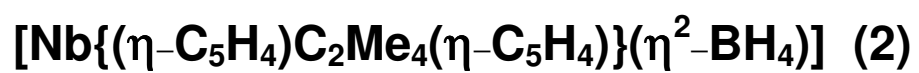


## Appendix A

### Crystallographic Data for



## A.1 Crystal Data and Structure Refinement for $[\text{Nb}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{Me}_4(\eta\text{-C}_5\text{H}_4)\}\{\eta^2\text{-BH}_4\}] (2)$

Empirical formula	$\text{C}_{16}\text{H}_{24}\text{BNb}$	
Formula weight	320.08	
Temperature	100 K	
Wavelength (Mo-K $\alpha$ )	0.71069 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 7.5840(2)$ Å	$\alpha = 98.334(2)^\circ$
	$b = 9.6590(4)$ Å	$\beta = 105.989(2)^\circ$
	$c = 11.3790(4)$ Å	$\gamma = 107.886(2)^\circ$
Volume	$738.19$ Å <sup>3</sup>	
Z	2.00	
Density (calculated)	$1.44$ Mg/m <sup>3</sup>	
Absorption coefficient	$0.76$ mm <sup>-1</sup>	
F(000)	327.56	
Crystal size	$0.30 \times 0.20 \times 0.15$ mm <sup>3</sup>	
$\theta$ range for data collection	$1.92$ to $26.65^\circ$ .	
Index ranges	$0 \leq h \leq 9$ , $-12 \leq k \leq 11$ , $-14 \leq l \leq 13$	
Reflections collected	6498	
Independent reflections	2844 [R(int) = 0.012]	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F	
Weighting scheme	Chebyshev parameters $1.45$ , $0.293$ and $0.737$	
Data / parameters [ $I > 3\sigma(I)$ ]	2772/259	
Goodness-of-fit on F	1.0515	
Largest final shift	0.002569	
Final R indices	$R = 0.0179$ , $R_w = 0.0206$	
Residual density	$0.38$ and $-0.50$ e.Å <sup>-3</sup>	

## A.2 Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for $[\text{Nb}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{Me}_4(\eta\text{-C}_5\text{H}_4)\}(\eta^2\text{-BH}_4)]$ (2)

$U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{\text{ij}}$  tensor.

	x	y	z	$U(\text{eq})$
Nb(1)	2674(1)	4698(1)	7276(1)	8
C(3)	4471(2)	3394(2)	6394(1)	19
C(2)	2684(2)	2344(2)	6359(1)	16
C(1)	2717(2)	2421(2)	7640(1)	13
C(5)	4560(2)	3570(2)	8451(1)	15
C(4)	5612(2)	4152(2)	7660(1)	17
C(21)	1143(2)	1428(2)	8072(1)	14
C(22)	-818(2)	1754(1)	7567(1)	12
C(26)	-2107(2)	1431(2)	8403(1)	18
C(6)	-252(2)	3410(1)	7538(1)	10
C(10)	-731(2)	3956(2)	6424(1)	12
C(9)	-42(2)	5551(2)	6817(1)	15
C(8)	862(2)	6001(2)	8138(1)	15
C(7)	769(2)	4705(2)	8602(1)	12
C(25)	-2121(2)	777(2)	6228(1)	17
C(24)	1933(2)	1777(2)	9523(1)	19
C(23)	860(2)	-227(2)	7581(2)	22
B(1)	4523(3)	6954(2)	6893(2)	21
H(101)	-1442	3389	5591	12
H(71)	1242	4699	9502	15
H(242)	2162	2829	9959	21
H(51)	5031	3819	9342	14
H(251)	-1444	900	5600	14
H(252)	-3253	1055	5936	23
H(31)	4782	3572	5657	17
H(253)	-2573	-272	6246	17
H(21)	1655	1648	5638	21
H(233)	-204	-901	7808	30
H(261)	-1486	2100	9258	22
H(263)	-2442	401	8465	22
H(241)	3196	1650	9794	30
H(81)	1593	7027	8626	18
H(41)	6871	4947	7948	22
H(262)	-3297	1558	8049	21
H(231)	2008	-425	7951	27
H(2)	3176	5757	6093	30
H(91)	-188	6197	6256	19
H(232)	547	-507	6642	26
H(1)	4530(30)	6570(20)	7925(19)	29(5)
H(243)	1030(30)	1130(20)	9813(18)	26(5)
H(3)	5950(40)	7130(30)	6720(20)	41(6)
H(4)	4000(40)	7880(30)	6890(20)	45(7)

