

Supporting Information

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Hungry for charge – how a beryllium scorpionate complex “eats” a weakly coordinating anion

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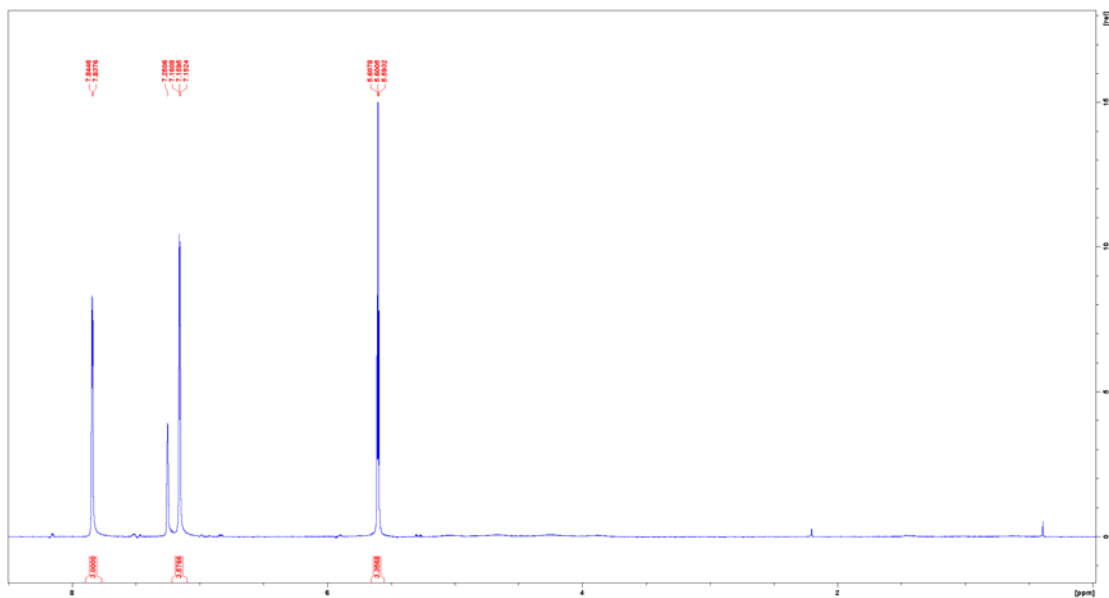
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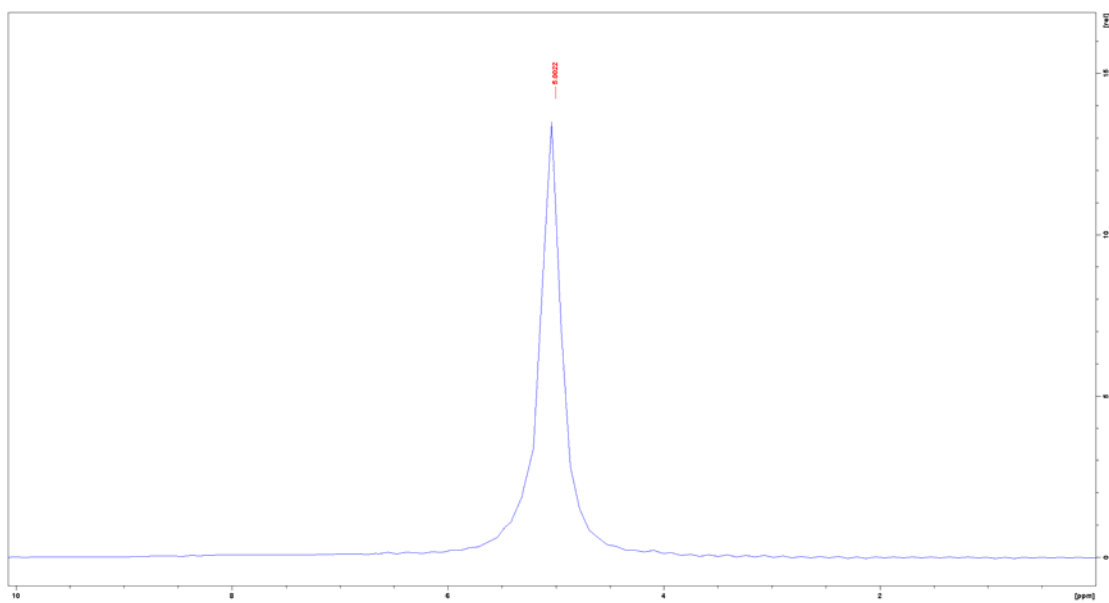
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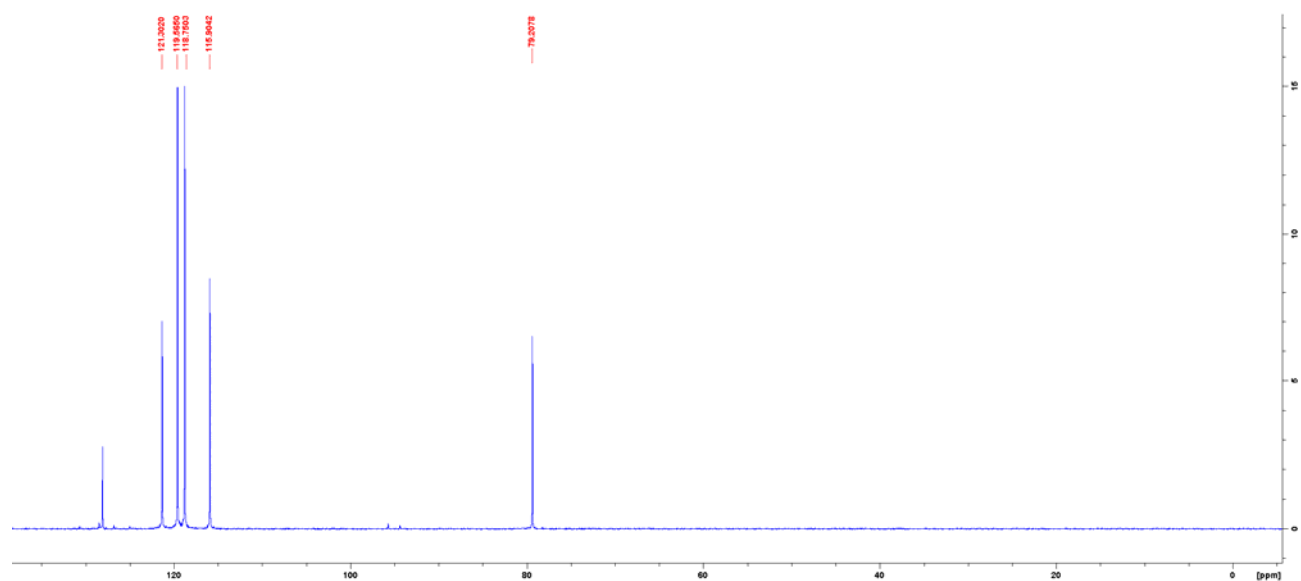
S1: ^1H NMR: 1 in C_6D_6



