Experimental

General Procedures

1-Hydroxy-2,2-dimethylbutan-3-one and 2,2-dimethyl-1-methoxybutan-3-one were prepared according to the literature procedures.[1] The manipulation of air sensitive compounds involved the use of anhydrous solvents and dry and deoxygenated nitrogen, employing standard Schlenk line techniques. Ethyl formate, hydrazine hydrochloride $LiBH_4$, $NaBH_4$, KBH_4, CaI_2, $KN(SiMe_3)_2$, and TlOAc were purchased from Aldrich. Paraformaldehyde, 2,2-dimethyl-3-butanone, dimethylsulfate, sodium methoxide, and KBH_4 were purchased from Acros.

Measurements. ^1H- and $^{13}C\{^1H\}$-NMR spectra were recorded in C_6D_6 and $CDCl_3$ on Bruker NMR spectrometers DPX-400 or DPX-250. Experiments for determining positive or negative ion mass spectra of the compounds were performed on a Bruker Esquire Ion Trap mass spectrometer (Bremen, Germany) equipped with an orthogonal electrospray source operated in positive ion mode. All samples were prepared in a solution containing the solvent system infused into the electrospray source at a rate of 5 - 10 ml min^{-1}. Optimal ESI conditions were: capillary voltage 3500 V, source temperature 250 ºC, the ESI drying gas was nitrogen. The ion trap was set to pass ions from m/z 50 - 2000 amu. Data were acquired in continuum mode until acceptable averaged data were obtained.

3-(2-Methoxy-1,1-dimethylethyl)pyrazole, pz*H. 62.5 g (1.16 mol) of sodium methoxide was placed in a 500 ml round-bottom flask in the drybox and then slurred in 70 ml of freshly distilled and degassed toluene under nitrogen. To this slurry was added dropwise 135.5 g (1.04 mol) of 2,2-dimethyl-1-methoxybutan-3-one, which yielded a pale yellow slurry. At room temperature, 85.7 g (1.16 mol) of ethyl formate was slowly added to this slurry to control the vigorous reaction. At about ½ of the required amount, the mixture began to boil. Then, it was cooled in an ice-water bath. After all of the ethyl formate was added, a clear orange yellow solution was obtained along with a little white precipitate at the bottom of the flask. The mixture was allowed to stir for about 1 hour until it cooled down to room temperature. The volatile materials including toluene were removed under vacuum and a thick dark yellow paste (about the half of the initial volume) was obtained. 350 ml of iced cold water was then added to the slurry which formed a yellow aqueous layer and a white organic layer. Then, the organic layer was separated off and to the aqueous layer was added dropwise 74.1 g (1.08 mol) of hydrazine monohydrochloride with slight cooling to control the vigourous reaction. After the addition was complete, the reaction mixture was cooled to room temperature and was stirred at room temperature overnight. The product was extracted with dichloromethane (4 × 100 ml). The solvent was removed from the combined organic extracts by rotary evaporator. 151 g (91 % of theory) of pure 3-(2-methoxy-1,1-dimethylethyl)pyrazole was obtained as a colorless oil upon vacuum distillation of the residue.

^1H-NMR (250 MHz, C_6D_6) δ: 10.68 (br, 1 H), 7.40 (d, 1 H, J =1 Hz), 6.06 (d, 1 H, J = 1 Hz), 3.19 (s, 2 H), 3.03 (s, 3H), 1.32 (s, 6 H). $^{13}C\{^1H\}$-NMR (C_6D_6): 153.62 (3-C, pz), 134.87 (5-C, pz), 102.00 (4-C, pz), 82.01(CH_2O), 58.88 (OCH_3), 36.05 (**C**Me_2), 25.52 (CMe_2)

GC-MS for $C_8H_{14}N_2O$: 154.33 g/mol

Anal. Calcd. for $C_8H_{14}N_2O$: C, 62.31; H, 9.15; N, 18.17. Found: C, 62.20; H, 9.54; N, 17.45.

Lithium (3-(2-methoxy-1,1-dimethylethyl)pyrazolyl){tris[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]borate}, Tp*Lipz*, 1. A mixture 2.14 g (13.9 mmol) of 2-methoxy-1,1-dimethylethyl)pyrazole and 0.0914 g (4.2 mmol) of ground $LiBH_4$ was heated heated at 230 °C for 16 h. Unreacted pyrazole was removed by sublimation at 75 °C under vacuum. Then, the residue was dissolved in hexane. Instead of lithium tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate, colorless crystals of lithium(3-(2-methoxy-1,1-dimethylethyl)pyrazolyl){tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]borate} were obtained (0.88 g, 34 %).

