

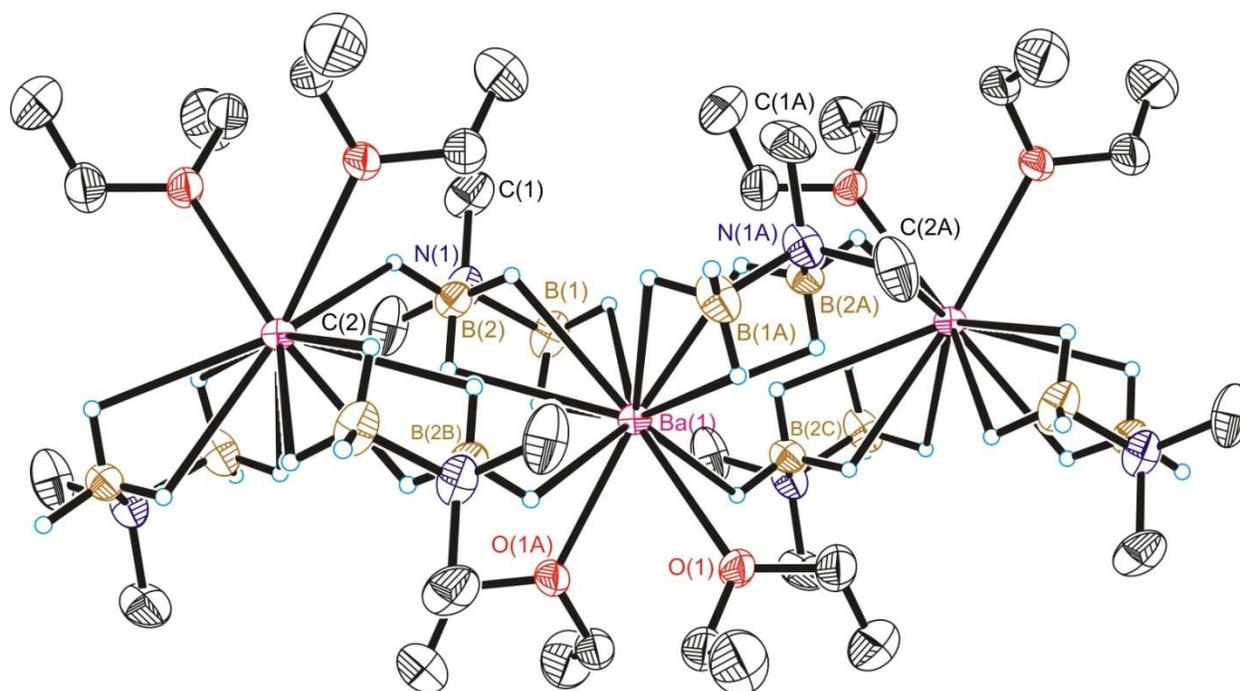
Supporting Information for

Synthesis and Structural Diversity of Barium *N,N*-Dimethylaminodiboranates

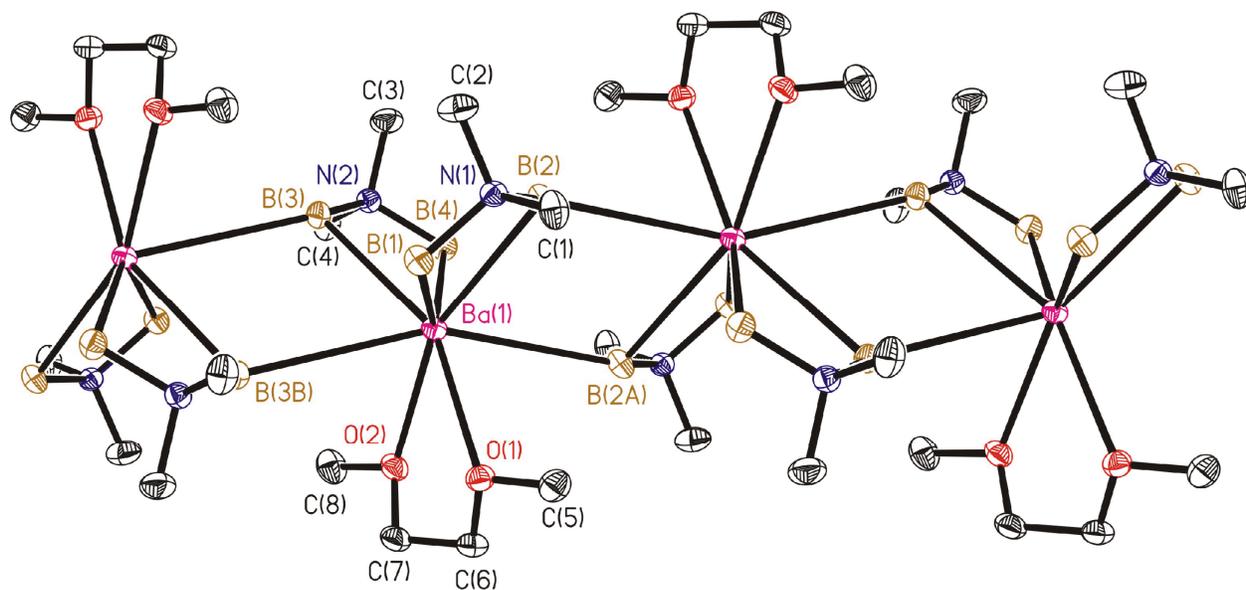
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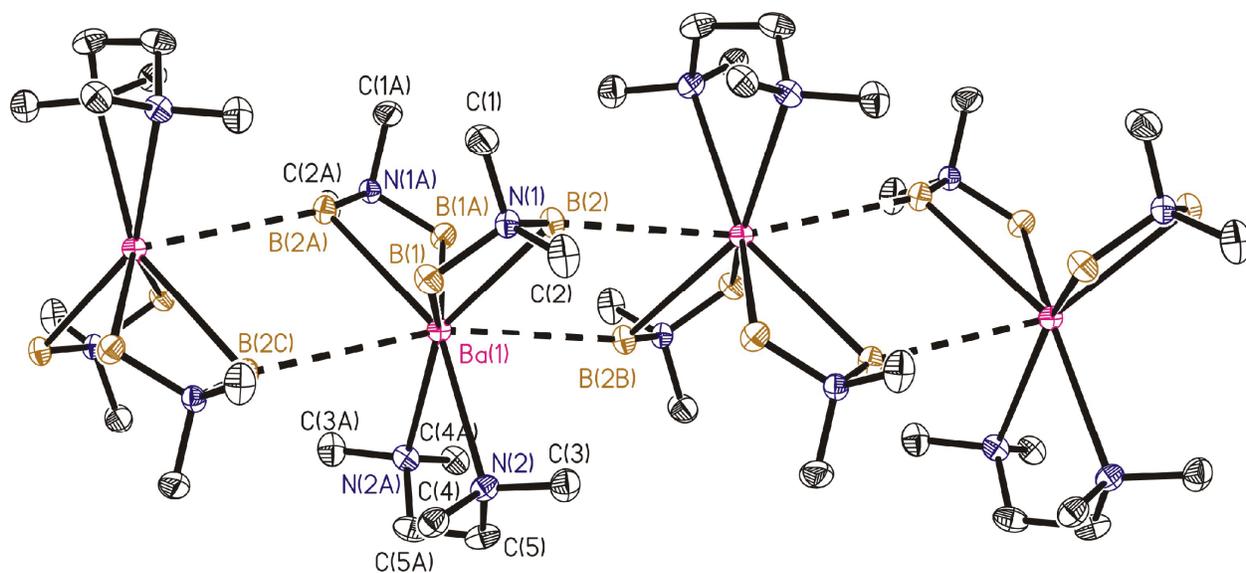
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**Figure S1.** Molecular structure of  $\text{Ba}(\text{H}_3\text{BNMe}_2\text{BH}_3)_2(\text{Et}_2\text{O})_2$ , **1**. Ellipsoids are drawn at the 35% probability level. The hydrogen atoms have been removed for clarity.