S2: ^9Be NMR: 1 in C_7D_8



S3: ^{13}C NMR: 1 in C_6D_6



Single-crystal X-ray analyses

Table S1: Single crystal structure data

Identification code	dnp_130m
Empirical formula	C ₁₃ H ₁₀ BB ₂ F ₉ N ₆ O
Formula weight	457.09
Density (calculated)	1.658 g·cm ⁻³
<i>F</i> (000)	912
Temperature	100(2) K
Crystal size	0.267 × 0.168 × 0.157 mm
Crystal colour	colorless
Crystal description	block
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	
<i>a</i> [Å]	10.4092(11)
<i>b</i> [Å]	12.9008(13)
<i>c</i> [Å]	13.8906(16)
<i>α</i> [°]	90
<i>β</i> [°]	100.978(6)
<i>γ</i> [°]	90
Volume	1831.2(3) Å ³
<i>Z</i>	4
Cell measurement reflections used	9913
Cell measurement <i>θ</i> min/max	2.54°/30.47°
Diffractometer control software	BRUKER D8 KAPPA APEX 2 (3.0-2009)
Diffractometer measurement device	Bruker D8 KAPPA series II with APEX II area detector system
Diffractometer measurement method	Data collection strategy APEX 2/COSMO
<i>θ</i> range for data collection	2.173°- 30.578°
Completeness to <i>θ</i> = 25.242°	100.0%
Completeness to <i>θ</i> _{max} = 30.578°	98.4%
Index ranges	-14 ≤ <i>h</i> ≤ 14
	-18 ≤ <i>k</i> ≤ 18
	-19 ≤ <i>l</i> ≤ 19
Computing data reduction	BRUKER D8 KAPPA APEX 2 (3.0-2009)
Absorption coefficient	0.170 mm ⁻¹
Absorption correction	Semi-empirical from equivalents

Computation absorption correction	BRUKER AXS SMART APEX 2 Vers. 3.0-2009
Max./min. Transmission	0.75/0.58
R_{merg} before/after correction	0.0496/0.0413
Computing structure solution	BRUKER D8 KAPPA APEX 2 (3.0-2009)
Computing structure refinement	SHELXL-2017/1 (Sheldrick, 2017)
Refinement method	Full-matrix least-squares on F^2
Reflections collected	34365
Independent reflections	5530
R_{int}	0.0300
Reflections with $I > 2\sigma(I)$	4423
Restraints	0
Parameter	284
GooF	1.054
Weighting details	$w = 1/[\sigma^2(F_{\text{obs}}^2) + (0.0641P)^2 + 1.3305P]$
	where $P = (F_{\text{obs}}^2 + 2F_{\text{calc}}^2)/3$
$R_1 [I > 2\sigma(I)]$	0.0472
$wR_2 [I > 2\sigma(I)]$	0.1364
$R_1 [\text{all data}]$	0.0617
$wR_2 [\text{all data}]$	0.1364
Largest diff. peak and hole	0.704/-0.401

