Table 2. NMR Spectral Data of M[B(CF=CF$_2$)$_4$] and Related Compounds[a,b]

compd	solvent	δ(^{19}F) F^1	δ(^{19}F) F^2(cis)	δ(^{19}F) F^2(trans)	δ (^{11}B)	δ(^{13}C) C−1	δ(^{13}C) C−2	J
[Me$_4$N][B(CF=CF$_2$)$_4$]	CD_3CN	−181.81	−123.74	−99.48	−21.29	137.05	160.77	$^1J_{CF}$ = 186.0, $^2J_{CF}$ = 62.5, $^2J_{CF}$ = 55.5, $^1J_{CB}$ = 61.8, C-1; $^1J_{CF}$ = 291.5, $^1J_{CF}$ = 272.6, $^2J_{CF}$ = 46.5, $^2J_{CB}$ = 7.8, C-2
[Me$_4$N][B(CF=CF$_2$)$_4$]	MeOH	−181.75	−123.81	−100.19	−20.83			$^2J_{F,F}$ = 89, $^3J_{F,F}$ = 111, $^3J_{F,F}$ = 26, $^2J_{B,F}$ = 21
[Me$_4$N][B(CF=CF$_2$)$_4$]	CH_2Cl_2	−183.39	−124.38	−100.00	−21.51			$^2J_{F,F}$ = 90, $^3J_{F,F}$ = 110, $^3J_{F,F}$ = 26, $^2J_{B,F}$ = 24
Cs[B(CF=CF$_2$)$_4$]	CH_3OH	−182.01	−123.94	−100.30	−20.84			
K [B(CF=CF$_2$)$_4$]	CH_3CN	−181.89	−123.63	−99.27	−20.73			$^2J_{F,F}$ = 90, $^3J_{F,F}$ = 110, $^3J_{F,F}$ = 27, $^2J_{B,F}$ = 24
K[CF$_2$=CFBF$_3$][c]	CH_3OH	−198.49	−122.94	−99.02				$^2J_{F,F}$ = 89, $^3J_{F,F}$ = 108, $^3J_{F,F}$ = 24, $^2J_{B,F}$ = 21
K[CF$_2$=CFBF$_3$]	CD_3CN	−195.73	123.97	−101.12	0.51[d]	135.62[d]	160.73[d]	$^2J_{F,F}$ = 93, $^3J_{F,F}$ = 110, $^3J_{F,F}$ = 25, $^2J_{B,F}$ =24
Cs[CF$_2$=CFB(CF$_3$)$_2$F][e]	CD_3CN	−195.7	−124.3	−99.5	−6.4	133	161.6	
[C$_6$H$_5$CH$_2$NMe$_3$][BCl$_4$]	CH_2Cl_2				6.00			
B(CF=CF$_2$)$_3$	CH_2Cl_2	−186.45	−90.83	−72.72	45.74			$^3J_{F,F}$ = 108, $^3J_{F,F}$ = 22, $^2J_{F,F}$ not observed

[a] J in Hz and δ in ppm. [b] The fluorine atoms F^2 at C-2 in ethenylborates are specified by cis and trans relative to the position of the boron atom. [c] Data for K[CF$_2$=CFBF$_3$] were taken from ref 7. [d] Present work. [e] Data for Cs[CF$_2$=CFB(CF$_3$)$_2$F] were taken from ref 6.

Table S1. Crystal data and structure refinement for $[NMe_4]$ $[B(CF=CF_2)_4]$.

Empirical formula	C12 H12 B F12 N	
Formula weight	409.04	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I-4	
Unit cell dimensions	a = 9.9305(9) Å	α = 90°.
	b = 9.9305(9) Å	β = 90°.
	c = 8.2531(10) Å	γ = 90°.
Volume	813.88(14) $Å^3$	
Z	2	
Density (calculated)	1.669 Mg/m^3	
Absorption coefficient	0.194 mm^{-1}	
F(000)	408	
Crystal size	0.35 x 0.20 x 0.15 mm^3	
Theta range for data collection	2.90 to 28.22°.	
Index ranges	-13<=h<=13, -12<=k<=12, -10<=l<=10	
Reflections collected	4751	
Independent reflections	981 [R(int) = 0.0547]	
Completeness to theta = 28.22°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.589 and 0.524	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	981 / 4 / 70	
Goodness-of-fit on F^2	0.921	
Final R indices [I>2sigma(I)]	R1 = 0.0489, wR2 = 0.1188	
R indices (all data)	R1 = 0.0847, wR2 = 0.1301	
Absolute structure parameter	1.0(18)	
Largest diff. peak and hole	0.264 and -0.159 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $[NMe_4]$ $[B(CF=CF_2)_4]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	0	5000	2500	38(1)
C(31) 1)	845(10)	5841(10)	1487(15)	178(5)
C(32) 2)	-160(30)	3701(18)	3170(20)	132(13)
B(1)	0	0	0	36(1)
C(1)	1204(3)	621(3)	1090(4)	45(1)
C(2)	1718(3)	253(3)	2451(5)	60(1)
F(1)	1872(2)	1710(2)	431(3)	77(1)
F(2)	2769(2)	812(2)	3189(3)	99(1)
F(3)	1287(2)	-767(2)	3339(3)	84(1)