^{1}H-NMR (400 MHz, $CHCl_3$) δ: 7.48 (s), 7.44 (s) , 6.14 (s), 6.04 (s), 3.61 (s), 3.38 (s), 3.34 (s), 1.56 (br), 1.29 (s), 1.24 (s), 0.863 (m); ^{11}B-NMR (500 MHz, C_6D_6) δ: 0.528 (s).

Anal. Calcd. For $LiC_{31}H_{50}BN_8O_4$: C, 60.39; H, 8.17 ; N, 18.17. Found: C, 59.21; H, 8.31; N, 17.72.

Positive Ion Mass Spectrum for $[LiC_{23}H_{36}BN_6O_3]$-Li^+ : 479.4

CCDC reference number is 290335.

Sodium tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate, NaTp*, 2. 3-(2-methoxy-1,1-dimethylethyl)pyrazole (10.2 g, 66.0 mmol) and sodium borohydride (0.757 g, 20.0 mmol) were mixed under nitrogen atmosphere and heated to 180 °C with stirring in a flask connected to a water-cooled condenser which was subsequently connected to a wet gas meter made up of water bath and a flask. The mixture was heated at 180 °C until about 1.5 L (60 mmol) hydrogen gas had been evolved, which was measured by water replacement. The reaction took about 4 h. The white solid was formed. The heating was stopped. The white solid was washed by adding 40 ml of hexane when the temperature of the oil bath was 80-90 °C. Sodium tris[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]hydroborate (7.81 g 79 % of theory) was obtained as a white solid. The product was recrystallized from 1:1 mixture of THF and chloroform as white crystals upon the evaporation of the solvent mixture. Single crystals were also obtained from a concentrated solution of NaTp* in THF at –20 °C.

^{1}H-NMR (400 MHz, C_6D_6) δ: 7.73 (d, 1 H, J =1 Hz), 5.96 (d, 1 H, J = 1 Hz), 3.25 (s, 2 H), 3.18 (s, 3H), 1.19 (s, 6 H)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, 1 H, J =1 Hz), 5.85 (d, 1 H, J = 1 Hz), 3.51 (s, 3 H), 3.44 (s, 1 H), 1.22 (s, 6 H); $^{13}C\{^1H\}$-NMR (250 MHz, $CDCl_3$) δ: 158.04 (3-C, pz), 134.24 (5-C, pz), 99.38 (4-C, pz), 83.63(CH_2O), 60.14 (OCH_3), 36.43 (CMe_2), 26.39 (CMe_2); ^{11}B-NMR (250 MHz,C_6D_6) δ: -2.21 (q).

Positive Ion Mass Spectrum: 471.3 for H^+- $[HBC_{24}H_{39}N_6O_3]^-$

Anal. Calcd. for $NaBC_{24}H_{40}N_6O_3$: C, 58.30; H, 8.15; N, 17.00. Found: C, 57.88; H, 8.14; N, 16.97.

CCDC reference number is 290332.

Sodium tetrakis[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]borate, $NaB(pz^*)_4$, 3. With an aim to increase the yield of the reaction yielding $NaTp^*$, the reaction was run for 5 h yielding sodium tris[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]hydroborate and sodium tetrakis[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]borate in 10:1 ratio. The latter compound was obtained as an over reaction product, isolated and recrystallized from 1:5 mixture of hexanes/benzene solution under nitrogen at room temperature overnight. It was characterized by the following data:

^{1}H-NMR (250 MHz, C_6D_6)δ: 7.89 (d, 1 H, J =0.9 Hz), 6.09 (d, 1 H, J = 0.9 Hz), 3.26 (s, 2 H), 3.10 (s, 3H), 1.26 (s, 6 H). $^{13}C\{^1H\}$-NMR (250 MHz, C_6D_6) δ: 157.99 (3-C, pz), 135.28 (5-C, pz), 101.08 (4-C, pz), 83.68(CH_2O), 59.07 (OCH_3), 36.32 (CMe_2), 25.70(CMe_2)

^{11}B-NMR (250 MHz,C_6D_6) δ: 1.13 (s)

Positive Ion Mass Spectrum: 669.7 for $NaBC_{32}H_{52}N_8O_4$-Na^+.
Negative Ion Mass Spectrum: 623.8 for $[BC_{32}H_{52}N_8O_4]^-$.