### A.3 Bond Lengths [Å] and Angles [°] for [Nb{(η-C<sub>5</sub>H<sub>4</sub>)C<sub>2</sub>Me<sub>4</sub>(η-C<sub>5</sub>H<sub>4</sub>)}(η<sup>2</sup>-BH<sub>4</sub>)] (2)

Nb(1)-C(3)	2.4274(15)	Nb(1)-C(2)	2.3635(13)
Nb(1)-C(1)	2.3041(13)	Nb(1)-C(5)	2.3119(13)
Nb(1)-C(4)	2.3849(15)	Nb(1)-C(6)	2.3105(14)
Nb(1)-C(10)	2.3249(14)	Nb(1)-C(9)	2.4017(14)
Nb(1)-C(8)	2.4253(14)	Nb(1)-C(7)	2.3596(14)
Nb(1)-B(1)	2.3752(17)	Nb(1)-H(2)	1.8564(1)
Nb(1)-H(1)	1.81(2)	C(3)-C(2)	1.407(2)
C(3)-C(4)	1.407(2)	C(3)-H(31)	0.9562(15)
C(2)-C(1)	1.4415(19)	C(2)-H(21)	0.9483(14)
C(1)-C(5)	1.4410(19)	C(1)-C(21)	1.531(2)
C(5)-C(4)	1.424(2)	C(5)-H(51)	0.9440(14)
C(4)-H(41)	0.9555(15)	C(21)-C(22)	1.5849(19)
C(21)-C(24)	1.5385(19)	C(21)-C(23)	1.5414(18)
C(22)-C(26)	1.538(2)	C(22)-C(6)	1.5305(17)
C(22)-C(25)	1.5396(18)	C(26)-H(261)	0.9820(15)
C(26)-H(263)	0.9672(14)	C(26)-H(262)	0.9350(15)
C(6)-C(10)	1.4406(18)	C(6)-C(7)	1.4416(18)
C(10)-C(9)	1.4220(19)	C(10)-H(101)	0.9368(13)
C(9)-C(8)	1.406(2)	C(9)-H(91)	0.9639(14)
C(8)-C(7)	1.4174(19)	C(8)-H(81)	0.9654(14)
C(7)-H(71)	0.9896(13)	C(25)-H(251)	0.9894(16)
C(25)-H(252)	0.9641(15)	C(25)-H(253)	0.9701(14)
C(24)-H(242)	1.0031(15)	C(24)-H(241)	0.9741(16)
C(24)-H(243)	0.94(2)	C(23)-H(233)	0.9910(17)
C(23)-H(231)	0.9467(16)	C(23)-H(232)	1.0039(16)
B(1)-H(2)	1.2907(17)	B(1)-H(1)	1.28(2)
B(1)-H(3)	1.12(3)	B(1)-H(4)	1.09(2)
C(3)-Nb(1)-C(2)	34.13(5)	C(3)-Nb(1)-C(1)	58.28(5)
C(2)-Nb(1)-C(1)	35.95(5)	C(3)-Nb(1)-C(5)	58.07(5)
C(2)-Nb(1)-C(5)	59.43(5)	C(1)-Nb(1)-C(5)	36.38(5)
C(3)-Nb(1)-C(4)	33.98(5)	C(2)-Nb(1)-C(4)	57.58(5)
C(1)-Nb(1)-C(4)	58.92(5)	C(5)-Nb(1)-C(4)	35.26(5)
C(3)-Nb(1)-C(6)	121.67(5)	C(2)-Nb(1)-C(6)	87.62(5)
C(1)-Nb(1)-C(6)	71.11(5)	C(5)-Nb(1)-C(6)	96.73(5)
C(4)-Nb(1)-C(6)	129.16(5)	C(3)-Nb(1)-C(10)	121.79(5)
C(2)-Nb(1)-C(10)	93.63(5)	C(1)-Nb(1)-C(10)	96.51(5)
C(5)-Nb(1)-C(10)	129.77(5)	C(4)-Nb(1)-C(10)	151.02(5)
C(3)-Nb(1)-C(9)	145.60(5)	C(2)-Nb(1)-C(9)	127.07(5)
C(1)-Nb(1)-C(9)	128.81(5)	C(5)-Nb(1)-C(9)	151.29(5)
C(4)-Nb(1)-C(9)	172.16(5)	C(3)-Nb(1)-C(8)	179.46(5)
C(2)-Nb(1)-C(8)	145.81(5)	C(1)-Nb(1)-C(8)	122.00(5)
C(5)-Nb(1)-C(8)	122.44(5)	C(4)-Nb(1)-C(8)	146.51(5)
C(3)-Nb(1)-C(7)	145.89(5)	C(2)-Nb(1)-C(7)	116.96(5)