Table 2: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dnp_130m. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
F(1)	123(1)	5901(1)	584(1)	49(1)
F(2)	2027(1)	5214(1)	1022(1)	45(1)
F(3)	571(1)	5056(1)	1925(1)	54(1)
F(4)	622(1)	7968(1)	700(1)	43(1)
F(5)	2388(1)	7203(1)	481(1)	48(1)
F(6)	2474(1)	8348(1)	1601(1)	47(1)
F(7)	2744(1)	5674(1)	3157(1)	51(1)
F(8)	3837(1)	6413(1)	2188(1)	32(1)
F(9)	3110(1)	7307(1)	3263(1)	38(1)
O(1)	621(1)	7053(1)	2419(1)	25(1)
N(1)	-2115(1)	7412(1)	1407(1)	17(1)
N(2)	-3263(1)	7694(1)	1679(1)	17(1)
N(3)	-1548(1)	6464(1)	3151(1)	17(1)
N(4)	-2764(1)	6773(1)	3264(1)	17(1)
N(5)	-996(1)	8470(1)	2993(1)	16(1)
N(6)	-2223(1)	8641(1)	3171(1)	17(1)
C(1)	-2357(2)	7377(1)	428(1)	20(1)
H(1)	-1732	7200	39	24
C(2)	-3661(2)	7638(1)	57(1)	22(1)
H(2)	-4085	7675	-611	27
C(3)	-4194(1)	7831(1)	873(1)	21(1)
H(3)	-5074	8029	868	25
C(4)	-1301(2)	5562(1)	3625(1)	21(1)
H(4)	-517	5173	3669	25
C(5)	-2366(2)	5275(1)	4045(1)	25(1)
H(5)	-2451	4672	4420	30
C(6)	-3271(2)	6065(1)	3793(1)	22(1)
H(6)	-4110	6099	3966	26
C(7)	-259(1)	9281(1)	3358(1)	20(1)
H(7)	641	9364	3334	24
C(8)	-1006(2)	9986(1)	3779(1)	24(1)
H(8)	-727	10624	4091	28
C(9)	-2243(2)	9551(1)	3643(1)	21(1)
H(9)	-2984	9845	3848	25
C(10)	1510(1)	6731(1)	1909(1)	18(1)
H(10)	-4228(19)	7985(15)	2916(14)	20(5)
C(11)	1074(2)	5711(1)	1349(2)	32(1)
C(12)	1756(2)	7573(1)	1163(1)	30(1)
C(13)	2821(2)	6528(1)	2639(1)	25(1)
B(1)	-3274(2)	7816(1)	2787(1)	17(1)
Be(1)	-822(2)	7299(1)	2421(1)	16(1)

Table 3: Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dnp_130m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(1)	31(1)	48(1)	58(1)	-33(1)	-16(1)	10(1)
F(2)	30(1)	40(1)	62(1)	-28(1)	0(1)	10(1)
F(3)	40(1)	27(1)	95(1)	0(1)	13(1)	-11(1)
F(4)	33(1)	49(1)	45(1)	23(1)	5(1)	7(1)
F(5)	41(1)	72(1)	34(1)	9(1)	19(1)	5(1)
F(6)	45(1)	29(1)	66(1)	7(1)	6(1)	-11(1)
F(7)	32(1)	54(1)	61(1)	32(1)	-4(1)	2(1)
F(8)	16(1)	42(1)	39(1)	-10(1)	4(1)	3(1)
F(9)	23(1)	57(1)	30(1)	-18(1)	-1(1)	1(1)
O(1)	17(1)	37(1)	21(1)	-3(1)	4(1)	6(1)
N(1)	16(1)	16(1)	17(1)	0(1)	1(1)	1(1)
N(2)	15(1)	15(1)	20(1)	0(1)	-1(1)	0(1)
N(3)	18(1)	13(1)	19(1)	-1(1)	2(1)	1(1)
N(4)	17(1)	16(1)	20(1)	0(1)	4(1)	-1(1)
N(5)	15(1)	14(1)	19(1)	-1(1)	1(1)	-1(1)
N(6)	17(1)	14(1)	18(1)	-1(1)	2(1)	2(1)
C(1)	25(1)	17(1)	17(1)	-1(1)	-1(1)	0(1)
C(2)	24(1)	19(1)	20(1)	1(1)	-6(1)	-2(1)
C(3)	17(1)	15(1)	26(1)	2(1)	-4(1)	-2(1)
C(4)	26(1)	15(1)	21(1)	0(1)	2(1)	2(1)
C(5)	34(1)	17(1)	25(1)	4(1)	8(1)	-2(1)
C(6)	25(1)	19(1)	22(1)	0(1)	7(1)	-4(1)
C(7)	20(1)	15(1)	23(1)	1(1)	-2(1)	-3(1)
C(8)	30(1)	14(1)	25(1)	-2(1)	-2(1)	-1(1)
C(9)	26(1)	15(1)	20(1)	-1(1)	2(1)	4(1)
C(10)	14(1)	18(1)	21(1)	-2(1)	2(1)	0(1)
C(11)	22(1)	26(1)	46(1)	-13(1)	1(1)	1(1)
C(12)	26(1)	32(1)	31(1)	6(1)	6(1)	-1(1)
C(13)	17(1)	31(1)	26(1)	0(1)	2(1)	2(1)
B(1)	16(1)	14(1)	21(1)	-1(1)	2(1)	0(1)
Be(1)	15(1)	16(1)	17(1)	0(1)	2(1)	1(1)

Table 4: Bond lengths [Å] for dnp_130m.

F(1)-C(11)	1.330(2)	N(1)-N(2)	1.3693(16)	N(6)-C(9)	1.3462(18)
F(2)-C(11)	1.332(2)	N(1)-Be(1)	1.759(2)	N(6)-B(1)	1.5462(19)
F(3)-C(11)	1.337(2)	N(2)-C(3)	1.3461(18)	C(1)-C(2)	1.398(2)
F(4)-C(12)	1.334(2)	N(2)-B(1)	1.549(2)	C(2)-C(3)	1.377(2)
F(5)-C(12)	1.340(2)	N(3)-C(4)	1.3382(18)	C(4)-C(5)	1.397(2)
F(6)-C(12)	1.324(2)	N(3)-N(4)	1.3638(16)	C(5)-C(6)	1.387(2)
F(7)-C(13)	1.327(2)	N(3)-Be(1)	1.746(2)	C(7)-C(8)	1.395(2)
F(8)-C(13)	1.3362(18)	N(4)-C(6)	1.3417(19)	C(8)-C(9)	1.385(2)
F(9)-C(13)	1.324(2)	N(4)-B(1)	1.5491(19)	C(10)-C(11)	1.552(2)
O(1)-C(10)	1.3352(17)	N(5)-C(7)	1.3385(18)	C(10)-C(12)	1.555(2)
O(1)-Be(1)	1.535(2)	N(5)-N(6)	1.3638(16)	C(10)-C(13)	1.560(2)
N(1)-C(1)	1.3362(19)	N(5)-Be(1)	1.733(2)		

Table 5: Bond angles [°] for dnp_130m.

