawn at the 15% level. Hydrogen atoms are omitted for clarity, except for H11 atom.