C(1)-Nb(1)-C(7)	87.68(5)	C(5)-Nb(1)-C(7)	93.88(5)
C(4)-Nb(1)-C(7)	127.68(5)	C(3)-Nb(1)-B(1)	89.77(6)
C(2)-Nb(1)-B(1)	121.40(6)	C(1)-Nb(1)-B(1)	144.02(6)
C(5)-Nb(1)-B(1)	114.49(6)	C(4)-Nb(1)-B(1)	85.47(6)
C(3)-Nb(1)-H(2)	79.60(4)	C(2)-Nb(1)-H(2)	100.92(4)
C(1)-Nb(1)-H(2)	135.86(4)	C(5)-Nb(1)-H(2)	129.21(4)
C(4)-Nb(1)-H(2)	93.97(4)	C(3)-Nb(1)-H(1)	100.6(7)
C(2)-Nb(1)-H(1)	134.1(7)	C(1)-Nb(1)-H(1)	131.1(7)
C(5)-Nb(1)-H(1)	94.7(7)	C(4)-Nb(1)-H(1)	79.2(7)
C(6)-Nb(1)-C(10)	36.21(4)	C(6)-Nb(1)-C(9)	58.67(5)
C(10)-Nb(1)-C(9)	34.97(5)	C(6)-Nb(1)-C(8)	58.31(5)
C(10)-Nb(1)-C(8)	57.83(5)	C(9)-Nb(1)-C(8)	33.87(5)
C(6)-Nb(1)-C(7)	35.94(4)	C(10)-Nb(1)-C(7)	59.34(5)
C(9)-Nb(1)-C(7)	57.65(5)	C(8)-Nb(1)-C(7)	34.43(5)
C(6)-Nb(1)-B(1)	144.87(6)	C(10)-Nb(1)-B(1)	115.74(6)
C(9)-Nb(1)-B(1)	86.70(6)	C(8)-Nb(1)-B(1)	90.10(6)
C(7)-Nb(1)-B(1)	121.64(6)	C(6)-Nb(1)-H(2)	131.06(3)
C(10)-Nb(1)-H(2)	94.89(3)	C(9)-Nb(1)-H(2)	79.12(3)
C(8)-Nb(1)-H(2)	100.02(3)	C(7)-Nb(1)-H(2)	133.90(3)
C(6)-Nb(1)-H(1)	135.7(7)	C(10)-Nb(1)-H(1)	129.3(7)
C(9)-Nb(1)-H(1)	94.4(7)	C(8)-Nb(1)-H(1)	79.5(7)
C(7)-Nb(1)-H(1)	100.7(7)	B(1)-Nb(1)-H(2)	32.69(4)
B(1)-Nb(1)-H(1)	32.2(7)	H(2)-Nb(1)-H(1)	64.8(7)
Nb(1)-C(3)-C(2)	70.45(8)	Nb(1)-C(3)-C(4)	71.36(8)
C(2)-C(3)-C(4)	108.71(13)	Nb(1)-C(3)-H(31)	121.68(11)
C(2)-C(3)-H(31)	123.77(15)	C(4)-C(3)-H(31)	127.45(16)
Nb(1)-C(2)-C(3)	75.42(8)	Nb(1)-C(2)-C(1)	69.78(7)
C(3)-C(2)-C(1)	108.12(13)	Nb(1)-C(2)-H(21)	123.64(11)
C(3)-C(2)-H(21)	127.39(15)	C(1)-C(2)-H(21)	124.36(15)
Nb(1)-C(1)-C(2)	74.27(8)	Nb(1)-C(1)-C(5)	72.10(7)
C(2)-C(1)-C(5)	107.06(13)	Nb(1)-C(1)-C(21)	121.15(9)
C(2)-C(1)-C(21)	126.88(13)	C(5)-C(1)-C(21)	126.00(12)
Nb(1)-C(5)-C(1)	71.52(7)	Nb(1)-C(5)-C(4)	75.17(8)
C(1)-C(5)-C(4)	107.26(12)	Nb(1)-C(5)-H(51)	123.4(1)
C(1)-C(5)-H(51)	126.07(15)	C(4)-C(5)-H(51)	126.41(14)
Nb(1)-C(4)-C(3)	74.66(9)	Nb(1)-C(4)-C(5)	69.57(8)
C(3)-C(4)-C(5)	108.83(13)	Nb(1)-C(4)-H(41)	120.41(11)
C(3)-C(4)-H(41)	125.98(16)	C(5)-C(4)-H(41)	125.16(15)
C(1)-C(21)-C(22)	108.7(1)	C(1)-C(21)-C(24)	108.35(11)
C(22)-C(21)-C(24)	111.98(12)	C(1)-C(21)-C(23)	108.46(12)
C(22)-C(21)-C(23)	112.70(11)	C(24)-C(21)-C(23)	106.53(11)
C(21)-C(22)-C(26)	112.33(11)	C(21)-C(22)-C(6)	108.32(11)
C(26)-C(22)-C(6)	109.16(11)	C(21)-C(22)-C(25)	112.22(11)
C(26)-C(22)-C(25)	106.07(11)	C(6)-C(22)-C(25)	108.7(1)
C(22)-C(26)-H(261)	113.21(13)	C(22)-C(26)-H(263)	110.88(13)
H(261)-C(26)-H(263)	108.80(14)	C(22)-C(26)-H(262)	110.55(13)
H(261)-C(26)-H(262)	106.52(15)	H(263)-C(26)-H(262)	106.58(14)
Nb(1)-C(6)-C(22)	121.16(9)	Nb(1)-C(6)-C(10)	72.44(8)
C(22)-C(6)-C(10)	125.53(11)	Nb(1)-C(6)-C(7)	73.89(8)
C(22)-C(6)-C(7)	127.28(12)	C(10)-C(6)-C(7)	107.14(11)

