Three new types of transition metal carboranylamidinate complexes

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Supplementary Information

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1. Magnetic moments

The magnetic moments were determined with the Gouy method at 293 K, using the magnetic balance Johnson Matthey MSB MK I. Diamagnetic correction have been applied as $\chi_{mol,\ corr} = \chi_{mol} - \chi_{mol,\ dia}$ while $\chi_{mol,\ dia}$ was calculated as the sum of the molar diamagnetic susceptibility of each atom. The molar diamagnetic susceptibility values of the atoms were taken from literature [S1] as $\chi^{O}_{mol,\ dia} = -4.61 \cdot 10^{-6}$ emu / mol, $\chi^{C(THF)}_{mol,\ dia} = -6 \cdot 10^{-6}$ emu / mol, $\chi^{Li}_{mol,\ dia} = -4.2 \cdot 10^{-6}$ emu / mol, $\chi^{Cl}_{mol,\ dia} = -2.6 \cdot 10^{-5}$ emu / mol, $\chi^{Mn(III)}_{mol,\ dia} = -1.1 \cdot 10^{-5}$ emu / mol, $\chi^{Mn(II)}_{mol,\ dia} = -1.4 \cdot 10^{-5}$ emu / mol.

S1 H. Landolt, R. Börnstein, O. Madelung, *Numerical data and functional relationships in science and technology: new series - Macroscopic and technical properties of matter*, Springer, Berlin, 1974.

Results:

Sample: $Mn_4Cl_6[(o\text{-}C_2B_{10}H_{10})C(N^iPr)(NH^iPr)]_2(THF)_4 \bullet THF$ (2)

χ_{mol}= 0.0354 emu / mol

$\chi_{mol,\ dia}$= $-4.89 \cdot 10^{-4}$ emu/mol

$\chi_{mol,\ corr}$ = 0.0359 emu / mol

μ/μ_B (for one Mn ion) = 4.60

Sample: $[Li(DME)_3][FeCl_2\{(o\text{-}C_2B_{10}H_{10})C(N^iPr)(NH^iPr)\}]$ (3)

χ_{mol}= 0.0133 emu / mol

$\chi_{mol,\ dia}$= $-2.32 \cdot 10^{-4}$ emu/mol

$\chi_{mol,\ corr}$ = 0.0135 emu / mol

μ/μ_B = 5.64

2. X-Ray crystallographic data for **2**, **3** and **4**

STRUCTURE REPORT for Compound 2

Crystallographer: P. Liebing
ID code: LI0266
Compound: $Mn_4Cl_6\{(C_2B_{10}H_{10})C(NiPr)(NHiPr)\}_2(THF)_4 \cdot THF$ (**2**)
Formula sum: $C_{38}H_{90}B_{20}Cl_6Mn_4N_4O_5$
Formula moieties: $C_{34}H_{82}B_{20}Cl_6Mn_4N_4O_4$, C_4H_8O

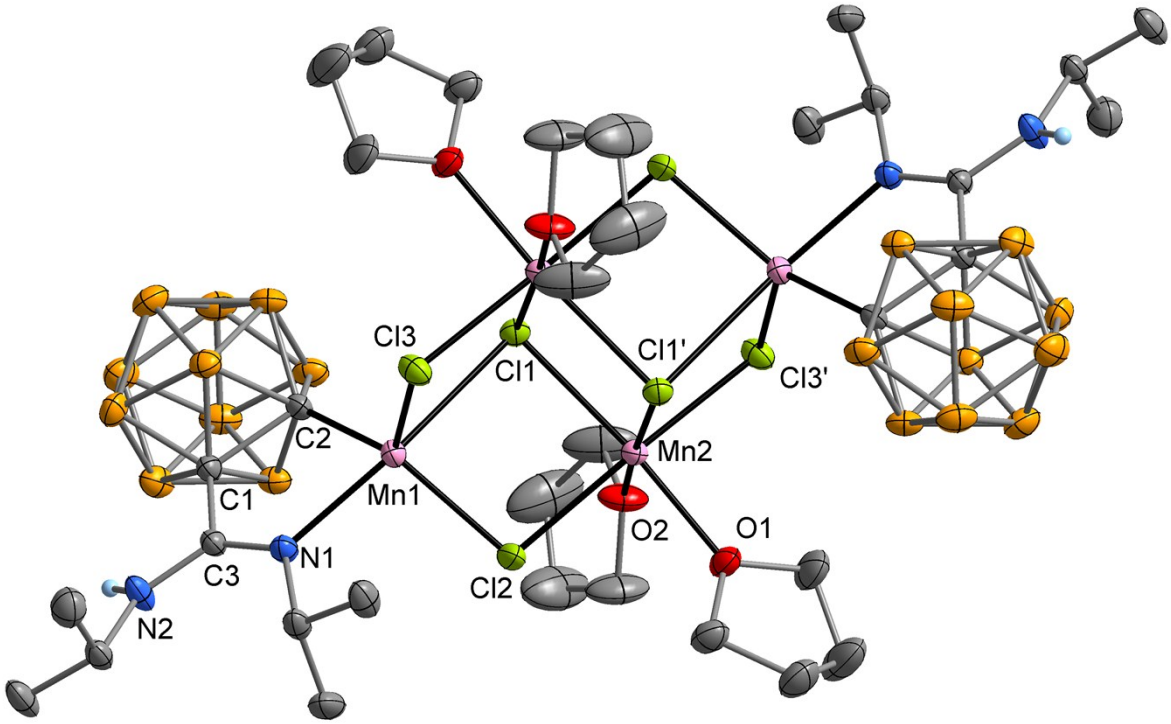

Figure S1. Molecular structure of **2**. Displacement ellipsoids with 50% probability, H atoms omitted for clarity.

Table S1. Crystallographic Data and Details on Structure Refinement for Compound **2**.

formula sum	$C_{38}H_{90}B_{20}Cl_6Mn_4N_4O_5$
formula weight	1331.79
crystal color / shape / size (mm)	colorless prisms / 0.24 × 0.20 × 0.17
crystal system	monoclinic
space group	$P2_1/n$
unit cell parameters	
a (Å)	10.7605(4)
b (Å)	19.0431(7)
c (Å)	16.0549(6)
α (deg)	90
β (deg)	92.892(3)
γ (deg)	90
unit cell volume V (Å^3)	3285.7(2)
molecules per cell z	2
crystallographic density ρ_{calcd} (g cm^{-3})	1.346
absorption coefficient μ (mm^{-1})	1.036
diffractometer	STOE IPDS 2T
radiation (λ [Å])	graphite-monochromated Mo-K_α (0.71073)
temperature (°C)	–120
scan type [S2]	ω scan (increment 1.5°, exposure 3 min)
completeness of dataset	100%
θ range of data collection (deg)	2.176 to 25.999
reflections collected	22893 (–13 ≤ h ≤ 13, –23 ≤ k ≤ 23, –19 ≤ l ≤ 19)
independent reflections	6452 (R_{int} = 0.0449)
independent reflections with I>2σ (I)	5387
structure solution method	heavy atom methods (SIR-97) [S36
refinement method	full-matrix least-squares on F^2 (SHELXL 2016/4) [S4]
absorption correction method	numerical
range of transmission factors	0.7950 to 0.8986
data / parameters / restraints	6452 / 374 / 70[a]
goodness of fit (GooF) [all data]	1.020
final R values	
R_1 [all data, I ≥ 2σ (I)]	0.0446, 0.0331
wR_2 [all data, I ≥ 2 σ (I)]]	0.0757, 0.0721
largest difference peak and hole	0.522 and –0.320 eÅ^{-3}
Extinction coefficient	–

Refinement special details: The free THF molecule (O3, C18–C21) is located on an inversion center and therefore disordered over two orientations (site occupancy factors constrained to 0.5). [a] Restraints on interatomic distances and anisotropic displacement parameters (SADI, SIMU) of the disordered atoms.

[S2] Stoe & Cie 2002. X-AREA. Stoe & Cie, Darmstadt, Germany.

[S3] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori & R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115-119.

[S4] G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3–8.

Table S2. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (x 10^3) for Compound **2**.