CCDC reference number is 290331.

Potassium tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate, KTp^*, 4.
3-(2-methoxy-1,1-dimethylethyl)pyrazole (43.38 mmol) and potassium borohydride (0.585 g, 10.84 mmol) were mixed under a nitrogen atmosphere and the resulting mixture was heated to 180 °C with stirring in a flask connected to a water-cooled condenser. After 4 h reaction at 180 °C, reaction mixture was cooled to 80 °C and 30 ml of hexane was added to extract unreacted 3-(2-methoxy-1,1-dimethylethyl)pyrazole. The mixture was centrifuged and then decantated. The white precipitate was dried under vacuum, and redissolved in THF. The unreacted potassium borohydride precipitated out. The mixture was filtered, and the THF extract was dried, yielding KTp^* as a white solid (2.10 g, 38 %). Single crystals was obtained from a concentrated solution of KTp^* in THF at –20 °C. The structure consists of two K^+ with two boron tripod ligands and a third ligand consisting of the pyrazole ring with its attached substituents.

^{1}H-NMR (400 MHz, C_6D_6) δ: 7.44 (s, 3H), 6.07 (s, 3H), 3.29 (s, 6H), 2.97 (s, 9H), 1.31 (s, 18H).

Anal. Calcd. For $KBC_{24}H_{40}N_6O_3$: C, 57.23; H, 8.06; N, 16.69 Found: C, 57.04; H, 8.24; N, 16.44.

Negative Ion Mass Spectrum: 471.8 for $[BC_{24}H_{40}N_6O_3]^-$.
Positive ion Mass Spectrum: 701.7 for $KBC_{32}H_{52}N_8O_4$-K^+.

CCDC reference number is 290330.

Thallium(I) tris[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]hydroborate, TlTp*, 6. Sodium tris[1-(3-(2-methoxy-1,1-dimethyl-)pyrazolyl)]hydroborate (2.15 g, 4.34 mmol) (1.27 g, 4.83 mmol) of thallium(I) acetate were mixed under nitrogen atmosphere. To this mixture was added 60 ml of dry dichloromethane. The mixture was stirred at room temperature overnight. Sodium acetate precipitated, and the solution was filtered and vacuum pumped to dryness, which resulted in 2.75 g (94 % of theory) of thallium tris[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]hydroborate as white powder. The product is air-stable. White single crystals as needles were obtained from the recrystallization of the product from 3:1 mixture of toluene/diethyl ether through slow evaporation of the solvent mixture.

^{1}H-NMR (400 MHz, C_6D_6) δ: 7.65 (s, 3H), 6.06 (s, 3H), 3.28 (s, 6H), 3.06 (s, 9H), 1.41 (s, 18H). ^{13}C{^{1}H}-NMR (400 MHz, C_6D_6) δ: 159.93 (br, 3-C, pz), 136.25 (5-C, pz), 102.21 (d, 4-C, pz), 83.21(CH_2O), 82.21(CH_2O), 58.69 (OCH_3), 36.96 (CMe_2), 27.39 (CMe_2), 25.67 (CMe_2); ^{11}B-NMR (400 MHz, C_6D_6) δ: -0.08 (q).

Anal. Calcd. for $TlBC_{24}H_{40}N_6O_3$: C, 42.66; H, 5.97; N, 12.44. Found: C, 42.72; H, 6.02; N, 12.53.

CCDC reference number is 290334.

Tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroboratocalcium iodide, Tp*CaI, 5. A solution of TlTp* (0.676 g, 1 mmol) in 20 ml THF was added dropwise to a slurry of CaI_2 (0.294 g, 1 mmol) in 15 ml THF. The resulting yellow mixture was stirred for 2 h. Formation of the thallium(I) iodide as a yellow precipitate was observed. The solution was filtered, and volatile components were removed under dynamic vacuum. The product was redissolved and crystallized from 25 ml toluene. The white precipitate was formed. The solution was filtered off. The white precipitate was dried under vacuum, yielding Tp*CaI (0.55 g, 65 %). The white colorless single crystals used for crystallography were obtained from a concentrated solution of the product in THF.