C(10)-O(1)-Be(1)	147.43(12)	N(2)-C(3)-C(2)	108.79(13)	F(6)-C(12)-F(5)	106.50(15)
C(1)-N(1)-N(2)	106.51(12)	N(3)-C(4)-C(5)	110.05(13)	F(4)-C(12)-F(5)	107.66(15)
C(1)-N(1)-Be(1)	141.24(12)	C(6)-C(5)-C(4)	104.77(13)	F(6)-C(12)-C(10)	111.81(14)
N(2)-N(1)-Be(1)	112.08(11)	N(4)-C(6)-C(5)	108.58(14)	F(4)-C(12)-C(10)	110.17(13)
C(3)-N(2)-N(1)	109.48(12)	N(5)-C(7)-C(8)	110.08(13)	F(5)-C(12)-C(10)	112.77(15)
C(3)-N(2)-B(1)	132.27(13)	C(9)-C(8)-C(7)	104.85(13)	F(9)-C(13)-F(7)	107.76(15)
N(1)-N(2)-B(1)	118.24(11)	N(6)-C(9)-C(8)	108.63(13)	F(9)-C(13)-F(8)	106.84(13)
C(4)-N(3)-N(4)	107.00(12)	O(1)-C(10)-C(11)	111.33(13)	F(7)-C(13)-F(8)	107.34(14)
C(4)-N(3)-Be(1)	139.31(12)	O(1)-C(10)-C(12)	110.79(13)	F(9)-C(13)-C(10)	111.07(13)
N(4)-N(3)-Be(1)	113.63(11)	C(11)-C(10)-C(12)	109.16(14)	F(7)-C(13)-C(10)	110.88(13)
C(6)-N(4)-N(3)	109.60(12)	O(1)-C(10)-C(13)	108.45(12)	F(8)-C(13)-C(10)	112.71(13)
C(6)-N(4)-B(1)	133.39(13)	C(11)-C(10)-C(13)	108.62(12)	N(6)-B(1)-N(2)	105.96(11)
N(3)-N(4)-B(1)	117.01(11)	C(12)-C(10)-C(13)	108.41(12)	N(6)-B(1)-N(4)	106.74(11)
C(7)-N(5)-N(6)	107.09(12)	F(1)-C(11)-F(2)	107.78(16)	N(2)-B(1)-N(4)	105.61(11)
C(7)-N(5)-Be(1)	138.82(12)	F(1)-C(11)-F(3)	106.11(15)	O(1)-Be(1)-N(5)	111.64(12)
N(6)-N(5)-Be(1)	114.05(11)	F(2)-C(11)-F(3)	107.58(16)	O(1)-Be(1)-N(3)	113.93(12)
C(9)-N(6)-N(5)	109.35(12)	F(1)-C(11)-C(10)	110.25(14)	N(5)-Be(1)-N(3)	100.18(11)
C(9)-N(6)-B(1)	133.79(12)	F(2)-C(11)-C(10)	114.41(14)	O(1)-Be(1)-N(1)	127.96(13)
N(5)-N(6)-B(1)	116.83(11)	F(3)-C(11)-C(10)	110.34(15)	N(5)-Be(1)-N(1)	99.43(10)
N(1)-C(1)-C(2)	110.46(14)	F(6)-C(12)-F(4)	107.69(15)	N(3)-Be(1)-N(1)	99.55(10)
C(3)-C(2)-C(1)	104.77(13)				

Computational calculations

For technical details of the quantum chemical calculations see manuscript text.

Fig. S4: Molecular structure of Cp^*Be^+ from the DFT calculations (B3LYP/TZVPP, see main text).

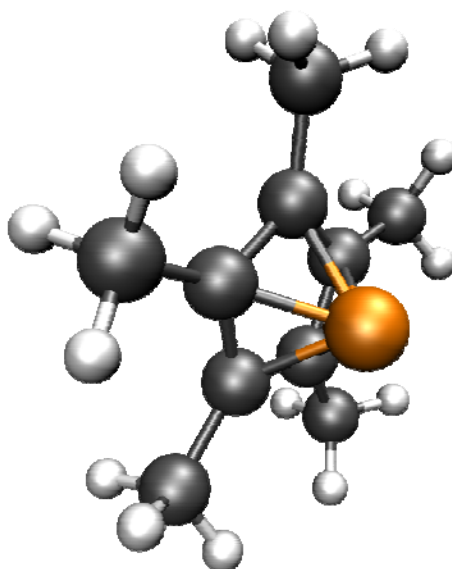


Fig. S5: Molecular structure of $\text{Cp}^*\text{BeOR}^{\text{F}}$ from the DFT calculations (B3LYP/TZVPP, see main text).