Atom	x	y	z	U_{eq} / Å^2
C(1)	-1300(2)	6911(1)	457(1)	19(1)
C(2)	-798(2)	7588(1)	-68(1)	20(1)
C(3)	-1723(2)	7076(1)	1330(1)	19(1)
C(4)	-1974(2)	7921(1)	2430(1)	25(1)
C(5)	-847(2)	7784(1)	3013(1)	35(1)
C(6)	-2361(2)	8688(1)	2452(1)	31(1)
C(7)	-2792(2)	6352(1)	2453(1)	24(1)
C(8)	-2649(3)	5576(1)	2655(1)	36(1)
C(9)	-4132(2)	6547(1)	2265(2)	37(1)
C(10)	1988(2)	10383(1)	2528(1)	33(1)
C(11)	2675(3)	10962(2)	2987(2)	47(1)
C(12)	3906(3)	10956(2)	2574(2)	69(1)
C(13)	3560(2)	10803(2)	1690(2)	46(1)
C(14)	3608(3)	8857(2)	-125(2)	68(1)
C(15)	4040(4)	8170(2)	139(2)	93(1)
C(16)	4182(5)	8187(2)	1049(2)	88(1)
C(17)	3823(3)	8893(2)	1311(2)	56(1)
C(18)	-409(14)	9671(7)	4366(8)	94(3)
C(19)	-643(15)	9606(7)	5249(8)	97(3)
C(20)	36(13)	10178(7)	5656(8)	89(3)
C(21)	550(13)	10582(7)	4976(6)	83(3)
B(1)	-2224(2)	7225(1)	-351(1)	23(1)
B(2)	-1177(2)	7462(1)	-1104(1)	25(1)
B(3)	-2062(2)	6304(1)	-167(2)	28(1)
B(4)	-1975(2)	6646(2)	-1186(2)	30(1)
B(5)	248(2)	6976(1)	322(1)	23(1)
B(6)	341(2)	7309(1)	-694(1)	26(1)
B(7)	-528(2)	6148(1)	246(1)	26(1)
B(8)	-913(3)	5982(1)	-816(2)	32(1)
B(9)	-373(3)	6697(1)	-1404(2)	30(1)
B(10)	525(2)	6393(1)	-510(2)	29(1)
N(1)	-1694(2)	7722(1)	1565(1)	21(1)
N(2)	-2031(2)	6484(1)	1731(1)	27(1)
O(1)	2440(1)	10390(1)	1695(1)	29(1)
O(2)	3175(2)	9198(1)	588(1)	36(1)
O(3)	42(7)	10354(4)	4186(3)	93(2)
CL1	263(1)	9251(1)	-551(1)	22(1)
CL2	629(1)	9028(1)	1589(1)	34(1)
CL3	-2646(1)	9323(1)	363(1)	26(1)
MN1	-967(1)	8515(1)	689(1)	21(1)
MN2	1543(1)	9882(1)	608(1)	20(1)

Table S3. Interatomic Distances for Compound **2**. Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z+1 #2 -x,-y+2,-z

Atom 1	Atom 2	d / Å	Atom 1	Atom 2	d / Å
C(1)	C(3)	1.528(3)	C(21)	C(20)#1	1.861(19)
C(1)	C(2)	1.647(3)	B(1)	B(2)	1.754(3)
C(1)	B(5)	1.695(3)	B(1)	B(4)	1.768(3)
C(1)	B(1)	1.702(3)	B(1)	B(3)	1.786(3)
C(1)	B(3)	1.711(3)	B(2)	B(6)	1.754(3)
C(1)	B(7)	1.715(3)	B(2)	B(9)	1.773(4)
C(2)	B(6)	1.708(3)	B(2)	B(4)	1.778(4)
C(2)	B(2)	1.710(3)	B(3)	B(8)	1.767(4)
C(2)	B(5)	1.716(3)	B(3)	B(4)	1.769(4)
C(2)	B(1)	1.724(3)	B(3)	B(7)	1.773(4)
C(2)	MN1	2.156(2)	B(4)	B(9)	1.779(4)
C(3)	N(1)	1.288(3)	B(4)	B(8)	1.786(4)
C(3)	N(2)	1.348(3)	B(5)	B(6)	1.756(3)
C(4)	N(1)	1.484(2)	B(5)	B(10)	1.774(3)
C(4)	C(5)	1.517(3)	B(5)	B(7)	1.787(4)
C(4)	C(6)	1.521(3)	B(6)	B(9)	1.778(4)
C(7)	N(2)	1.474(3)	B(6)	B(10)	1.780(4)
C(7)	C(9)	1.505(3)	B(7)	B(8)	1.764(3)
C(7)	C(8)	1.518(3)	B(7)	B(10)	1.765(4)
C(10)	O(1)	1.446(3)	B(8)	B(9)	1.773(4)
C(10)	C(11)	1.500(3)	B(8)	B(10)	1.782(4)
C(11)	C(12)	1.511(4)	B(9)	B(10)	1.786(3)
C(12)	C(13)	1.477(4)	N(1)	MN1	2.232(2)
C(13)	O(1)	1.440(3)	O(1)	MN2	2.178(1)
C(14)	O(2)	1.416(3)	O(2)	MN2	2.188(2)
C(14)	C(15)	1.445(5)	O(3)	C(20)#1	1.050(1)
C(15)	C(16)	1.462(5)	O(3)	C(19)#1	1.090(2)
C(16)	C(17)	1.465(5)	CL1	MN2#2	2.548(1)
C(17)	O(2)	1.445(3)	CL1	MN2	2.558(1)
C(18)	O(3)	1.423(11)	CL1	MN1	2.819(1)
C(18)	C(19)	1.458(8)	CL2	MN1	2.395(1)
C(19)	C(20)	1.449(9)	CL2	MN2	2.501(1)
C(19)	C(18)#1	1.868(19)	CL3	MN1	2.409(1)
C(20)	C(21)	1.467(7)	CL3	MN2#2	2.513(1)
C(20)	C(21)#1	1.861(19)	MN2	CL3#2	2.513(1)
C(21)	O(3)	1.424(10)	MN2	CL1#2	2.548(1)

Table S4. Interatomic Angles (deg.) for Compound **2**. Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z+1 #2 -x,-y+2,-z