^{1}H-NMR (250 MHz, C_6D_6)δ: 7.46 (s, 3H), 5.79 (s, 3H), 3.59 (s, 6H), 3.52 (s, 9H), 1.21 (s, 18 H). ^{13}C{^{1}H}-NMR (400 MHz, C_6D_6) δ: 161.22 (3-C, pz), 137.00 (5-C, pz), 102.08 (4-C, pz), 83.50(CH_2O), 62.96 (OCH_3), 37.22 ($\boldsymbol{C}Me_2$), 27.51($C\boldsymbol{Me_2}$); ^{11}B-NMR (80 MHz,C_6D_6) δ: -2.79 (q).

Positive Ion Mass Spectrum: 511.6 for $C_{24}H_{40}N_6O_3BCa^+$.

CCDC reference number is 290333.

Tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroboratocalcium bis(trimethylsilyl)amide, Tp*CaN(SiMe$_3$)$_2$, 7. A solution of TlTp* (0.669 g, 0.990 mmol) in 10 ml benzene was added dropwise to a solution of Ca[N(SiMe$_3$)$_2$]$_2$ (0.357 g, 0.990 mmol) in 10 ml benzene. The reaction mixture turned dark green as the addition is continued. Benzene was removed under dynamic vacuum giving a mixture of Tp*CaN(SiMe$_3$)$_2$ and TlN(SiMe$_3$)$_2$. TlN(SiMe$_3$)$_2$ was removed by vacuum sublimation at a cold finger at 90-100 °C. The resulting dark brown residue was redissolved in benzene and then the Schlenk flask was dipped into the oil bath at 80 °C. A dark precipitate (presumably the Tl metal) was separated by Schlenk filtration. The product was obtained as a yellow solid (0.43 g, 65 % upon removal of the benzene under dynamic vacuum.

^{1}H-NMR (250 MHz, C$_6$D$_6$)δ: 7.89 (s, 3H), 5.86 (s, 3H), 3.50 (s, 6H), 3.24 (s, 9H), 1.19 (s, 18 H).
^{11}B-NMR (80 MHz,C$_6$D$_6$) δ: -2.81 (q)

The crystal structures of **1-6** have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 290330 – 290335.

Table S1. Crystallographic data for **1-6**.

	1	**2**	**3**	**4**	**5**	**6**
Empirical Form.	$C_{31}H_{50}BLiN_8O_4$	$C_{24}H_{40}BN_6NaO_3$	$C_{32}H_{52}BN_8NaO_4$	$C_{56}H_{94}B_2K_2N_{14}O_7$	$C_{24}H_{40}BCaIN_6O_3$	$C_{24}H_{40}BN_6O_3Tl$
Formula Wt.	616.54	494.42	646.62	1175.28	638.41	675.80
Crystal System	monoclinic	cubic	monoclinic	triclinic	cubic	orthorhombic
a/ Å	11.365(2)	22.056(2)	13.3825(10)	13.163(1)	15.072(2)	7.870(1)
b/ Å	14.028(2)		18.570(2)	13.629(1)		14.415(1)
c/ Å	22.125(3)		14.715(2)	21.637(2)		24.533(3)
α/º				75.219(4)		
β/º	103.156(8)		97.993(6)	78.293(5)		
γ/º				63.403(5)		
U/ Å^3	3434.8(9)	10729.5(17)	3621.3(7)	3338.3(5)	3423.8(8)	2783.2(5)
T / K	200(2)	200(2)	150(2)	150(2)	150(2)	150(2)
Space Group	$P2_1/n$	$\bar{I}\,43d$	$P\ 2_1/n$	$P\,\bar{1}$	$P2_13$	$P\ 2_12_12_1$
Z	4	16	4	2	4	4
μ(Mo-Kα)/ mm^{-1}	0.080	0.095	0.089	0.199	1.115	5.839
Reflections Measured	43385	63372	40021	63668	53576	39208
Unique refl. Rint	6056, 0.034	860, 0.046	6388, 0.031	11749, 0.034	2021, 0.049	6330, 0.061
R1(I>2σI)	0.0477	0.0269	0.0425	0.0444	0.0430	0.0273
wR2(all data)	0.1358	0.0701	0.1159	0.1193	0.1208	0.0506

Reference:

[1] Krämer, W.; Elbe, H.-L. **1983** US Pat. 4,371,708