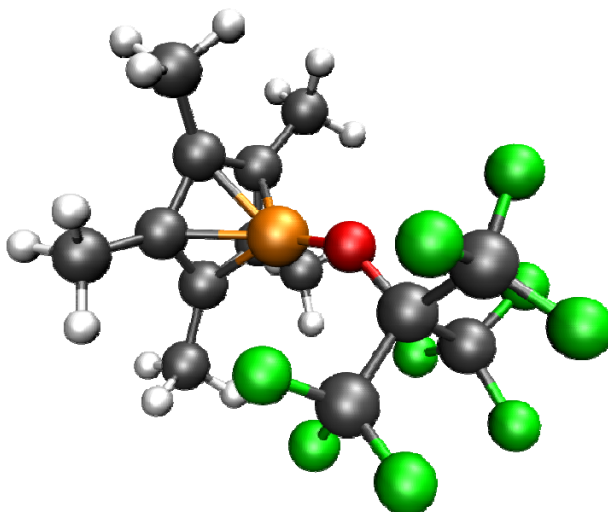


Fig. S6: Molecular structure of TpBe^+ from the DFT calculations (B3LYP/TZVPP, see main text).

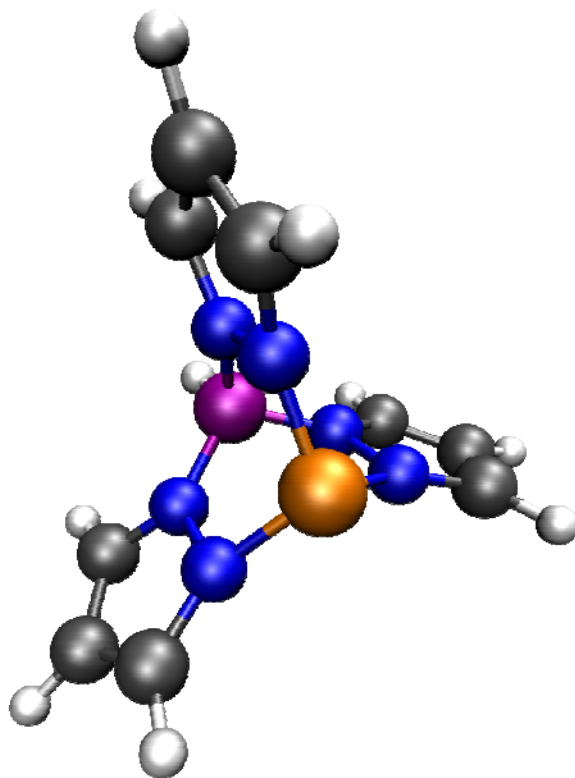


Fig. S7: Molecular structure of $\text{Cp}^*\text{BeFAl}(\text{OR}^{\text{F}})_3$ from the DFT calculations (B3LYP/TZVPP, see main text).

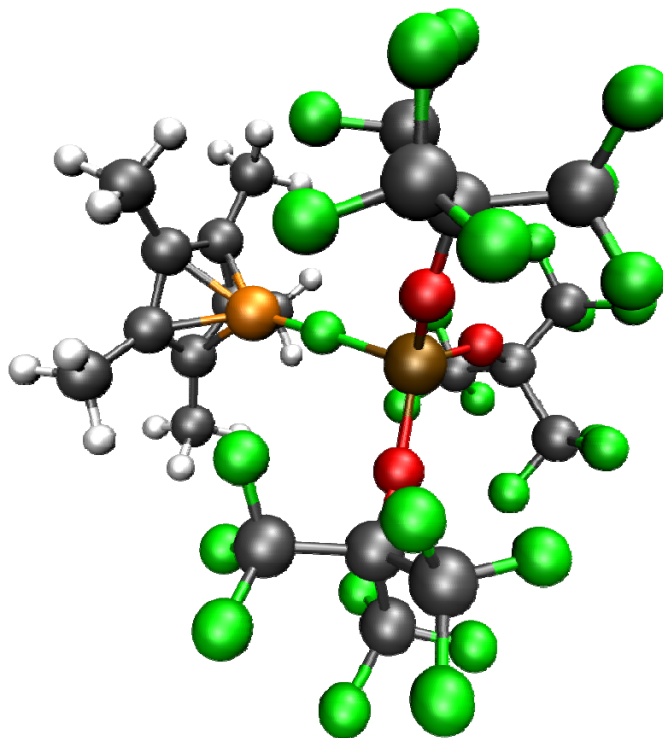


Fig. S8: Molecular structure of TpBeOR^{F} from the DFT calculations (B3LYP/TZVPP, see main text).