Atom 1	Atom 2	Atom 3	Angle / °	Atom 1	Atom 2	Atom 3	Angle / °
C(3)	C(1)	C(2)	115.37(15)	B(6)	B(5)	B(10)	60.55(14)
C(3)	C(1)	B(5)	116.27(16)	C(1)	B(5)	B(7)	58.97(13)
C(2)	C(1)	B(5)	61.79(13)	C(2)	B(5)	B(7)	106.22(16)
C(3)	C(1)	B(1)	115.85(16)	B(6)	B(5)	B(7)	107.72(16)
C(2)	C(1)	B(1)	61.92(12)	B(10)	B(5)	B(7)	59.43(14)
B(5)	C(1)	B(1)	114.65(15)	C(2)	B(6)	B(2)	59.17(12)
C(3)	C(1)	B(3)	121.24(17)	C(2)	B(6)	B(5)	59.37(12)
C(2)	C(1)	B(3)	112.98(15)	B(2)	B(6)	B(5)	108.26(17)
B(5)	C(1)	B(3)	114.87(16)	C(2)	B(6)	B(9)	106.37(17)
B(1)	C(1)	B(3)	63.11(14)	B(2)	B(6)	B(9)	60.27(14)
C(3)	C(1)	B(7)	121.62(16)	B(5)	B(6)	B(9)	108.41(18)
C(2)	C(1)	B(7)	112.89(16)	C(2)	B(6)	B(10)	106.55(17)
B(5)	C(1)	B(7)	63.19(14)	B(2)	B(6)	B(10)	108.59(18)
B(1)	C(1)	B(7)	114.72(16)	B(5)	B(6)	B(10)	60.21(14)
B(3)	C(1)	B(7)	62.31(14)	B(9)	B(6)	B(10)	60.27(15)
C(1)	C(2)	B(6)	108.68(16)	C(1)	B(7)	B(8)	104.46(17)
C(1)	C(2)	B(2)	108.62(15)	C(1)	B(7)	B(10)	104.20(17)
B(6)	C(2)	B(2)	61.76(13)	B(8)	B(7)	B(10)	60.64(15)
C(1)	C(2)	B(5)	60.49(12)	C(1)	B(7)	B(3)	58.73(13)
B(6)	C(2)	B(5)	61.71(13)	B(8)	B(7)	B(3)	59.95(14)
B(2)	C(2)	B(5)	112.25(16)	B(10)	B(7)	B(3)	108.46(17)
C(1)	C(2)	B(1)	60.63(12)	C(1)	B(7)	B(5)	57.85(13)
B(6)	C(2)	B(1)	112.08(16)	B(8)	B(7)	B(5)	108.06(17)
B(2)	C(2)	B(1)	61.44(13)	B(10)	B(7)	B(5)	59.92(14)
B(5)	C(2)	B(1)	112.47(16)	B(3)	B(7)	B(5)	107.50(17)
C(1)	C(2)	MN1	108.32(12)	B(7)	B(8)	B(3)	60.27(14)
B(6)	C(2)	MN1	132.05(14)	B(7)	B(8)	B(9)	108.03(18)
B(2)	C(2)	MN1	129.85(14)	B(3)	B(8)	B(9)	107.80(18)
B(5)	C(2)	MN1	115.03(12)	B(7)	B(8)	B(10)	59.70(14)
B(1)	C(2)	MN1	112.20(13)	B(3)	B(8)	B(10)	107.96(17)
N(1)	C(3)	N(2)	131.46(18)	B(9)	B(8)	B(10)	60.33(15)
N(1)	C(3)	C(1)	117.51(17)	B(7)	B(8)	B(4)	108.05(17)
N(2)	C(3)	C(1)	110.99(17)	B(3)	B(8)	B(4)	59.71(15)
N(1)	C(4)	C(5)	109.91(18)	B(9)	B(8)	B(4)	60.01(15)
N(1)	C(4)	C(6)	109.60(17)	B(10)	B(8)	B(4)	108.23(19)
C(5)	C(4)	C(6)	111.25(19)	B(8)	B(9)	B(2)	108.02(18)
N(2)	C(7)	C(9)	111.37(18)	B(8)	B(9)	B(6)	107.78(17)
N(2)	C(7)	C(8)	106.25(18)	B(2)	B(9)	B(6)	59.21(14)
C(9)	C(7)	C(8)	111.7(2)	B(8)	B(9)	B(4)	60.36(16)
O(1)	C(10)	C(11)	105.54(19)	B(2)	B(9)	B(4)	60.06(15)
C(10)	C(11)	C(12)	101.5(2)	B(6)	B(9)	B(4)	107.54(17)
C(13)	C(12)	C(11)	103.9(2)	B(8)	B(9)	B(10)	60.08(15)
O(1)	C(13)	C(12)	105.9(2)	B(2)	B(9)	B(10)	107.46(17)

Atom 1	Atom 2	Atom 3	Angle / °	Atom 1	Atom 2	Atom 3	Angle / °
O(2)	C(14)	C(15)	107.0(3)	B(6)	B(9)	B(10)	59.91(14)
C(14)	C(15)	C(16)	106.7(3)	B(4)	B(9)	B(10)	108.31(18)
C(15)	C(16)	C(17)	107.0(3)	B(7)	B(10)	B(5)	60.65(13)
O(2)	C(17)	C(16)	105.2(2)	B(7)	B(10)	B(6)	107.66(17)
O(3)	C(18)	C(19)	110.6(9)	B(5)	B(10)	B(6)	59.24(13)
C(20)	C(19)	C(18)	105.5(9)	B(7)	B(10)	B(8)	59.66(14)
C(20)	C(19)	C(18)#1	9.3(8)	B(5)	B(10)	B(8)	107.86(17)
C(18)	C(19)	C(18)#1	97.3(11)	B(6)	B(10)	B(8)	107.30(18)
C(19)	C(20)	C(21)	105.1(8)	B(7)	B(10)	B(9)	107.39(18)
C(19)	C(20)	C(21)#1	11.3(9)	B(5)	B(10)	B(9)	107.28(17)
C(21)	C(20)	C(21)#1	97.6(10)	B(6)	B(10)	B(9)	59.82(14)
O(3)	C(21)	C(20)	111.1(9)	B(8)	B(10)	B(9)	59.58(15)
O(3)	C(21)	C(20)#1	34.1(4)	C(3)	N(1)	C(4)	121.02(17)
C(20)	C(21)	C(20)#1	82.4(10)	C(3)	N(1)	MN1	117.77(13)
C(1)	B(1)	C(2)	57.45(11)	C(4)	N(1)	MN1	120.72(12)
C(1)	B(1)	B(2)	104.14(16)	C(3)	N(2)	C(7)	132.70(18)
C(2)	B(1)	B(2)	58.90(12)	C(13)	O(1)	C(10)	109.26(16)
C(1)	B(1)	B(4)	104.66(17)	C(13)	O(1)	MN2	125.19(13)
C(2)	B(1)	B(4)	106.46(16)	C(10)	O(1)	MN2	125.53(13)
B(2)	B(1)	B(4)	60.65(14)	C(14)	O(2)	C(17)	107.4(2)
C(1)	B(1)	B(3)	58.69(13)	C(14)	O(2)	MN2	125.58(15)
C(2)	B(1)	B(3)	105.82(16)	C(17)	O(2)	MN2	125.69(15)
B(2)	B(1)	B(3)	107.84(17)	C(20)#1	O(3)	C(19)#1	85.3(8)
B(4)	B(1)	B(3)	59.70(14)	C(20)#1	O(3)	C(18)	15.4(12)
C(2)	B(2)	B(1)	59.66(12)	C(19)#1	O(3)	C(18)	95.1(9)
C(2)	B(2)	B(6)	59.07(12)	C(20)#1	O(3)	C(21)	96.4(9)
B(1)	B(2)	B(6)	108.45(16)	C(19)#1	O(3)	C(21)	18.6(12)
C(2)	B(2)	B(9)	106.50(16)	C(18)	O(3)	C(21)	102.6(10)
B(1)	B(2)	B(9)	108.36(18)	MN2#2	CL1	MN2	95.925(18)
B(6)	B(2)	B(9)	60.53(14)	MN2#2	CL1	MN1	87.873(17)
C(2)	B(2)	B(4)	106.58(16)	MN2	CL1	MN1	88.563(16)
B(1)	B(2)	B(4)	60.05(14)	MN1	CL2	MN2	100.25(2)
B(6)	B(2)	B(4)	108.65(18)	MN1	CL3	MN2#2	98.47(2)
B(9)	B(2)	B(4)	60.14(15)	C(2)	MN1	N(1)	81.00(7)
C(1)	B(3)	B(8)	104.50(18)	C(2)	MN1	CL2	126.52(6)
C(1)	B(3)	B(4)	104.24(17)	N(1)	MN1	CL2	99.15(5)
B(8)	B(3)	B(4)	60.66(15)	C(2)	MN1	CL3	118.92(5)
C(1)	B(3)	B(7)	58.96(13)	N(1)	MN1	CL3	106.63(5)
B(8)	B(3)	B(7)	59.78(14)	CL2	MN1	CL3	112.20(2)
B(4)	B(3)	B(7)	108.41(18)	C(2)	MN1	CL1	87.29(5)
C(1)	B(3)	B(1)	58.21(12)	N(1)	MN1	CL1	166.76(5)
B(8)	B(3)	B(1)	107.97(18)	CL2	MN1	CL1	82.845(18)
B(4)	B(3)	B(1)	59.62(14)	CL3	MN1	CL1	84.416(18)
B(7)	B(3)	B(1)	107.92(17)	O(1)	MN2	O(2)	87.23(6)
B(1)	B(4)	B(3)	60.68(14)	O(1)	MN2	CL2	87.50(4)
B(1)	B(4)	B(2)	59.30(14)	O(2)	MN2	CL2	87.90(5)