**Figure S2.** Molecular structure of Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(dme), **2**. Ellipsoids are drawn at the 35% probability level. The hydrogen atoms have been removed for clarity.



**Figure S3.** Molecular structure of  $\text{Ba}(\text{H}_3\text{BNMe}_2\text{BH}_3)_2(\text{tmeda})$ , **3**. Ellipsoids are drawn at the 35% probability level. The hydrogen atoms have been removed for clarity. The dashed lines reflect the increased bridging  $\text{Ba}\cdots\text{B}$  distances relative to **1** and **2**.

**Table S1.** Selected Bond Lengths and Angles for Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>O)<sub>2</sub>, **1**.

Bond Lengths (Å)			
Ba(1)-O(1)	2.800(3)	Ba(1)-H(1A)	2.79(4)
Ba(1)-B(1)	3.216(6)	Ba(1)-H(1B)	2.78(5)
Ba(1)-B(2)	3.265(6)	Ba(1)-H(2A)	2.88(5)
Ba(1)-B(2)'	3.477(5)	Ba(1)-H(2B)	2.79(4)
Bond Angles (deg)			
B(1)-Ba(1)-B(2)	47.31(13)	B(1)-Ba(1)-B(1)'	124.1(3)
O(1)-Ba(1)-B(1)	146.10(13)	B(1)-Ba(1)-B(2)'	97.04(17)
O(1)-Ba(1)-B(2)	154.76(12)	B(1)-Ba(1)-B(2)''	112.77(14)
O(1)-Ba(1)-B(1)'	85.89(15)	B(1)-Ba(1)-B(2)'''	76.61(14)
O(1)-Ba(1)-B(2)'	93.17(12)	B(2)-Ba(1)-B(2)'	107.3(2)
O(1)-Ba(1)-B(2)''	87.41(11)	B(2)-Ba(1)-B(2)''	69.10(14)
O(1)-Ba(1)-B(2)'''	77.08(12)	B(2)-Ba(1)-B(2)'''	123.61(15)
O(1)-Ba(1)-O(1)'	71.91(13)	B(2)''-Ba(1)-B(2)'''	160.89(19)

Symmetry transf. used to generate equivalent atoms: ' = -x+2, y, -z+3/2; '' = -x+2, -y, -z+1; ''' = x, -y, z+1/2.