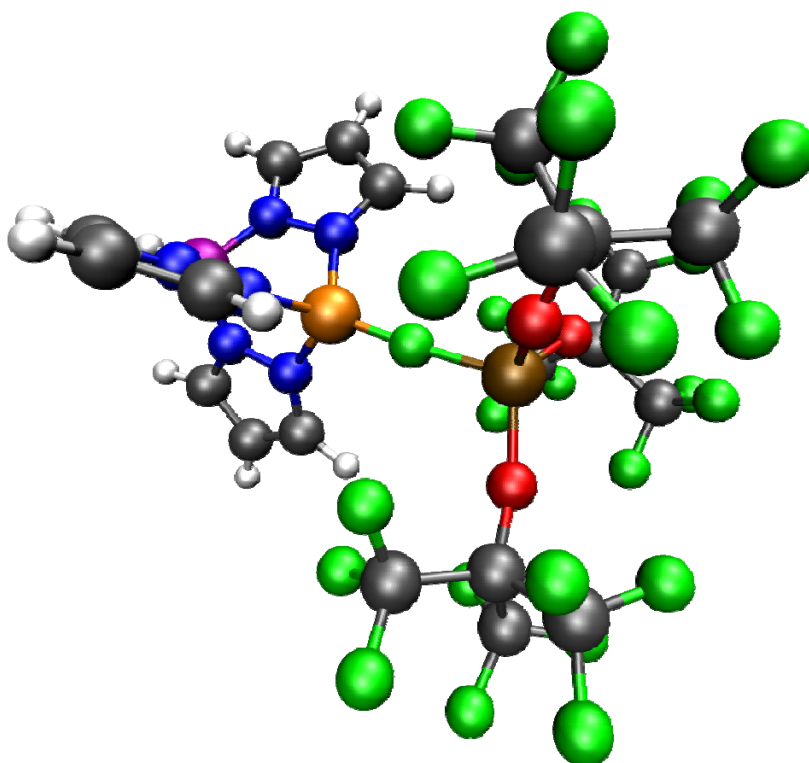


Fig. S9: Molecular structure of $\text{TpBeFAl(OR}^{\text{F}}\text{)}_3$ from the DFT calculations (B3LYP/TZVPP, see main text).