Atom 1	Atom 2	Atom 3	Angle / °	Atom 1	Atom 2	Atom 3	Angle / °
B(3)	B(4)	B(2)	107.56(16)	O(1)	MN2	CL3#2	91.46(4)
B(1)	B(4)	B(9)	107.49(17)	O(2)	MN2	CL3#2	86.87(5)
B(3)	B(4)	B(9)	107.42(18)	CL2	MN2	CL3#2	174.70(2)
B(2)	B(4)	B(9)	59.80(14)	O(1)	MN2	CL1#2	92.74(5)
B(1)	B(4)	B(8)	107.98(17)	O(2)	MN2	CL1#2	175.17(5)
B(3)	B(4)	B(8)	59.62(14)	CL2	MN2	CL1#2	96.93(2)
B(2)	B(4)	B(8)	107.23(18)	CL3#2	MN2	CL1#2	88.305(19)
B(9)	B(4)	B(8)	59.63(15)	O(1)	MN2	CL1	172.75(4)
C(1)	B(5)	C(2)	57.72(12)	O(2)	MN2	CL1	96.49(5)
C(1)	B(5)	B(6)	104.33(16)	CL2	MN2	CL1	86.431(18)
C(2)	B(5)	B(6)	58.92(13)	CL3#2	MN2	CL1	94.941(19)
C(1)	B(5)	B(10)	104.68(16)	CL1#2	MN2	CL1	84.075(18)
C(2)	B(5)	B(10)	106.46(15)				

STRUCTURE REPORT for Compound 3

Crystallographer: F. Engelhardt
ID code: FE0004
Compound: $[FeCl_2\{(C2B10H10)C(NiPr)(NHiPr)\}][Li(DME)_2]$(**3**)
Formula sum: $C_{21}H_{55}B_{10}Cl_2FeLiN_2O_6$
Formula moieties: $C_9H_{25}B_{10}N_2FeCl_2$, $C_{12}H_{30}O_6Li$

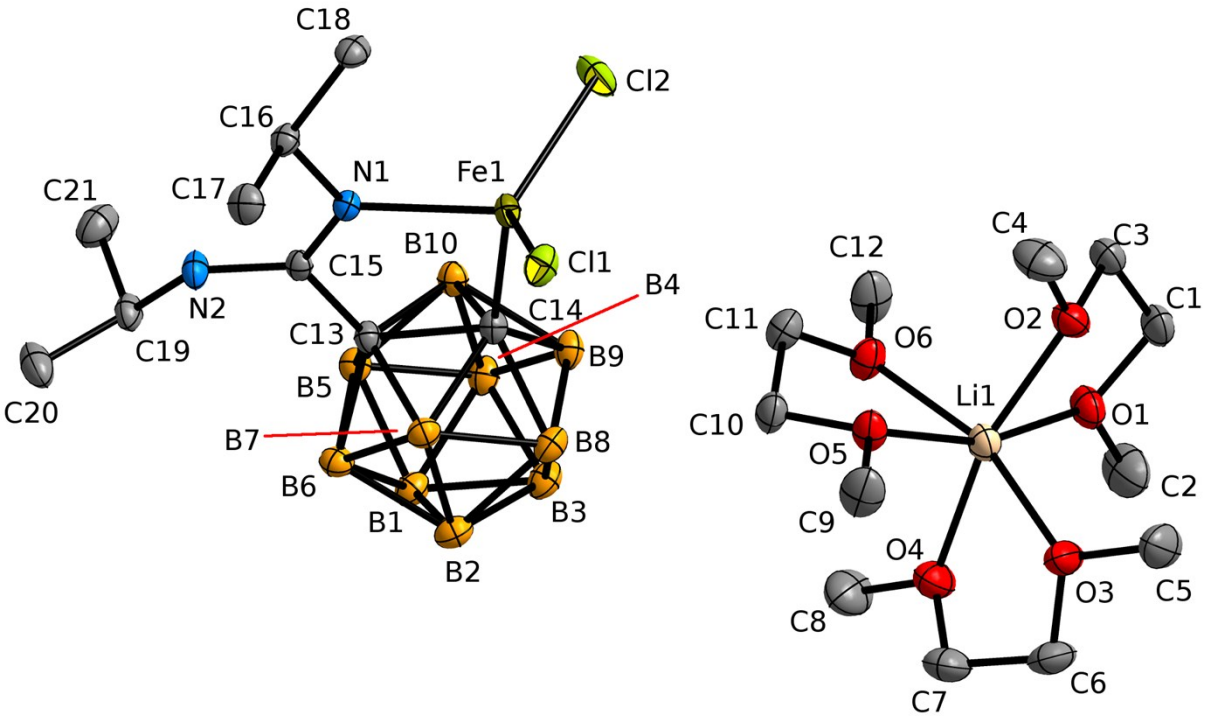

Figure S2. Molecular structure of **3** in the crystal. Anisotropic displacement parameters are shown at the 50% probability level, H atoms omitted for clarity.

Table S5. Crystallographic Data and Details on Structure Refinement for Compound **3**.

formula sum	$C_{21}H_{55}B_{10}Cl_2N_2O_6FeLi$
formula weight	673.46
crystal color / shape / size (mm)	orange block / 0.42 × 0.30 × 0.19
crystal system	monoclinic
space group	$P2_1/n$
unit cell parameters	
a (Å)	14.304(5)
b (Å)	15.457(4)
c (Å)	18.237(5)
α (deg)	90
β (deg)	110.13(2)
γ (deg)	90
unit cell volume V (Å^3)	3786(2)
molecules per cell z	4
crystallographic density ρ_{calcd} (g cm^{-3})	1.182
absorption coefficient μ (mm^{-1})	0.573
diffractometer	STOE IPDS 2T
radiation (λ [Å])	graphite-monochromated Mo-Kα (0.71073)
temperature (°C)	–173
scan type [S2]	ω scan (increment 1°, exposure 8 min)
completeness of dataset	97.2%
θ range of data collection (deg)	1.775 to 29.194
reflections collected	27045 ($-19 \le h \le 19$, $-21 \le k \le 17$, $-24 \le l \le 24$)
independent reflections	9728 (R_{int} = 0.0395)
independent reflections with $I>2\sigma(I)$	7588
structure solution method	dual-space algorithms (SHELXT- 2014/5) [S5]
refinement method	full-matrix least-squares on F^2 (SHELXL-2016/4) [S4]
absorption correction method	numerical
range of transmission factors	0.9771 to 0.9545
data / parameters / restraints	9728 / 431 / 738
goodness of fit (GooF) [all data]	0.950
final R values	
R_1 [all data, $I \ge 2\sigma(I)$]	0.0561, 0.0364
wR_2 [all data, $I \ge 2\sigma(I)$]]	0.0787, 0.0734
largest difference peak and hole	0.506 and –0.473 eÅ^{-3}

Refinement special details: None

[S5] G. M. Sheldrick, G. M. *Acta Cryst.* 2015, **A71**, 3–8.

Table S6. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (x 10^3) for Compound **3**.

Atom	x	y	z	U_{eq} / $Å^2$
C(13)	8232(1)	3030(1)	8142(1)	15(1)
C(14)	8189(1)	3929(1)	7604(1)	17(1)
C(15)	8679(1)	2263(1)	7849(1)	15(1)
C(16)	9354(1)	1708(1)	6908(1)	17(1)
C(17)	8477(1)	1219(1)	6344(1)	24(1)
C(18)	10009(1)	2073(1)	6478(1)	22(1)
C(19)	8595(1)	1187(1)	8902(1)	21(1)
C(20)	7966(2)	372(1)	8754(1)	33(1)
C(21)	9621(2)	1053(1)	9502(1)	33(1)
N(1)	8989(1)	2428(1)	7272(1)	14(1)
N(2)	8684(1)	1469(1)	8154(1)	21(1)
B(1)	7336(1)	3865(1)	9060(1)	21(1)
B(2)	6523(1)	3912(1)	8066(1)	22(1)
B(3)	7281(1)	4821(1)	8505(1)	23(1)
B(4)	8457(1)	4424(1)	9135(1)	20(1)
B(5)	8415(1)	3279(1)	9097(1)	18(1)
B(6)	7221(1)	2962(1)	8435(1)	19(1)
B(79	7117(1)	3364(1)	7490(1)	18(1)
B(8)	7149(1)	4502(1)	7539(1)	21(1)
B(9)	8322(1)	4814(1)	8187(1)	20(1)
B(10)	9021(1)	3866(1)	8544(1)	18(1)
Fe(1)	8862(1)	3667(1)	6787(1)	16(1)
Li(1)	3537(2)	2543(2)	4820(2)	24(1)
O(1)	2842(1)	1452(1)	4211(1)	29(1)
C(1)	2196(1)	1025(1)	4538(1)	31(1)
O(2)	2672(1)	2127(1)	5498(1)	27(1)
C(2)	3146(2)	891(1)	3719(1)	45(1)
Cl(2)	10301(1)	4444(1)	7099(1)	32(1)
O(3)	4869(1)	2030(1)	5599(1)	32(1)
Cl(1)	7816(1)	3561(1)	5532(1)	24(1)
C(3)	1832(1)	1675(1)	4986(1)	29(1)
O(4)	4507(1)	2631(1)	4151(1)	34(1)
C(4)	2419(2)	2641(1)	6047(1)	41(1)
C(8)	4380(2)	3128(1)	3467(1)	45(1)
C(7)	5502(1)	2634(1)	4675(1)	38(1)
O(6)	2521(1)	3351(1)	4028(1)	26(1)
C(6)	5617(1)	1932(1)	5259(1)	38(1)
O(5)	3812(1)	3765(1)	5412(1)	25(1)
C(5)	4944(2)	1399(1)	6179(1)	45(1)
C(9)	4666(2)	4004(1)	6048(1)	38(1)
C(10)	3477(1)	4442(1)	4855(1)	27(1)
C(12)	1662(2)	3141(1)	3380(1)	36(1)