1) site occupation factor 0.77
2) site occupation factor 0.23

Table S3. Bond lengths [Å] for $[NMe_4]$ $[B(CF=CF_2)_4]$.

N(1)-C(32)	1.411(11)
N(1)-C(31)	1.449(8)
B(1)-C(1)	1.618(3)
C(1)-C(2)	1.287(4)
C(1)-F(1)	1.381(4)
C(2)-F(3)	1.321(4)
C(2)-F(2)	1.330(4)

Table S4. Angles [°] for $[NMe_4]$ $[B(CF=CF_2)_4]$.

C(32)#1-N(1)-C(32)	134.1(18)
C(32)#2-N(1)-C(32)	98.7(6)
C(31)#1-N(1)-C(31)	109.5(11)
C(31)-N(1)-C(31)#3	109.4(5)
C(1)-B(1)-C(1)#4	108.01(11)
C(1)-B(1)-C(1)#5	112.4(2)
C(1)-B(1)-C(1)#6	108.01(11)
C(2)-C(1)-F(1)	112.1(3)
C(2)-C(1)-B(1)	132.1(3)
F(1)-C(1)-B(1)	115.7(2)
C(1)-C(2)-F(3)	125.0(3)
C(1)-C(2)-F(2)	126.3(4)
F(3)-C(2)-F(2)	108.7(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,z #2 y-1/2,-x+1/2,-z+1/2 #3 -y+1/2,x+1/2,-z+1/2
#4 -y,x,-z #5 -x,-y,z #6 y,-x,-z

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[NMe_4]\ [B(CF=CF_2)_4]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	39(2)	39(2)	35(2)	0	0	0
C(31)	156(8)	185(10)	193(12)	85(9)	91(8)	14(6)
C(32)	118(16)	111(16)	170(30)	111(18)	-106(19)	-60(14)
B(1)	30(2)	30(2)	47(4)	0	0	0
C(1)	40(2)	44(2)	51(2)	-4(1)	-2(1)	-1(1)
C(2)	62(2)	49(2)	69(2)	-3(2)	-22(2)	4(2)
F(1)	64(1)	76(1)	90(2)	15(1)	-16(1)	-31(1)
F(2)	94(2)	92(2)	110(2)	-17(2)	-59(2)	-8(1)
F(3)	108(2)	76(2)	69(1)	16(1)	-33(2)	5(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[NMe_4]$ $[B(CF=CF_2)_4]$.

	x	y	z	U(eq)
H(31A) 1)	1472	5273	876	267
H(31B) 1)	1353	6468	2170	267
H(31C) 1)	279	6350	731	267
H(32A) 2)	-1100	3579	3506	198
H(32B) 2)	432	3600	4106	198
H(32C) 2)	68	3023	2350	198

1) site occupation factor 0.77
2) site occupation factor 0.23

Table S7. Torsion angles [°] for $[NMe_4]$ $[B(CF=CF_2)_4]$.

C(1)#4-B(1)-C(1)-C(2)	154.9(3)
C(1)#5-B(1)-C(1)-C(2)	35.8(3)
C(1)#6-B(1)-C(1)-C(2)	-83.3(3)
C(1)#4-B(1)-C(1)-F(1)	-29.0(2)
C(1)#5-B(1)-C(1)-F(1)	-148.1(3)
C(1)#6-B(1)-C(1)-F(1)	92.8(3)
F(1)-C(1)-C(2)-F(3)	-179.4(3)
B(1)-C(1)-C(2)-F(3)	-3.2(5)
F(1)-C(1)-C(2)-F(2)	-0.3(5)
B(1)-C(1)-C(2)-F(2)	175.9(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,z #2 y-1/2,-x+1/2,-z+1/2 #3 -y+1/2,x+1/2,-z+1/2
#4 -y,x,-z #5 -x,-y,z #6 y,-x,-z