**Table S2.** Selected Bond Lengths and Angles for Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(dme), **2**.

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Bond Lengths (Å)			
Ba(1)-O(1)	2.8233(15)	Ba(1)-H(11)	2.873(16)
Ba(1)-O(2)	2.8150(14)	Ba(1)-H(12)	2.781(17)
Ba(1)-B(1)	3.260(3)	Ba(1)-H(21)	2.920(17)
Ba(1)-B(2)	3.271(2)	Ba(1)-H(22)	2.806(17)
Ba(1)-B(2)'	3.412(3)	Ba(1)-H(31)	2.813(18)
Ba(1)-B(3)	3.252(3)	Ba(1)-H(32)	2.848(16)
Ba(1)-B(3)''	3.461(3)	Ba(1)-H(41)	2.850(17)
Ba(1)-B(4)	3.251(3)	Ba(1)-H(42)	2.772(18)
Bond Angles (deg)			
B(1)-Ba(1)-B(2)	47.20(6)	O(1)-Ba(1)-O(2)	60.09(4)
B(1)-Ba(1)-B(2)'	112.93(6)	O(1)-Ba(1)-B(1)	86.32(5)
B(1)-Ba(1)-B(3)	101.66(6)	O(1)-Ba(1)-B(2)	102.10(6)
B(1)-Ba(1)-B(3)''	76.52(6)	O(1)-Ba(1)-B(3)	154.31(5)
B(1)-Ba(1)-B(4)	133.15(6)	O(1)-Ba(1)-B(4)	137.96(5)
B(2)-Ba(1)-B(2)'	75.76(7)	O(1)-Ba(1)-B(2)'	72.58(5)
B(2)-Ba(1)-B(3)	101.12(7)	O(1)-Ba(1)-B(3)''	87.76(5)
B(2)-Ba(1)-B(3)''	121.13(6)	O(2)-Ba(1)-B(1)	134.17(5)
B(2)-Ba(1)-B(4)	98.39(7)	O(2)-Ba(1)-B(2)	158.91(5)
B(2)'-Ba(1)-B(3)	124.24(6)	O(2)-Ba(1)-B(3)	98.80(5)
B(2)'-Ba(1)-B(3)''	157.03(6)	O(2)-Ba(1)-B(4)	90.02(6)
B(2)'-Ba(1)-B(4)	77.56(6)	O(2)-Ba(1)-B(2)'	87.35(5)
B(3)-Ba(1)-B(3)''	70.81(7)	O(2)-Ba(1)-B(3)''	72.27(5)
B(3)-Ba(1)-B(4)	47.33(6)		
B(3)''-Ba(1)-B(4)	112.06(6)		

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Symmetry transformations used to generate equivalent atoms: ' = -x+1, -y, -z; '' = -x, -y, -z.

**Table S3.** Selected Bond Lengths and Angles for Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(tmeda), **3**.

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Bond Lengths (Å)			
Ba(1)-B(1)	3.237(3)	Ba(1)-H(12)	2.794(17)
Ba(1)-B(2)	3.261(3)	Ba(1)-H(21)	2.794(16)
Ba(1)-B(2)'	3.512(3)	Ba(1)-H(22)	2.851(16)
Ba(1)-N(2)	2.9965(15)	Ba(1)-H(23)'	2.832(17)
Ba(1)-H(11)	2.808(17)		
Bond Angles (deg)			
B(1)-Ba(1)-B(2)	47.29(6)	B(2)-Ba(1)-B(2)'	103.11(10)
B(1)-Ba(1)-B(1)'	132.15(10)	B(2)-Ba(1)-N(2)	99.04(6)
B(1)-Ba(1)-B(2)'	100.02(7)	B(2)-Ba(1)-N(2)'	154.39(6)
B(1)-Ba(1)-N(2)	85.66(6)	N(2)-Ba(1)-B(2)'	154.39(6)
B(1)-Ba(1)-N(2)'	140.03(6)	N(2)'-Ba(1)-B(2)'	99.04(6)
B(2)-Ba(1)-B(1)'	100.02(7)	N(2)-Ba(1)-N(2)'	63.24(6)

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Symmetry transformations used to generate equivalent atoms: ' = -x+2, y, -z+<sup>3</sup>/<sub>2</sub>

**Table S4.** Selected Bond Lengths and Angles for Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(12-crown 4)(thf)·thf, **4'**.

Bond Lengths (Å)			
Ba(1)-O(1)	2.854(4)	Ba(1)-H(11)	2.8983
Ba(1)-O(11)	2.864(4)	Ba(1)-H(12)	2.7544
Ba(1)-O(12)	2.904(4)	Ba(1)-H(21)	3.095
Ba(1)-O(13)	2.922(4)	Ba(1)-H(23)	2.847
Ba(1)-O(14)	2.838(4)	Ba(1)-H(31)	2.7848
Ba(1)-B(1)	3.270(7)	Ba(1)-H(32)	2.9063
Ba(1)-B(2)	3.399(7)	Ba(1)-H(41)	2.8249
Ba(1)-B(3)	3.278(7)	Ba(1)-H(43)	2.9513
Ba(1)-B(4)	3.316(8)		
Bond Angles (deg)			
O(1)-Ba(1)-O(11)	140.52(12)	O(12)-Ba(1)-B(1)	170.88(16)
O(1)-Ba(1)-O(12)	118.48(12)	O(13)-Ba(1)-B(1)	129.46(16)
O(1)-Ba(1)-O(13)	66.74(12)	O(14)-Ba(1)-B(1)	92.53(15)
O(1)-Ba(1)-O(14)	82.60(12)	O(1)-Ba(1)-B(2)	114.85(15)
O(11)-Ba(1)-O(12)	57.71(13)	O(11)-Ba(1)-B(2)	74.40(15)
O(11)-Ba(1)-O(13)	86.23(11)	O(12)-Ba(1)-B(2)	125.49(16)
O(11)-Ba(1)-O(14)	58.29(13)	O(13)-Ba(1)-B(2)	149.11(17)
O(12)-Ba(1)-O(13)	55.95(12)	O(14)-Ba(1)-B(2)	91.29(17)
O(12)-Ba(1)-O(14)	85.04(11)	O(1)-Ba(1)-B(3)	76.29(15)
O(13)-Ba(1)-O(14)	57.88(12)	O(11)-Ba(1)-B(3)	136.56(16)
B(1)-Ba(1)-B(2)	45.67(17)	O(12)-Ba(1)-B(3)	87.04(15)
B(1)-Ba(1)-B(3)	99.23(19)	O(13)-Ba(1)-B(3)	94.37(16)
B(1)-Ba(1)-B(4)	105.1(2)	O(14)-Ba(1)-B(3)	150.41(16)
B(2)-Ba(1)-B(3)	116.27(19)	O(1)-Ba(1)-B(4)	122.16(15)
B(2)-Ba(1)-B(4)	87.1(2)	O(11)-Ba(1)-B(4)	95.72(16)
B(3)-Ba(1)-B(4)	46.83(17)	O(12)-Ba(1)-B(4)	74.36(17)
O(1)-Ba(1)-B(1)	69.76(15)	O(13)-Ba(1)-B(4)	119.16(18)
O(11)-Ba(1)-B(1)	113.65(16)	O(14)-Ba(1)-B(4)	153.22(16)