C(11)	2466(1)	4201(1)	4307(1)	27(1)

Table S7. Interatomic Distances for Compound **3**.

Atom 1	Atom 2	d / Å	Atom 1	Atom 2	d / Å
Fe(1)	Cl(2)	2.280(1)	C(14)	B(7)	1.713(2)
Fe(1)	Cl(1)	2.269(1)	C(13)	B(5)	1.713(2)
Li(1)	O(5)	2.143(3)	C(13)	B(7)	1.709(2)
Li(1)	O(4)	2.143(3)	C(13)	B(6)	1.708(2)
Li(1)	O(2)	2.128(3)	C(13)	B(10)	1.706(2)
Li(1)	O(3)	2.101(3)	C(14)	B(9)	1.702(2)
N11	Fe(1)	2.090(1)	C(14)	B(8)	1.700(2)
Li(1)	O(6)	2.077(3)	C(13)	C(14)	1.690(2)
Li(1)	O(1)	2.074(3)	C(13)	C(15)	1.527(2)
C(14)	Fe(1)	2.073(1)	C(16)	C(18)	1.522(2)
B(3)	B(4)	1.789(3)	C(16)	C(17)	1.521(2)
B(6)	B(7)	1.789(2)	C(19)	C(20)	1.517(2)
B(2)	B(3)	1.788(3)	C(19)	C(21)	1.513(3)
B(5)	B(6)	1.788(3)	C(1)	C(3)	1.497(2)
B(1)	B(2)	1.787(3)	C(10)	C(11)	1.495(3)
B(5)	B(10)	1.787(2)	C(7)	C(6)	1.490(3)
B(1)	B(4)	1.786(2)	C161	N11	1.481(2)
B(3)	B(8)	1.778(2)	C191	N21	1.479(2)
B(4)	B(9)	1.778(2)	O(2)	C(3)	1.425(2)
B(1)	B(3)	1.777(2)	O(1)	C(1)	1.423(2)
B(4)	B(10)	1.777(2)	O(5)	C(10)	1.422(2)
B(2)	B(7)	1.776(2)	O(4)	C(8)	1.422(2)
B(2)	B(8)	1.775(2)	O(6)	C(11)	1.421(2)
B(3)	B(9)	1.775(2)	O(1)	C(2)	1.420(2)
B(1)	B(6)	1.774(2)	O(2)	C(4)	1.419(2)
B(2)	B(6)	1.772(2)	O(6)	C(12)	1.418(2)
B(1)	B(5)	1.771(2)	O(3)	C(6)	1.418(2)
B(4)	B(5)	1.771(2)	O(3)	C(5)	1.416(2)
B(9)	B(10)	1.767(2)	O(4)	C(7)	1.415(2)
B(7)	B(8)	1.761(2)	O(5)	C(9)	1.415(2)
B(8)	B(9)	1.755(3)	C(15)	N(2)	1.347(2)
C(14)	B(10)	1.719(2)	C(15)	N(1)	1.302(2)

Table S8. Interatomic Angles for Compound **3**.

Atom 1	Atom 2	Atom 3	Angle / °	Atom 1	Atom 2	Atom 3	Angle / °
C(15)	C(13)	C(14)	111.74(9)	C(13)	B(6)	B(1)	104.56(11)
C(15)	C(13)	B(10)	116.25(12)	B(2)	B(6)	B(1)	60.50(10)
C(14)	C(13)	B(10)	60.81(9)	C(13)	B(6)	B(7)	58.46(9)
C(15)	C(13)	B(6)	124.24(11)	B(2)	B(6)	B(7)	59.86(9)
C(14)	C(13)	B(6)	111.49(11)	B(1)	B(6)	B(7)	107.73(11)
B(10)	C(13)	B(6)	114.82(10)	C(13)	B(6)	B(5)	58.62(9)
C(15)	C(13)	B(7)	113.17(11)	B(2)	B(6)	B(5)	108.14(12)
C(14)	C(13)	B(7)	60.54(9)	B(1)	B(6)	B(5)	59.62(9)
B(10)	C(13)	B(7)	112.99(11)	B(7)	B(6)	B(5)	107.38(11)
B(6)	C(13)	B(7)	63.15(9)	C(13)	B(7)	C(14)	59.22(9)
C(15)	C(13)	B(5)	126.43(12)	C(13)	B(7)	B(8)	105.39(12)
C(14)	C(13)	B(5)	111.54(10)	C(14)	B(7)	B(8)	58.55(9)
B(10)	C(13)	B(5)	63.03(9)	C(13)	B(7)	B(2)	104.74(11)
B(6)	C(13)	B(5)	63.10(9)	C(14)	B(7)	B(2)	105.98(11)
B(7)	C(13)	B(5)	114.84(11)	B(8)	B(7)	B(2)	60.24(9)
C(13)	C(14)	B(8)	109.02(10)	C(13)	B(7)	B(6)	58.39(9)
C(13)	C(14)	B(9)	108.94(10)	C(14)	B(7)	B(6)	106.62(12)
B(8)	C(14)	B(9)	62.11(10)	B(8)	B(7)	B(6)	107.87(11)
C(13)	C(14)	B(7)	60.24(9)	B(2)	B(7)	B(6)	59.66(9)
B(8)	C(14)	B(7)	62.16(10)	C(14)	B(8)	B(9)	59.01(9)
B(9)	C(14)	B(7)	112.90(11)	C(14)	B(8)	B(7)	59.29(9)
C(13)	C(14)	B(10)	60.04(8)	B(9)	B(8)	B(7)	108.06(12)
B(8)	C(14)	B(10)	112.89(10)	C(14)	B(8)	B(2)	106.61(11)
B(9)	C(14)	B(10)	62.20(9)	B(9)	B(8)	B(2)	108.66(12)
B(7)	C(14)	B(10)	112.07(10)	B(7)	B(8)	B(2)	60.30(9)
C(13)	C(14)	Fe(1)	108.91(8)	C(14)	B(8)	B(3)	106.49(12)
B(8)	C(14)	Fe(1)	131.48(9)	B(9)	B(8)	B(3)	60.36(10)
B(9)	C(14)	Fe(1)	128.71(9)	B(7)	B(8)	B(3)	108.63(11)
B(7)	C(14)	Fe(1)	115.49(9)	B(2)	B(8)	B(3)	60.44(9)
B(10)	C(14)	Fe(1)	111.80(9)	C(14)	B(9)	B(8)	58.88(9)
N(1)	C(15)	N(2)	123.95(12)	C(14)	B(9)	B(10)	59.37(9)
N(1)	C(15)	C(13)	115.54(11)	B(8)	B(9)	B(10)	107.98(12)
N(2)	C(15)	C(13)	120.40(11)	C(14)	B(9)	B(3)	106.45(12)
N(1)	C(16)	C(17)	109.98(12)	B(8)	B(9)	B(3)	60.44(10)
N(1)	C(16)	C(18)	109.00(11)	B(10)	B(9)	B(3)	108.52(11)
C(17)	C(16)	C(18)	110.26(12)	C(14)	B(9)	B(4)	106.64(11)
N(2)	C(19)	C(21)	109.76(12)	B(8)	B(9)	B(4)	108.73(12)
N(2)	C(19)	C(20)	108.27(13)	B(10)	B(9)	B(4)	60.20(9)
C(21)	C(19)	C(20)	112.55(14)	B(3)	B(9)	B(4)	60.46(10)
C(15)	N(1)	C(16)	119.06(11)	C(13)	B(10)	C(14)	59.15(9)
C(15)	N(1)	Fe(1)	121.18(9)	C(13)	B(10)	B(9)	105.29(12)
C(16)	N(1)	Fe(1)	119.53(8)	C(14)	B(10)	B(9)	58.43(9)
C(15)	N(2)	C(19)	131.25(11)	C(13)	B(10)	B(4)	104.88(11)
B(5)	B(1)	B(6)	60.56(9)	C(14)	B(10)	B(4)	105.92(12)