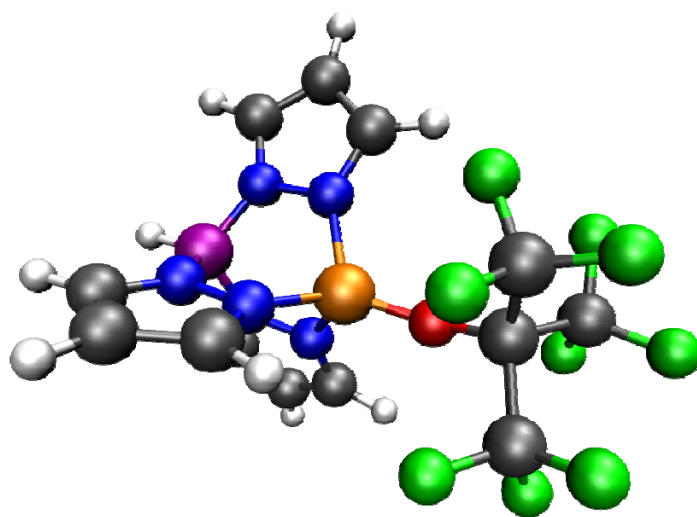


Fig. S10: LOL plot of Cp^*Be^+ in the C-C-Be plane

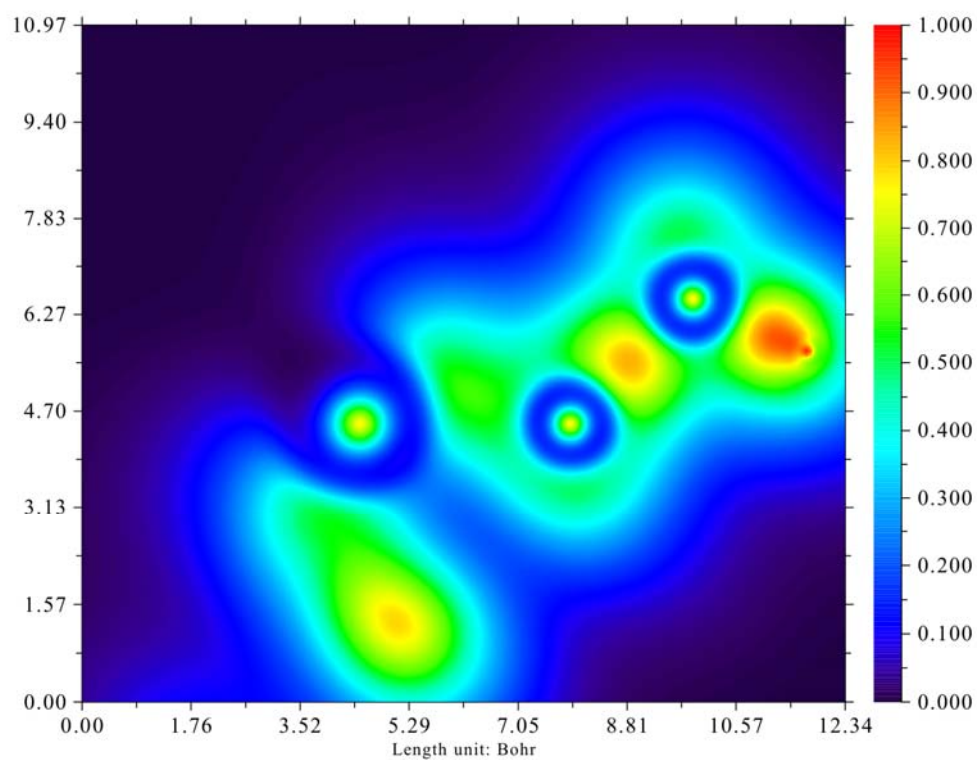


Fig. S11: LOL plot of $\text{Cp}^*\text{BeOR}^{\text{F}}$ in the C-Be-O plane

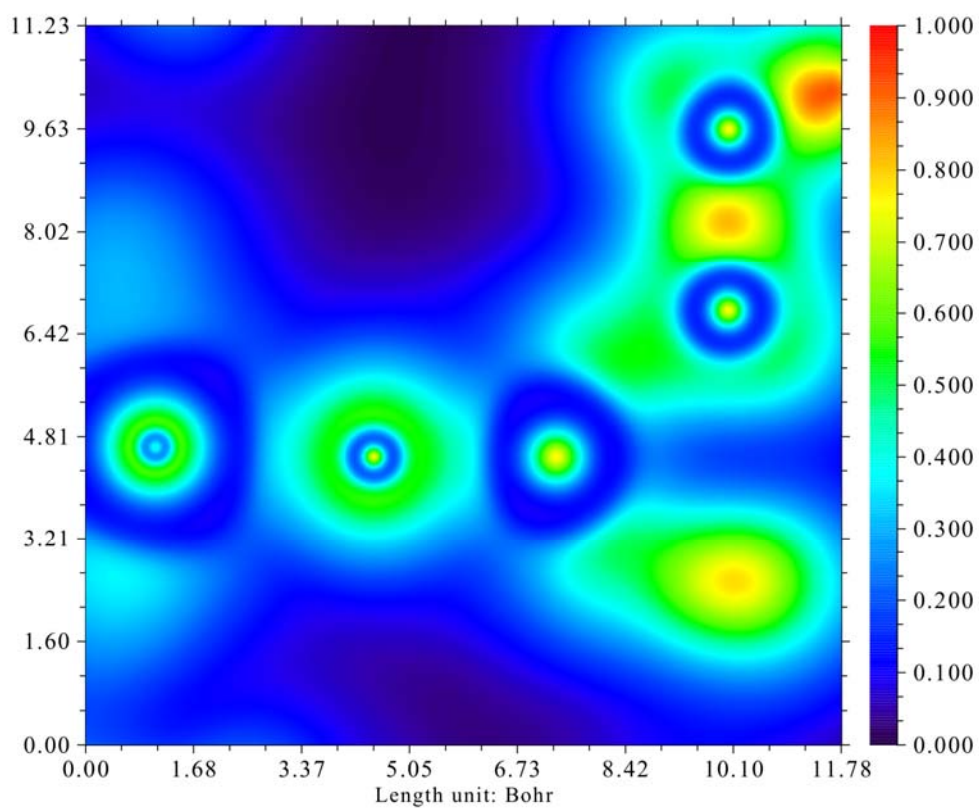


Fig. S12: LOL plot of $\text{Cp}^*\text{BeFAl}(\text{OR}^{\text{F}})_3$ in the C-Be-F plane