**Table S5.** Selected Bond Lengths and Angles for Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(18-crown-6)·2(thf), **5'**.

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Bond Lengths (Å)			
Ba(1)-B(1)	3.458(15)	Ba(1)-O(12)	2.789(3)
Ba(1)-B(2)	3.396(13)	Ba(1)-O(15)	2.792(3)
Ba(1)-B(3)	3.354(16)	Ba(1)-O(18)	2.798(3)
Ba(1)-B(4)	3.458(14)		
Bond Angles (deg)			
O(12)-Ba(1)-O(12)'	180	O(15)-Ba(1)-B(1)	92.7(3)
O(12)-Ba(1)-O(15)	60.44(10)	O(15)-Ba(1)-B(2)	77.8(2)
O(12)-Ba(1)-O(15)'	119.56(10)	O(15)-Ba(1)-B(3)	112.6(2)
O(12)-Ba(1)-O(18)	119.96(11)	O(15)-Ba(1)-B(4)	68.4(2)
O(12)-Ba(1)-O(18)'	60.04(11)	O(15)-Ba(1)-B(1)'	87.3(3)
O(15)-Ba(1)-O(15)'	180	O(15)-Ba(1)-B(2)'	102.2(2)
O(15)-Ba(1)-O(18)	60.45(10)	O(15)-Ba(1)-B(3)'	67.4(2)
O(15)-Ba(1)-O(18)'	119.55(10)	O(15)-Ba(1)-B(4)'	111.6(2)
O(18)-Ba(1)-O(18)'	180	O(18)-Ba(1)-B(1)	113.0(2)
O(12)-Ba(1)-B(1)	79.2(4)	O(18)-Ba(1)-B(2)	69.6(2)
O(12)-Ba(1)-B(2)	107.0(3)	O(18)-Ba(1)-B(3)	94.2(3)
O(12)-Ba(1)-B(3)	98.7(3)	O(18)-Ba(1)-B(4)	75.2(3)
O(12)-Ba(1)-B(4)	74.8(2)	O(18)-Ba(1)-B(1)'	67.0(2)
O(12)-Ba(1)-B(1)'	100.8(4)	O(18)-Ba(1)-B(2)'	110.4(2)
O(12)-Ba(1)-B(2)'	73.0(3)	O(18)-Ba(1)-B(3)'	85.8(3)
O(12)-Ba(1)-B(3)'	81.3(3)	O(18)-Ba(1)-B(4)'	104.8(3)
O(12)-Ba(1)-B(4)'	105.2(2)		

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Symmetry transformations used to generate equivalent atoms: -x,-y+1,-z+2

**Table S6.** Selected Bond Lengths and Angles for Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(teeda), **6**.

Bond Lengths (Å)			
Ba(1)-B(1)	3.243(4)	Ba(1)-H(12)	2.92(4)
Ba(1)-B(1)'	3.324(5)	Ba(1)-H(13)'	2.582(5)
Ba(1)-B(2)	3.255(5)	Ba(1)-H(21)	2.88(4)
Ba(1)-B(3)	3.191(6)	Ba(1)-H(22)	2.83(4)
Ba(1)-B(4)	3.173(6)	Ba(1)-H(31)	2.76(4)
Ba(1)-N(3)	2.970(3)	Ba(1)-H(33)	2.73(5)
Ba(1)-N(4)	2.947(4)	Ba(1)-H(41)	2.78(5)
Ba(1)-H(11)	2.78(4)	Ba(1)-H(42)	2.59(4)
Bond Angles (deg)			
B(1)-Ba(1)-B(2)	47.17(13)	B(3)-Ba(1)-B(4)	48.58(13)
B(1)-Ba(1)-B(3)	88.43(13)	B(3)-Ba(1)-N(3)	151.38(11)
B(1)-Ba(1)-B(4)	136.66(13)	B(3)-Ba(1)-N(4)	123.31(12)
B(1)-Ba(1)-N(3)	110.12(11)	B(3)-Ba(1)-B(1)'	85.74(15)
B(1)-Ba(1)-N(4)	125.94(12)	B(4)-Ba(1)-N(3)	111.75(11)
B(1)-Ba(1)-B(1)'	76.06(12)	B(4)-Ba(1)-N(4)	85.57(14)
B(2)-Ba(1)-B(3)	107.83(12)	B(4)-Ba(1)-B(1)'	101.91(16)
B(2)-Ba(1)-B(4)	131.55(15)	N(3)-Ba(1)-N(4)	67.37(9)
B(2)-Ba(1)-N(3)	100.72(11)	N(3)-Ba(1)-B(1)'	78.274(11)
B(2)-Ba(1)-N(4)	79.94(11)	N(4)-Ba(1)-B(1)'	140.11(9)
B(2)-Ba(1)-B(1)'	119.66(12)		

Symmetry transformations used to generate equivalent atoms: -x,-y+1,-z.