Atom 1	Atom 2	Atom 3	Angle / °	Atom 1	Atom 2	Atom 3	Angle / °
B(5)	B(1)	B(3)	108.28(11)	B(9)	B(10)	B(4)	60.22(9)
B(6)	B(1)	B(3)	108.14(11)	C(13)	B(10)	B(5)	58.68(8)
B(5)	B(1)	B(4)	59.72(9)	C(14)	B(10)	B(5)	106.74(12)
B(6)	B(1)	B(4)	108.15(11)	B(9)	B(10)	B(5)	107.82(11)
B(3)	B(1)	B(4)	60.27(10)	B(4)	B(10)	B(5)	59.59(9)
B(5)	B(1)	B(2)	108.23(11)	C(14)	Fe(1)	N(1)	82.49(5)
B(6)	B(1)	B(2)	59.67(9)	C(14)	Fe(1)	Cl(1)	115.55(5)
B(3)	B(1)	B(2)	60.18(10)	N(1)	Fe(1)	Cl(1)	106.97(4)
B(4)	B(1)	B(2)	108.16(11)	C(14)	Fe(1)	Cl(2)	108.74(5)
B(6)	B(2)	B(8)	107.92(11)	N(1)	Fe(1)	Cl(2)	115.93(4)
B(6)	B(2)	B(7)	60.48(9)	Cl(1)	Fe(1)	Cl(2)	120.96(2)
B(8)	B(2)	B(7)	59.46(9)	O(1)	Li(1)	O(6)	91.38(13)
B(6)	B(2)	B(1)	59.83(9)	O(1)	Li(1)	O(3)	102.25(12)
B(8)	B(2)	B(1)	107.27(13)	O(6)	Li(1)	O(3)	162.16(15)
B(7)	B(2)	B(1)	107.70(12)	O(1)	Li(1)	O(2)	78.32(10)
B(6)	B(2)	B(3)	107.84(13)	O(6)	Li(1)	O(2)	100.24(13)
B(8)	B(2)	B(3)	59.82(9)	O(3)	Li(1)	O(2)	93.83(11)
B(7)	B(2)	B(3)	107.47(12)	O(1)	Li(1)	O(5)	163.02(15)
B(1)	B(2)	B(3)	59.65(10)	O(6)	Li(1)	O(5)	77.51(10)
B(9)	B(3)	B(8)	59.19(9)	O(3)	Li(1)	O(5)	91.43(12)
B(9)	B(3)	B(1)	107.61(12)	O(2)	Li(1)	O(5)	90.91(11)
B(8)	B(3)	B(1)	107.62(11)	O(1)	Li(1)	O(4)	91.82(11)
B(9)	B(3)	B(2)	107.17(11)	O(6)	Li(1)	O(4)	90.05(11)
B(8)	B(3)	B(2)	59.74(9)	O(3)	Li(1)	O(4)	78.19(11)
B(1)	B(3)	B(2)	60.17(10)	O(2)	Li(1)	O(4)	165.83(15)
B(9)	B(3)	B(4)	59.85(10)	O(5)	Li(1)	O(4)	100.88(12)
B(8)	B(3)	B(4)	107.26(11)	C(2)	O(1)	C(1)	111.42(13)
B(1)	B(3)	B(4)	60.07(10)	C(2)	O(1)	Li(1)	129.63(13)
B(2)	B(3)	B(4)	107.99(12)	C(1)	O(1)	Li(1)	114.50(12)
B(5)	B(4)	B(10)	60.45(8)	O(1)	C(1)	C(3)	108.27(13)
B(5)	B(4)	B(9)	107.99(10)	C(4)	O(2)	C(3)	112.00(13)
B(10)	B(4)	B(9)	59.58(9)	C(4)	O(2)	Li(1)	125.58(13)
B(5)	B(4)	B(1)	59.76(9)	C(3)	O(2)	Li(1)	107.20(12)
B(10)	B(4)	B(1)	107.54(11)	C(5)	O(3)	C(6)	112.23(14)
B(9)	B(4)	B(1)	107.17(13)	C(5)	O(3)	Li(1)	125.64(13)
B(5)	B(4)	B(3)	107.83(12)	C(6)	O(3)	Li(1)	112.94(13)
B(10)	B(4)	B(3)	107.41(11)	O(2)	C(3)	C(1)	108.25(14)
B(9)	B(4)	B(3)	59.69(10)	C(7)	O(4)	C(8)	112.67(14)
B(1)	B(4)	B(3)	59.67(10)	C(7)	O(4)	Li(1)	108.22(13)
C(13)	B(5)	B(4)	104.86(10)	C(8)	O(4)	Li(1)	128.39(14)
C(13)	B(5)	B(1)	104.46(12)	O(4)	C(7)	C(6)	108.55(15)
B(4)	B(5)	B(1)	60.52(9)	C(12)	O(6)	C(11)	111.82(13)
C(13)	B(5)	B(10)	58.29(8)	C(12)	O(6)	Li(1)	129.76(13)
B(4)	B(5)	B(10)	59.96(8)	C(11)	O(6)	Li(1)	114.74(12)
B(1)	B(5)	B(10)	107.76(11)	O(3)	C(6)	C(7)	108.65(15)
C(13)	B(5)	B(6)	58.28(9)	C(9)	O(5)	C(10)	112.10(13)

Atom 1	Atom 2	Atom 3	Angle / °	Atom 1	Atom 2	Atom 3	Angle / °
B(4)	B(5)	B(6)	108.19(12)	C(9)	O(5)	Li(1)	126.92(13)
B(1)	B(5)	B(6)	59.82(10)	C(10)	O(5)	Li(1)	109.28(12)
B(10)	B(5)	B(6)	107.02(11)	O(5)	C(10)	C(11)	107.78(13)
C(13)	B(6)	B(2)	104.94(11)	O(6)	C(11)	C(10)	108.06(13)

STRUCTURE REPORT for Compound 4

Crystallographer: F. Engelhardt
ID code: FE0019
Compound: $[Mo_2\{(C_2B_{10}H_{10})C(N^iPr)(NH^iPr)\}_2(COOCH_3)_2]$ (**4**)
Formula sum: $C_{19}H_{44}B_{10}N_2O_4Mo$
Formula moieties: $C_{22}H_{56}B_{20}N_4O_4Mo_2$, $4(C_4H_8O)$