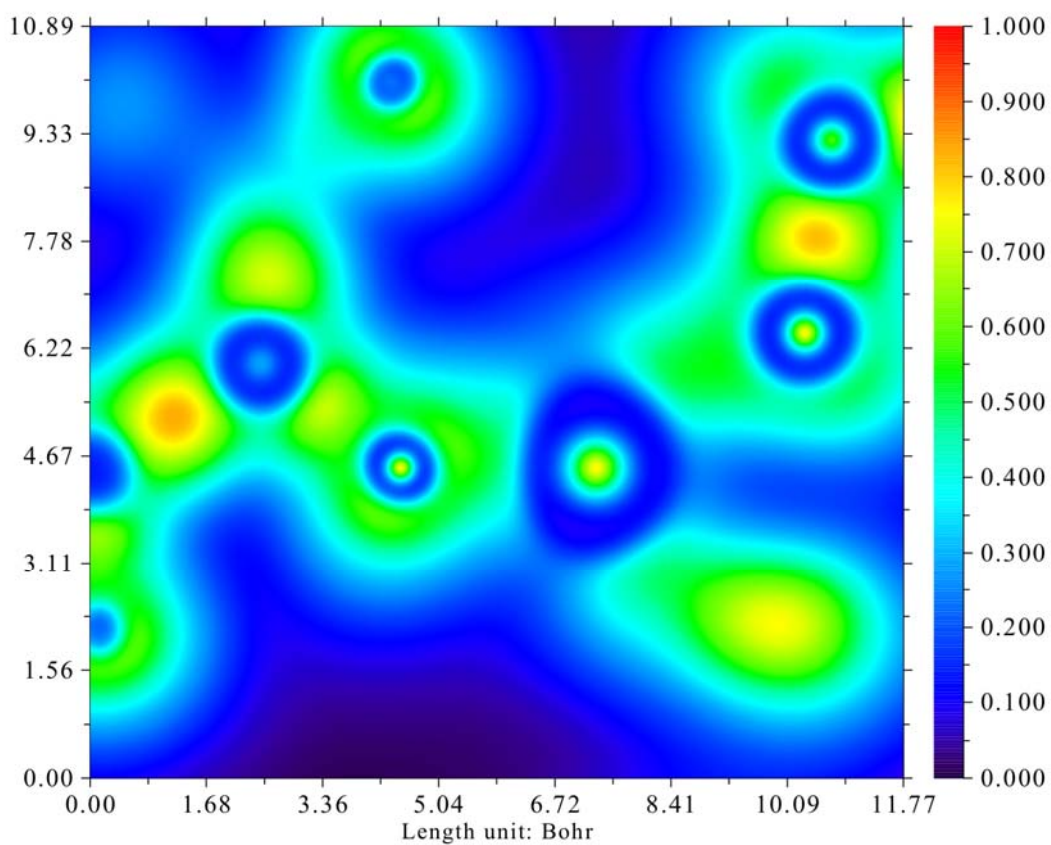


Fig. S13: LOL plot of TpBe^+ in the Be-N-N plane

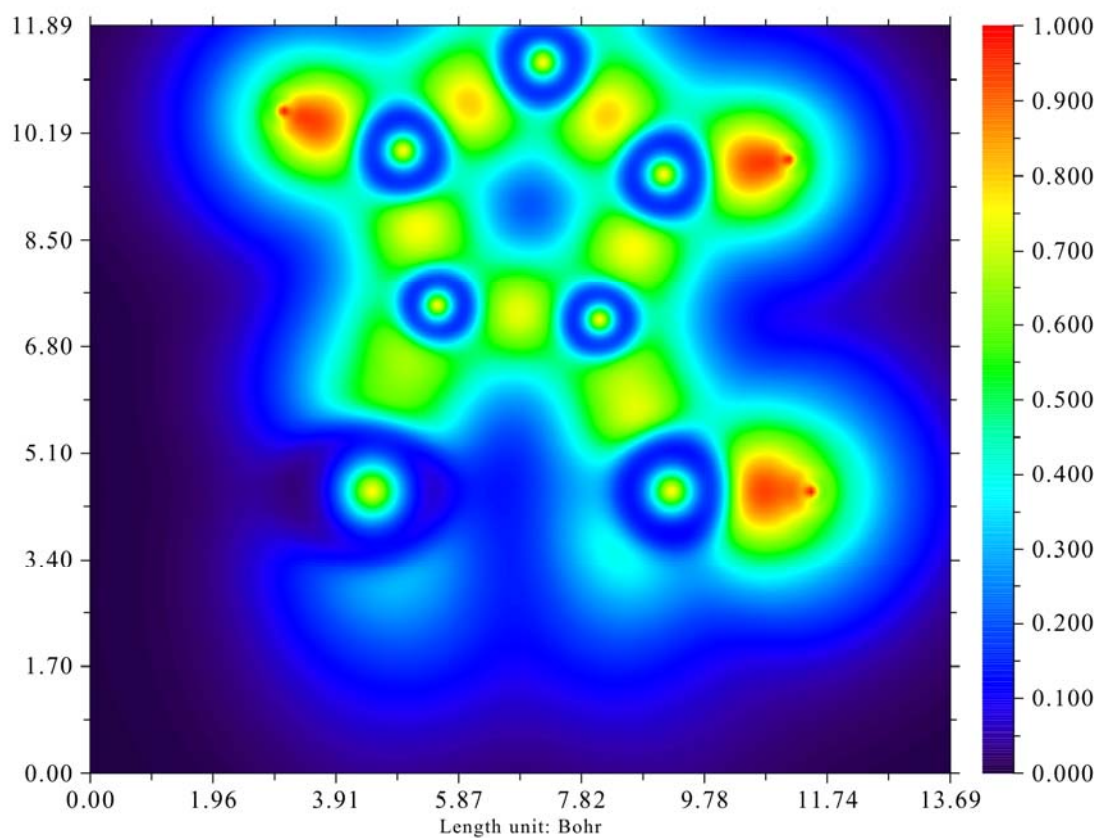


Fig. S14: LOL plot of TpBeORF in the N-Be-O plane.

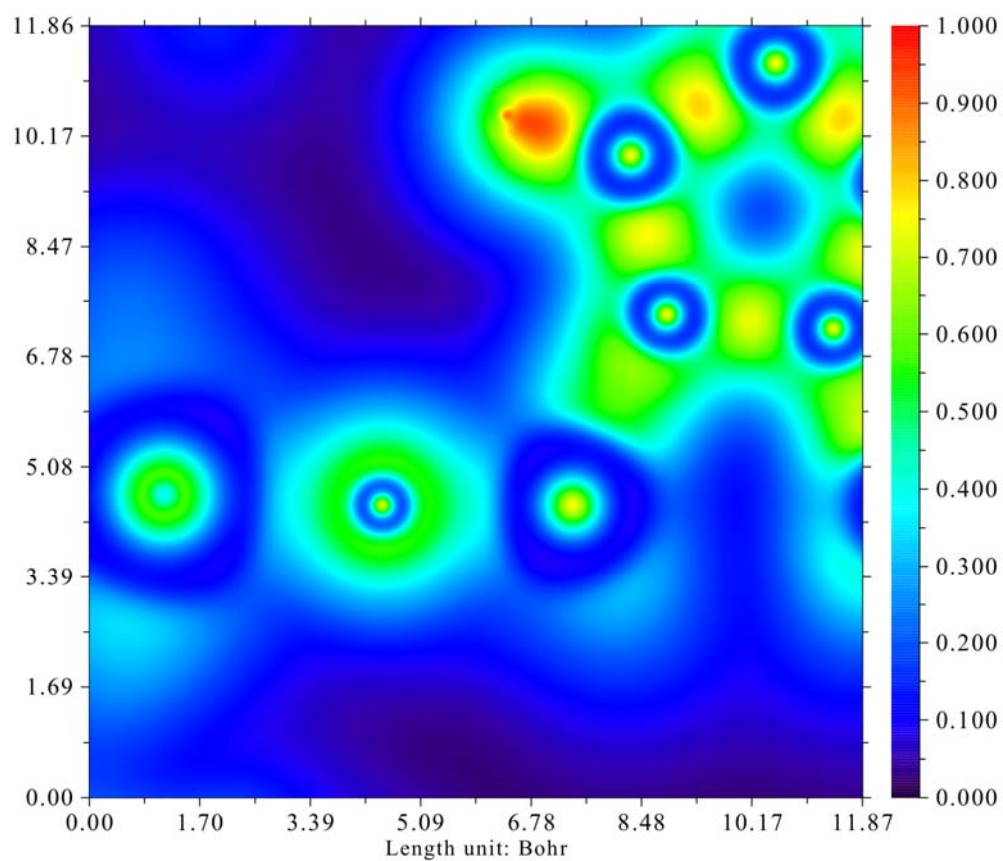


Fig. S15: LOL plot of TpBeFAl(ORF)₃ in the N-Be-F plane