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Nb(1)-C(10)-C(6)	71.35(7)	Nb(1)-C(10)-C(9)	75.47(8)
C(6)-C(10)-C(9)	107.61(11)	Nb(1)-C(10)-H(101)	122.11(11)
C(6)-C(10)-H(101)	127.66(13)	C(9)-C(10)-H(101)	124.61(13)
Nb(1)-C(9)-C(10)	69.56(8)	Nb(1)-C(9)-C(8)	73.98(8)
C(10)-C(9)-C(8)	108.71(12)	Nb(1)-C(9)-H(91)	122.48(11)
C(10)-C(9)-H(91)	124.58(14)	C(8)-C(9)-H(91)	126.71(14)
Nb(1)-C(8)-C(9)	72.15(8)	Nb(1)-C(8)-C(7)	70.25(8)
C(9)-C(8)-C(7)	108.79(12)	Nb(1)-C(8)-H(81)	116.71(11)
C(9)-C(8)-H(81)	124.97(14)	C(7)-C(8)-H(81)	125.65(14)
Nb(1)-C(7)-C(6)	70.17(8)	Nb(1)-C(7)-C(8)	75.32(8)
C(6)-C(7)-C(8)	107.74(12)	Nb(1)-C(7)-H(71)	123.3(1)
C(6)-C(7)-H(71)	126.65(13)	C(8)-C(7)-H(71)	125.48(13)
C(22)-C(25)-H(251)	113.36(13)	C(22)-C(25)-H(252)	109.58(13)
H(251)-C(25)-H(252)	106.47(13)	C(22)-C(25)-H(253)	109.46(12)
H(251)-C(25)-H(253)	109.14(14)	H(252)-C(25)-H(253)	108.71(14)
C(21)-C(24)-H(242)	114.23(12)	C(21)-C(24)-H(241)	109.21(14)
H(242)-C(24)-H(241)	106.60(14)	C(21)-C(24)-H(243)	110.2(12)
H(242)-C(24)-H(243)	106.7(12)	H(241)-C(24)-H(243)	109.8(12)
C(21)-C(23)-H(233)	110.30(14)	C(21)-C(23)-H(231)	111.70(14)
H(233)-C(23)-H(231)	106.27(14)	C(21)-C(23)-H(232)	111.89(13)
H(233)-C(23)-H(232)	109.59(15)	H(231)-C(23)-H(232)	106.88(16)
Nb(1)-B(1)-H(2)	50.97(6)	Nb(1)-B(1)-H(1)	48.9(9)
H(2)-B(1)-H(1)	99.8(9)	Nb(1)-B(1)-H(3)	123.0(12)
H(2)-B(1)-H(3)	109.4(12)	H(1)-B(1)-H(3)	112.7(15)
Nb(1)-B(1)-H(4)	120.1(13)	H(2)-B(1)-H(4)	109.5(13)
H(1)-B(1)-H(4)	107.2(16)	H(3)-B(1)-H(4)	116.8(18)
Nb(1)-H(2)-B(1)	96.34(8)	Nb(1)-H(1)-B(1)	99.0(12)