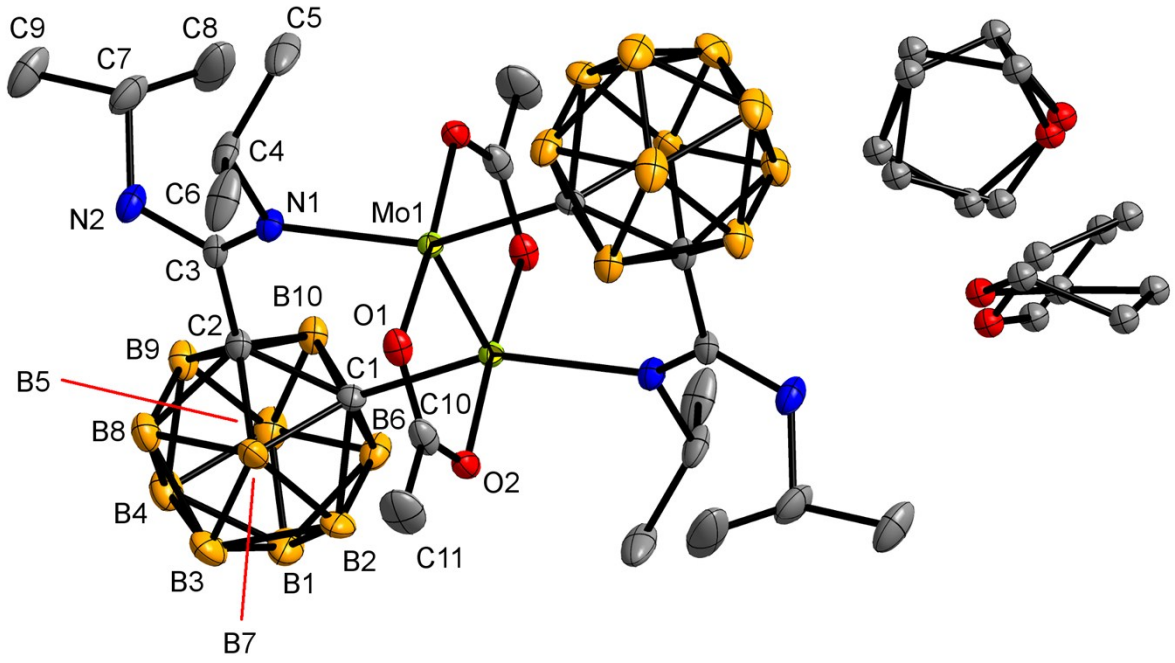

Figure S3. Molecular structure of **4** including disorder in the crystal, showing disorder of the two non-coordinated THF molecules. Anisotropic displacement parameters are shown at the 50% probability level. C and O atoms of disordered THF moieties are shown as spheres of arbitrary size. Only half of the molecule is contained within the asymmetric unit. The other half is generated by an inversion center lying on the midpoint of the Mo-Mo-bond.

Table S9. Crystallographic Data and Details on Structure Refinement for Compound **4**.

formula sum	$C_{19}H_{44}B_{10}N_2O_4Mo$
formula weight	568.60
crystal color / shape / size (mm)	colorless prisms / 0.27 × 0.15 × 0.12
crystal system	monoclinic
space group	$P2_1/n$
unit cell parameters	
a (Å)	9.4087(4)
b (Å)	17.8661(8)
c (Å)	16.6682(7)
α (deg)	90
β (deg)	93.737(3)
γ (deg)	90
unit cell volume V (Å^3)	2795.9(2)
molecules per cell z	4
crystallographic density ρ_{calcd} (g cm^{-3})	1.351
absorption coefficient μ (mm^{-1})	0.498
diffractometer	STOE IPDS 2T
radiation (λ [Å])	graphite-monochromated Mo-Kα (0.71073)
temperature (°C)	–173
scan type [S2]	ω scan (increment 1.5°, exposure 3 min)
completeness of dataset	100%
θ range of data collection (deg)	2.280 to 25.349
reflections collected	24078 (–11 ≤ h ≤ 11, –21 ≤ k ≤ 21, –20 ≤ l ≤ 20)
independent reflections	5122 (R_{int} = 0.0517)
independent reflections with I>2σ (I)	4037
structure solution method	dual-space algorithms (SHELXT 2014/5) [S5]
refinement method	full-matrix least-squares on F^2 (SHELXL 2016/4) [S4]
absorption correction method	none
range of transmission factors	–
data / parameters / restraints	5122 / 425 / 1090[a]
goodness of fit (GooF) [all data]	1.024
final R values	
R1 [all data, I ≥ 2σ (I)]	0.0514, 0.0358
wR2 [all data, I ≥ 2 σ (I)]]	0.0833, 0.0777
largest difference peak and hole	0.387 and –0.674 eÅ–3
Extinction coefficient	–

Refinement special details: The lattice solvent molecules (THF) are disordered over two positions. Refinement was stabilized by applying appropriate restraints (SAME, RIGU and SIMU) to the interatomic distances and the thermal displacement parameters.

Table S10. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (x 10^3) for Compound **4**.

Atom 1	x	y	z	U(eq)
B(1)	2849(4)	2242(2)	3256(2)	31(1)
N(1)	5396(2)	1133(1)	6110(1)	17(1)
O(1)	7489(2)	246(1)	5106(1)	20(1)
C(1)	3962(3)	1206(2)	4386(2)	16(1)
Mo(1)	5516(1)	1(1)	5568(1)	13(1)
B(2)	4260(4)	1607(2)	3475(2)	24(1)
N(2)	4263(3)	2242(2)	6490(2)	24(1)
O(2)	6397(2)	218(1)	3884(1)	19(1)
C(2)	4035(3)	1878(2)	5088(2)	17(1)
C(3)	4606(3)	1711(2)	5947(2)	17(1)
B(3)	4529(4)	2577(2)	3654(2)	30(1)
B(8)	4411(4)	2733(2)	4695(2)	24(1)
C(8)	2365(5)	1526(3)	7099(3)	60(1)
B(7)	5231(4)	1898(2)	4358(2)	22(1)
C(7)	3593(4)	2059(2)	7254(2)	34(1)
B(6)	2526(4)	1374(2)	3726(2)	23(1)
C(6)	7829(3)	1071(2)	6734(2)	40(1)
B(5)	1682(4)	2196(2)	4060(2)	27(1)
C(5)	5808(5)	520(2)	7457(2)	42(1)
C(4)	6271(3)	1138(2)	6897(2)	26(1)
B(4)	2932(4)	2945(2)	4012(2)	29(1)
B(9)	2651(4)	2507(2)	4935(2)	22(1)
C(9)	3142(4)	2789(2)	7626(2)	40(1)
B(10)	2410(3)	1531(2)	4770(2)	20(1)
C(10)	7517(3)	295(2)	4348(2)	22(1)
C(11)	8897(4)	462(2)	3995(2)	37(1)
O(1A)	589(12)	4262(6)	4328(5)	63(3)
C(1A)	536(7)	3998(4)	5130(3)	34(2)
C(2A)	1665(17)	3421(7)	5186(7)	39(3)
C(3A)	1430(20)	3018(7)	4402(8)	41(3)
C(4A)	760(20)	3608(7)	3832(7)	42(3)
O(1A')	660(20)	4142(10)	4237(10)	108(5)
C(1A')	1674(9)	4215(4)	4949(5)	39(2)
C(2A')	1470(20)	3479(7)	5326(9)	41(4)
C(3A')	1420(30)	2946(8)	4639(10)	38(4)
C(4A')	880(30)	3395(11)	3933(10)	64(5)
O(1B)	5833(12)	3916(7)	3835(8)	38(3)
C(1B)	6977(12)	4423(6)	4001(9)	39(3)
C(2B)	6746(11)	5014(5)	3381(6)	71(3)
C(3B)	5131(11)	5092(5)	3323(8)	73(3)
C(4B)	4630(13)	4330(6)	3507(9)	48(3)
O(1B')	6068(11)	3928(6)	3610(7)	37(3)

C(1B')	6619(13)	4545(7)	4070(11)	61(4)
C(2B')	5518(10)	5154(5)	4013(9)	79(3)
C(3B')	4185(10)	4741(6)	3808(7)	68(3)
C(4B')	4618(12)	4070(5)	3357(7)	41(3)

Table S11. Interatomic Distances for Compound **4**. Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1.