**Table S7.** Selected Bond Lengths and Angles for Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(pmdta), **7**.

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Bond Angles (Å)			
Ba(1) ···B(1)	3.158(7)	Ba(1)-H(11)	2.88(4)
Ba(1) ···B(2)	3.173(7)	Ba(1)-H(12)	2.68(4)
Ba(1) ···B(3)	3.262(9)	Ba(1)-H(21)	2.71(5)
Ba(1) ···B(4)	3.163(8)	Ba(1)-H(22)	2.73(4)
Ba(1)-N(3)	2.905(5)	Ba(1)-H(31)	2.63(5)
Ba(1)-N(4)	2.916(4)	Ba(1)-H(32)	2.77(5)
Ba(1)-N(5)	2.884(4)	Ba(1)-H(41)	2.85(5)
		Ba(1)-H(42)	2.88(5)
Bond Angles (deg)			
B(1)-Ba(1)-B(2)	49.12(18)	B(3)-Ba(1)-B(4)	49.1(2)
B(1)-Ba(1)-B(3)	94.1(2)	B(3)-Ba(1)-N(3)	89.56(19)
B(1)-Ba(1)-B(4)	139.2(2)	B(3)-Ba(1)-N(4)	148.65(18)
B(1)-Ba(1)-N(3)	91.19(17)	B(3)-Ba(1)-N(5)	126.52(18)
B(1)-Ba(1)-N(4)	100.44(17)	B(4)-Ba(1)-N(3)	103.40(19)
B(1)-Ba(1)-N(5)	127.32(17)	B(4)-Ba(1)-N(4)	120.17(18)
B(2)-Ba(1)-B(3)	111.4(2)	B(4)-Ba(1)-N(5)	78.94(17)
B(2)-Ba(1)-B(4)	121.1(2)	N(3)-Ba(1)-N(4)	62.71(14)
B(2)-Ba(1)-N(3)	134.47(16)	N(3)-Ba(1)-N(5)	117.62(14)
B(2)-Ba(1)-N(4)	98.97(16)	N(4)-Ba(1)-N(5)	63.36(13)
B(2)-Ba(1)-N(5)	82.45(16)		

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**Table S8.** Selected Bond Lengths and Angles for Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(diglyme)<sub>2</sub>, **8**.

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Bond Lengths (Å)			
Ba(1)-O(1)	2.9474(13)	Ba(1)-B(3)	3.051(2)
Ba(1)-O(2)	2.8353(14)	Ba(1)-H(11)	2.79(2)
Ba(1)-O(3)	2.9698(14)	Ba(1)-H(12)	2.830(16)
Ba(1)-O(4)	2.8905(13)	Ba(1)-H(21)	2.847(17)
Ba(1)-O(5)	2.9539(13)	Ba(1)-H(22)	2.918(19)
Ba(1)-O(6)	2.8273(13)	Ba(1)-H(31)	2.773(17)
Ba(1)-B(1)	3.266(3)	Ba(1)-H(32)	2.931(15)
Ba(1)-B(2)	3.280(3)	Ba(1)-H(33)	2.952(15)
Bond Angles (deg)			
O(1)-Ba(1)-O(2)	56.26(4)	O(1)-Ba(1)-B(1)	104.11(6)
O(1)-Ba(1)-O(3)	114.72(4)	O(2)-Ba(1)-B(1)	89.86(6)
O(1)-Ba(1)-O(4)	65.56(4)	O(3)-Ba(1)-B(1)	69.20(5)
O(1)-Ba(1)-O(5)	123.73(4)	O(4)-Ba(1)-B(1)	121.74(5)
O(1)-Ba(1)-O(6)	167.24(4)	O(5)-Ba(1)-B(1)	101.79(6)
O(2)-Ba(1)-O(3)	58.83(4)	O(6)-Ba(1)-B(1)	87.20(6)
O(2)-Ba(1)-O(4)	119.09(4)	O(1)-Ba(1)-B(2)	85.86(6)
O(2)-Ba(1)-O(5)	167.48(4)	O(2)-Ba(1)-B(2)	114.98(6)
O(2)-Ba(1)-O(6)	118.95(4)	O(3)-Ba(1)-B(2)	116.23(6)
O(4)-Ba(1)-O(3)	169.00(4)	O(4)-Ba(1)-B(2)	74.70(5)
O(5)-Ba(1)-O(3)	121.03(4)	O(5)-Ba(1)-B(2)	76.85(6)
O(6)-Ba(1)-O(3)	63.41(4)	O(6)-Ba(1)-B(2)	106.42(6)
O(4)-Ba(1)-O(5)	58.29(4)	O(1)-Ba(1)-B(3)	87.82(5)
O(4)-Ba(1)-O(6)	113.65(4)	O(2)-Ba(1)-B(3)	81.10(6)
O(5)-Ba(1)-O(6)	57.91(4)	O(3)-Ba(1)-B(3)	88.74(5)
B(1)-Ba(1)-B(2)	47.05(6)	O(4)-Ba(1)-B(3)	80.27(5)
B(1)-Ba(1)-B(3)	157.68(6)	O(5)-Ba(1)-B(3)	86.39(6)
B(2)-Ba(1)-B(3)	154.59(6)	O(6)-Ba(1)-B(3)	79.58(5)

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**Table S9.** Selected Bond Lengths and Angles for [Ba(15-crown-5)<sub>2</sub>] [H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>]<sub>2</sub>, **9**.