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#### A.4 Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for $[\text{Nb}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{Me}_4(\eta\text{-C}_5\text{H}_4)\}(\eta^2\text{-BH}_4)] (2)$

The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
Nb(1)	8(1)	10(1)	8(1)	2(1)	3(1)	3(1)
C(3)	22(1)	24(1)	21(1)	7(1)	13(1)	15(1)
C(2)	20(1)	18(1)	15(1)	1(1)	7(1)	11(1)
C(1)	14(1)	13(1)	15(1)	4(1)	6(1)	9(1)
C(5)	13(1)	17(1)	15(1)	5(1)	2(1)	9(1)
C(4)	12(1)	21(1)	23(1)	7(1)	8(1)	9(1)
C(21)	15(1)	11(1)	15(1)	4(1)	4(1)	6(1)
C(22)	12(1)	10(1)	13(1)	3(1)	4(1)	4(1)
C(26)	18(1)	16(1)	21(1)	8(1)	10(1)	4(1)
C(6)	9(1)	12(1)	12(1)	3(1)	5(1)	4(1)
C(10)	9(1)	16(1)	13(1)	5(1)	4(1)	5(1)
C(9)	14(1)	16(1)	20(1)	9(1)	8(1)	9(1)
C(8)	14(1)	12(1)	21(1)	3(1)	10(1)	6(1)
C(7)	11(1)	13(1)	13(1)	2(1)	7(1)	5(1)
C(25)	16(1)	13(1)	16(1)	1(1)	2(1)	2(1)
C(24)	20(1)	20(1)	16(1)	10(1)	4(1)	5(1)
C(23)	24(1)	12(1)	30(1)	6(1)	6(1)	9(1)
B(1)	20(1)	17(1)	25(1)	9(1)	9(1)	2(1)

#### A.5 Additional Structural Information for $[\text{Nb}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{Me}_4(\eta\text{-C}_5\text{H}_4)\}(\eta^2\text{-BH}_4)] (2)$

Nb-Cp <sup>1</sup> <sub>cent</sub>	2.0240 Å
Nb-Cp <sup>1</sup> <sub>ave</sub>	2.33584(14) Å
Nb-Cp <sup>2</sup> <sub>cent</sub>	2.030 Å
Nb-Cp <sup>2</sup> <sub>ave</sub>	2.3644(14) Å
C <sub>ipso</sub> -C <sub>ipso</sub>	2.6835 Å
Between Cp planes, $\alpha$	52.2°
Cp <sup>1</sup> <sub>norm</sub> -Nb-Cp <sup>2</sup> <sub>norm</sub> , $\beta$	127.8°
Cp <sup>1</sup> <sub>cent</sub> -Nb-Cp <sup>2</sup> <sub>cent</sub> , $\chi$	134.38°
C <sub>ipso</sub> -Cp plane, $\phi$	-2.4, ° -2.6°