Bond Lengths (Å)			
Ba(1)-O(1)	2.891(3)	Ba(1)-O(4)	2.813(3)
Ba(1)-O(2)	2.818(3)	Ba(1)-O(5)	2.815(3)
Ba(1)-O(3)	2.824(3)		
Bond Angles (deg)			
O(1)-Ba(1)-O(2)	59.27(11)	O(1)-Ba(1)-O(2)'	120.73(11)
O(1)-Ba(1)-O(3)	100.10(11)	O(1)-Ba(1)-O(3)'	79.90(11)
O(1)-Ba(1)-O(4)	100.55(12)	O(1)-Ba(1)-O(4)'	79.45(12)
O(1)-Ba(1)-O(5)	58.43(11)	O(1)-Ba(1)-O(5)'	121.57(11)
O(2)-Ba(1)-O(3)	58.58(10)	O(2)-Ba(1)-O(3)'	121.42(10)
O(2)-Ba(1)-O(4)	106.50(10)	O(2)-Ba(1)-O(4)'	73.50(10)
O(2)-Ba(1)-O(5)	110.05(11)	O(2)-Ba(1)-O(5)'	69.95(11)
O(3)-Ba(1)-O(4)	58.19(8)	O(3)-Ba(1)-O(4)'	121.81(8)
O(3)-Ba(1)-O(5)	106.00(9)	O(3)-Ba(1)-O(5)'	74.00(9)
O(4)-Ba(1)-O(5)	59.17(9)	O(4)-Ba(1)-O(5)'	120.83(9)

Symmetry transformations used to generate equivalent atoms: -x+1,-y+1,-z

**Table S10.** Selected Bond Lengths and Angles for [Na(12-crown-4)<sub>2</sub>][Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>3</sub>(thf)<sub>2</sub>], **10**.

Bond Lengths (Å)			
Ba(1) ···B(1)	3.255(5)	Ba(1)-H(42)	2.7928(5)
Ba(1) ···B(2)	3.258(6)	Ba(1)-H(51)	2.8408(6)
Ba(1) ···B(3)	3.260(5)	Ba(1)-H(52)	2.7926(6)
Ba(1) ···B(4)	3.237(5)	Ba(1)-H(61)	2.8500(6)
Ba(1) ···B(5)	3.255(6)	Ba(1)-H(62)	2.9311(6)
Ba(1) ···B(6)	3.291(6)	B(1)-N(1)	1.575(6)
Ba(1)-H(11)	2.8292(5)	B(2)-N(1)	1.587(6)
Ba(1)-H(12)	2.7949(5)	B(3)-N(2)	1.572(6)
Ba(1)-H(21)	2.8151(6)	B(4)-N(2)	1.585(6)
Ba(1)-H(22)	2.8708(6)	B(5)-N(3)	1.593(6)
Ba(1)-H(31)	2.7969(5)	B(6)-N(3)	1.566(6)
Ba(1)-H(32)	2.8093(5)	Ba(1)-O(1)	2.871(3)
Ba(1)-H(41)	2.7686(5)	Ba(1)-O(2)	2.867(3)
Bond Angles (deg)			
B(1)-Ba(1)-B(2)	46.92(13)	B(1)-N(1)-B(2)	110.1(3)
B(1)-Ba(1)-B(3)	100.95(14)	B(3)-N(2)-B(4)	112.2(3)
B(1)-Ba(1)-B(4)	144.64(14)	B(5)-N(3)-B(6)	112.2(4)
B(1)-Ba(1)-B(5)	100.38(15)	B(3)-Ba(1)-O(1)	87.39(12)
B(1)-Ba(1)-B(5)	112.54(15)	B(3)-Ba(1)-O(2)	79.61(12)
B(1)-Ba(1)-O(1)	115.79(11)	O(1)-Ba(1)-O(2)	166.31(9)
B(1)-Ba(1)-O(2)	71.41(12)		

Symmetry transformations used to generate equivalent atoms: -x+1,-y,-z+1 and -x,-y,-z+2

**Crystallographic studies.**<sup>S1</sup> Single crystals obtained from diethyl ether (**1**, **2**, **3** and **8**) or tetrahydrofuran (**4'**, **5'**, **6,7**, **9**, and **10**) were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to -80 °C in a cold nitrogen gas stream on the diffractometer. Standard peak search and indexing procedures, followed by least-squares refinement yielded the cell dimensions given in Table 2. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background and Lorentz and polarization effects. No corrections for crystal decay were necessary but face-indexed absorption corrections were applied. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. Except where noted, all unique data were used in the least-squares refinements. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. Unless otherwise specified, correct atomic position(s) were deduced from an E-map (SHELX) and from subsequent least-squares refinement and difference Fourier calculations. Except where noted, hydrogen atoms attached to boron were located in the difference maps and hydrogen atoms attached to carbon were placed in idealized positions with C-H (methyl) = 0.98 Å and C-H (methylene) = 0.99 Å; the methyl groups were allowed to rotate about their respective C-N or C-O axes to find the best least-squares positions. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms. The displacement parameters for borane and methylene hydrogens were set equal to 1.2 times  $U_{eq}$  for the attached boron or carbon atom, and those for methyl hydrogens were set to 1.5 times  $U_{eq}$ , unless stated otherwise. No corrections for isotropic extinction were necessary unless stated otherwise. Successful convergence was indicated by the maximum shift/error of 0.000(5) for the last cycle. A final analysis of variance between observed and calculated structure factors showed no apparent errors.

**Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>O)<sub>2</sub>, (1).** The systematic absences  $hkl$  ( $h + k \neq 2n$ ) and  $h0l$  ( $l \neq 2n$ ) were consistent with the space groups  $Cc$  and  $C2/c$ . The centrosymmetric space group  $C2/c$  was chosen, and this choice was confirmed by successful refinement of the proposed model. The

reflection ( $\bar{2}23$ ) was a statistical outlier and was deleted; the remaining 2112 unique data were used in the least squares refinement. The quantity minimized by the least-squares program was  $\Sigma w(F_o^2 - F_c^2)^2$ , where  $w = \{[\sigma(F_o)]^2 + (0.0444P)^2\}^{-1}$  and  $P = (F_o^2 + 2F_c^2)/3$ . The largest peak in the final Fourier difference map ( $1.03 \text{ e}\text{\AA}^{-3}$ ) was located  $1.02 \text{ \AA}$  from Ba1.

**Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(dme), (2).** The systematic absences  $0k0$  ( $k \neq 2n$ ) and  $h0l$  ( $l \neq 2n$ ) were uniquely consistent with the space group  $P2_1/c$ , which was confirmed by the success of the subsequent refinement. The quantity minimized by the least-squares program was  $\Sigma w(F_o^2 - F_c^2)^2$ , where  $w = \{[\sigma(F_o)]^2 + (0.0135P)^2\}^{-1}$  and  $P = (F_o^2 + 2F_c^2)/3$ . All hydrogen atoms were located in the difference maps, and their positions were refined with independent isotropic displacement parameters. The largest peak in the final Fourier difference map ( $0.80 \text{ e}\text{\AA}^{-3}$ ) was located  $1.33 \text{ \AA}$  from Ba1.

**Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(tmeda), (3).** The systematic absences  $hkl$  ( $h + k \neq 2n$ ) and  $h0l$  ( $l \neq 2n$ ) were consistent with the space groups  $Cc$  and  $C2/c$ . The centrosymmetric space group  $C2/c$  was chosen, and this choice was confirmed by successful refinement of the proposed model. Correct positions for the Ba atoms were deduced from a Patterson map (SHELXTL). The quantity minimized by the least-squares program was  $\Sigma w(F_o^2 - F_c^2)^2$ , where  $w = \{[\sigma(F_o)]^2 + (0.0077P)^2\}^{-1}$  and  $P = (F_o^2 + 2F_c^2)/3$ . The largest peak in the final Fourier difference map ( $0.33 \text{ e}\text{\AA}^{-3}$ ) was located  $1.13 \text{ \AA}$  from Ba1.

**Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(12-crown-4)(thf)·thf, (4').** The triclinic lattice and the average values of the normalized structure factors suggested the space group  $P\bar{1}$ , which was confirmed by the success of the subsequent refinement. The reflections ( $\bar{1}01$ ),  $(021)$ ,  $(101)$ , and  $(\bar{1}\bar{1}1)$  were statistical outliers and were deleted; the remaining 11617 unique data were used in the least squares refinement. The coordinated 12-crown-4 ligand in molecule 2 and the non-coordinated thf molecule closest to molecule 2 were each disordered over two positions. The site occupancy factors (SOFs) for the two disordered components in each molecule were constrained to sum to one; the SOF for the major occupancy components refined to 0.575 for the 12-crown-4 molecule and 0.588 for the thf molecule. The quantity minimized by the least-squares program was  $\Sigma w(F_o^2$

-  $F_c^2$ )<sup>2</sup>, where  $w = \{[\sigma(F_o)]^2 + (0.0130P)^2\}^{-1}$  and  $P = (F_o^2 + 2F_c^2)/3$ . The C-C and C-O distances in the disordered thf molecule were fixed at  $1.52 \pm 0.01$  and  $1.48 \pm 0.01$  Å, respectively, and the chemically equivalent C-O distances in the disordered 12-crown-4 ligand were constrained to be equal within  $\pm 0.01$  Å; the same constraint was applied to the C-C distances in this ligand. The displacement parameters for the disordered atoms of the 12-crown-4 molecules were constrained to be near-isotropic to produce satisfactory ellipsoids. The largest peak in the final Fourier difference map ( $0.90 \text{ eÅ}^{-3}$ ) was located 1.05 Å from O12.

**Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(18-crown-6)·2thf, (5').** Although the unit cell proved to be primitive, the diffraction record was suggestive of both end- and body-centering. The systematic absences also showed signs of pseudosymmetry, with many of the  $0kl$  and  $hk0$  reflections being weak. The systematic absences  $0kl$  ( $k + l \neq 2n$ ) and  $hk0$  ( $h \neq 2n$ ) were consistent with space groups  $Pna2_1$  and  $Pnma$ ; both space groups were investigated, and the latter was confirmed by the success of the subsequent refinement of the proposed model. All 4150 unique data were used in the least squares refinement. The aminodiboranate ligands are disordered over two positions, as are two of the atoms within one of the tetrahydrofuran solvate molecules. The site occupancy factors (SOFs) for the two components within each disordered aminodiboranate ligand and thf molecule are exactly 0.5 owing to the location of these groups relative to crystallographic mirror planes. The quantity minimized by the least-squares program was  $\sum w(F_o^2 - F_c^2)^2$ , where  $w = \{[\sigma(F_o^2)]^2 + (0.0511P)^2 + 3.23P\}^{-1}$  and  $P = (F_o^2 + 2F_c^2)/3$ . The C-C and C-O distances within the tetrahydrofuran solvate molecules were constrained to be  $1.48 \pm 0.01$  and  $1.54 \pm 0.01$  Å, respectively. The largest peak in the final Fourier difference map ( $0.79 \text{ eÅ}^{-3}$ ) was located 0.96 Å from Ba1. The pseudosymmetry arises from the location of the barium atoms at Wyckoff positions  $a$  in the  $Pnma$  space group, so that they do not contribute to reflections of the type  $hkl$  where  $h + l \neq 2n$  or  $k \neq 2n$ .

**Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(teeda), (6).** The triclinic lattice and the average values of the normalized structure factors suggested the space group  $P\bar{1}$ , which was confirmed by the success of the subsequent refinement of the proposed model. The quantity minimized by the least-

squares program was  $\Sigma w(F_o^2 - F_c^2)^2$ , where  $w = \{[\sigma(F_o^2)]^2\}^{-1}$  and  $P = (F_o^2 + 2F_c^2)/3$ . The largest peak in the final Fourier difference map ( $2.21 \text{ e}\text{\AA}^{-3}$ ) was located  $1.49 \text{ \AA}$  from H11A.

**Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(pmdta), (7).** The systematic absences  $0k0$  ( $k \neq 2n$ ) and  $h0l$  ( $h + l \neq 2n$ ) were uniquely consistent with the space group  $P2_1/n$ . All 4479 unique data were used in the least squares refinement. The quantity minimized by the least-squares program was  $\Sigma w(F_o^2 - F_c^2)^2$ , where  $w = \{[\sigma(F_o^2)]^2 + (0.028P)^2\}^{-1}$  and  $P = (F_o^2 + 2F_c^2)/3$ . The largest peak in the final Fourier difference map ( $0.90 \text{ e}\text{\AA}^{-3}$ ) was located  $0.89 \text{ \AA}$  from H31.

**Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>(diglyme)<sub>2</sub>, (8).** The systematic absences  $0k0$  ( $k \neq 2n$ ) and  $h0l$  ( $l \neq 2n$ ) were uniquely consistent with the space group  $P2_1/c$ , which was confirmed by the success of the subsequent refinement. The quantity minimized by the least-squares program was  $\Sigma w(F_o^2 - F_c^2)^2$ , where  $w = \{[\sigma(F_o^2)]^2 + (0.0168P)^2\}^{-1}$  and  $P = (F_o^2 + 2F_c^2)/3$ . The chemically equivalent B–H distances within the BH<sub>3</sub> units were constrained to be equal within  $\pm 0.01 \text{ \AA}$ . An isotropic extinction parameter was refined to a final value of  $x = 0.38(7) \times 10^{-6}$  where  $F_c$  is multiplied by the factor  $k[1 + F_c^2 x \lambda^3 / \sin 2\theta]^{-1/4}$  with  $k$  being the overall scale factor. The largest peak in the final Fourier difference map ( $1.62 \text{ e}\text{\AA}^{-3}$ ) was located  $1.50 \text{ \AA}$  from H31.

**[Ba(15-crown-5)<sub>2</sub>][H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>]<sub>2</sub>, (9).** The systematic absences  $0k0$  ( $k \neq 2n$ ) and  $h0l$  ( $l \neq 2n$ ) were uniquely consistent with the space group  $P2_1/c$ , which was confirmed by the success of the subsequent refinement. All 4043 unique data were used in the least squares refinement. Three pairs of adjacent carbon atoms in the 15-crown-5 ligand were disordered over two positions for a total of six disordered carbon atoms each disordered over two positions. The site occupancy factors (SOFs) for the two disordered components were constrained to sum to one; the SOF for the major occupancy components refined to 0.506. The quantity minimized by the least-squares program was  $\Sigma w(F_o^2 - F_c^2)^2$ , where  $w = \{[\sigma(F_o^2)]^2 + (0.082P)^2 + 0.262P\}^{-1}$  and  $P = (F_o^2 + 2F_c^2)/3$ . Constraints were placed on the carbon-carbon bond distances for the disordered atoms in the 15-crown-5 ring so that the bond lengths would be equal within  $\pm 0.01 \text{ \AA}$ . A similarity constraint was placed on the shapes of the thermal ellipsoids for these disordered atoms. The largest peak in the final Fourier difference map ( $1.60 \text{ e}\text{\AA}^{-3}$ ) was located  $0.95 \text{ \AA}$  from

barium.

**[Na(12-crown-4)<sub>2</sub>][Ba(H<sub>3</sub>BNMe<sub>2</sub>BH<sub>3</sub>)<sub>3</sub>(thf)<sub>2</sub>], (10).** The triclinic lattice and the average values of the normalized structure factors suggested the space group  $P\bar{1}$ , which was confirmed by the success of the subsequent refinement. Correct positions for the barium and the non-hydrogen atoms of the aminodiboranate ligands were deduced from an E-map. The 12-crown-4 rings are disordered over two positions. The C-O and C-C distances within these rings were restrained to  $1.47 \pm 0.01$  and  $1.52 \pm 0.01$  Å, respectively. The disordered rings were assigned site occupancy factors (SOFs) of 0.5 except for the ring defined by oxygen atoms O45-O48 and the associated carbon atoms. For these rings a common site occupancy factor was refined so that the SOFs for the two disordered components summed to one; the sof of the major occupancy site refined to 0.645(5). The quantity minimized by the least-squares program was  $\sum w(F_o^2 - F_c^2)^2$ , where  $w = \{[\sigma(F_o^2)]^2 + (0.035P)^2\}^{-1}$  and  $P = (F_o^2 + 2F_c^2)/3$ . The largest peak in the final Fourier difference map ( $2.19 \text{ e}\text{\AA}^{-3}$ ) was located  $0.97$  Å from Ba2.

## References

(S1) Brumaghim, J. L.; Priepot, J. G.; Girolami, G. S. *Organometallics* **1999**, *18*, 2139-2144.