Atom 1	Atom 2	d / Å	Atom 1	Atom 2	d / Å
B(1)	B(2)	1.767(5)	B(8)	B(4)	1.780(5)
B(1)	B(6)	1.772(5)	B(8)	B(7)	1.787(5)
B(1)	B(4)	1.776(5)	C(8)	C(7)	1.505(5)
B(1)	B(3)	1.778(6)	C(7)	C(9)	1.518(4)
B(1)	B(5)	1.788(6)	B(6)	B(10)	1.772(5)
N(1)	C(3)	1.291(4)	B(6)	B(5)	1.776(5)
N(1)	C(4)	1.502(3)	C(6)	C(4)	1.514(5)
N(1)	Mo(1)	2.222(2)	B(5)	B(9)	1.758(5)
O(1)	C(10)	1.267(4)	B(5)	B(10)	1.782(5)
O(1)	Mo(1)	2.101(2)	B(5)	B(4)	1.786(5)
C(1)	C(2)	1.675(4)	C(5)	C(4)	1.528(5)
C(1)	B(6)	1.712(4)	B(4)	B(9)	1.761(5)
C(1)	B(2)	1.718(4)	B(9)	B(10)	1.779(5)
C(1)	B(7)	1.721(4)	C(10)	C(11)	1.490(4)
C(1)	B(10)	1.732(4)	O(1A)	C(1A)	1.421(9)
C(1)	Mo(1)#1	2.211(3)	O(1A)	C(4A)	1.447(10)
Mo(1)	Mo(1)#1	2.069(1)	C(1A)	C(2A)	1.478(11)
Mo(1)	O(2)#1	2.109(2)	C(2A)	C(3A)	1.495(10)
B(2)	B(7)	1.758(5)	C(3A)	C(4A)	1.526(10)
B(2)	B(6)	1.760(5)	O(1A')	C(4A')	1.446(12)
B(2)	B(3)	1.774(5)	O(1A')	C(1A')	1.478(13)
N(2)	C(3)	1.363(4)	C(1A')	C(2A')	1.475(12)
N(2)	C(7)	1.493(4)	C(2A')	C(3A')	1.487(12)
N(2)	H(2A)	0.976(18)	C(3A')	C(4A')	1.489(12)
O(2)	C(10)	1.273(4)	O(1B)	C(1B)	1.421(11)
C(2)	C(3)	1.526(4)	O(1B)	C(4B)	1.431(11)
C(2)	B(10)	1.702(4)	C(1B)	C(2B)	1.484(12)
C(2)	B(8)	1.708(4)	C(2B)	C(3B)	1.523(12)
C(2)	B(7)	1.711(4)	C(3B)	C(4B)	1.479(12)
C(2)	B(9)	1.727(4)	O(1B')	C(1B')	1.421(11)
B(3)	B(8)	1.768(5)	O(1B')	C(4B')	1.424(10)
B(3)	B(4)	1.778(5)	C(1B')	C(2B')	1.502(11)
B(3)	B(7)	1.785(5)	C(2B')	C(3B')	1.476(11)
B(8)	B(9)	1.775(5)	C(3B')	C(4B')	1.484(10)

Table S12. Interatomic Angles for Compound **4**. Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1

Atom 1	Atom 2	Atom 3	Angle / °	Atom 1	Atom 2	Atom 3	Angle / °
B(1)	B(2)	B(3)	60.3(2)	C(1)	B(2)	B(1)	106.7(2)
B(1)	B(3)	B(4)	59.9(2)	C(1)	B(2)	B(3)	106.8(2)
B(1)	B(3)	B(7)	107.3(3)	C(1)	B(2)	B(6)	58.95(18)
B(1)	B(4)	B(3)	60.0(2)	C(1)	B(2)	B(7)	59.34(18)
B(1)	B(4)	B(5)	60.3(2)	C(1)	B(6)	B(1)	106.7(2)
B(1)	B(4)	B(8)	107.4(3)	C(1)	B(6)	B(10)	59.58(17)
B(1)	B(6)	B(5)	60.5(2)	C(1)	B(6)	B(2)	59.29(18)
B(10)	B(5)	B(1)	107.4(2)	C(1)	B(6)	B(5)	107.1(2)
B(10)	B(5)	B(4)	107.7(2)	C(1)	B(7)	B(2)	59.17(18)
B(10)	B(6)	B(1)	108.6(2)	C(1)	B(7)	B(3)	106.2(3)
B(10)	B(6)	B(5)	60.31(19)	C(1)	B(7)	B(8)	106.1(2)
B(10)	C(1)	Mo(1)#1	120.30(18)	C(1)	C(2)	B(10)	61.69(17)
B(10)	C(2)	B(7)	113.9(2)	C(1)	C(2)	B(7)	61.10(17)
B(10)	C(2)	B(8)	114.2(2)	C(1)	C(2)	B(8)	111.9(2)
B(10)	C(2)	B(9)	62.49(18)	C(1)	C(2)	B(9)	111.6(2)
B(2)	B(1)	B(3)	60.1(2)	C(1)#1	Mo(1)	N(1)	152.92(9)
B(2)	B(1)	B(4)	108.0(3)	C(10)	O(1)	Mo(1)	117.11(18)
B(2)	B(1)	B(5)	107.8(2)	C(10)	O(2)	Mo(1)#1	116.89(18)
B(2)	B(1)	B(6)	59.7(2)	C(1A)	C(2A)	C(3A)	102.5(9)
B(2)	B(3)	B(1)	59.7(2)	C(1A)	O(1A)	C(4A)	106.3(8)
B(2)	B(3)	B(4)	107.6(3)	C(1A')	C(2A')	C(3A')	103.9(11)
B(2)	B(3)	B(7)	59.22(19)	C(1B)	C(2B)	C(3B)	102.1(8)
B(2)	B(6)	B(1)	60.0(2)	C(1B)	O(1B)	C(4B)	108.3(10)
B(2)	B(6)	B(10)	108.3(2)	C(1B')	O(1B')	C(4B')	109.3(9)
B(2)	B(6)	B(5)	108.6(3)	C(2)	B(10)	B(5)	105.2(2)
B(2)	B(7)	B(3)	60.1(2)	C(2)	B(10)	B(6)	104.6(2)
B(2)	B(7)	B(8)	107.4(3)	C(2)	B(10)	B(9)	59.45(18)
B(2)	C(1)	B(10)	112.1(2)	C(2)	B(10)	C(1)	58.39(17)
B(2)	C(1)	B(7)	61.49(19)	C(2)	B(7)	B(2)	105.0(2)
B(2)	C(1)	Mo(1)#1	112.91(18)	C(2)	B(7)	B(3)	104.5(2)
B(3)	B(1)	B(5)	108.1(3)	C(2)	B(7)	B(8)	58.42(18)
B(3)	B(4)	B(5)	108.1(3)	C(2)	B(7)	C(1)	58.43(16)
B(3)	B(4)	B(8)	59.6(2)	C(2)	B(8)	B(3)	105.3(2)
B(3)	B(7)	B(8)	59.4(2)	C(2)	B(8)	B(4)	105.3(2)
B(3)	B(8)	B(4)	60.1(2)	C(2)	B(8)	B(7)	58.56(18)
B(3)	B(8)	B(7)	60.3(2)	C(2)	B(8)	B(9)	59.42(18)
B(3)	B(8)	B(9)	107.7(3)	C(2)	B(9)	B(10)	58.06(17)
B(4)	B(1)	B(3)	60.1(2)	C(2)	B(9)	B(4)	105.3(2)
B(4)	B(1)	B(5)	60.1(2)	C(2)	B(9)	B(5)	105.2(2)
B(4)	B(3)	B(7)	108.4(3)	C(2)	B(9)	B(8)	58.36(18)
B(4)	B(5)	B(1)	59.6(2)	C(2)	C(1)	B(10)	59.92(17)
B(4)	B(8)	B(7)	108.2(3)	C(2)	C(1)	B(2)	108.4(2)
B(4)	B(9)	B(10)	109.0(2)	C(2)	C(1)	B(6)	108.5(2)

B(4)	B(9)	B(8)	60.5(2)	C(2)	C(1)	B(7)	60.47(18)
B(5)	B(9)	B(10)	60.50(19)	C(2)	C(1)	Mo(1)#1	132.48(17)
B(5)	B(9)	B(4)	61.0(2)	C(2A)	C(3A)	C(4A)	104.0(8)
B(5)	B(9)	B(8)	109.0(3)	C(2A')	C(1A')	O(1A')	99.6(10)
B(6)	B(1)	B(3)	107.7(2)	C(2A')	C(3A')	C(4A')	104.8(10)
B(6)	B(1)	B(4)	107.8(3)	C(2B')	C(3B')	C(4B')	105.3(8)
B(6)	B(1)	B(5)	59.8(2)	C(3)	C(2)	B(10)	118.4(2)
B(6)	B(10)	B(5)	59.96(19)	C(3)	C(2)	B(7)	117.7(2)
B(6)	B(10)	B(9)	106.9(2)	C(3)	C(2)	B(8)	117.7(2)
B(6)	B(2)	B(1)	60.3(2)	C(3)	C(2)	B(9)	118.8(2)
B(6)	B(2)	B(3)	108.4(3)	C(3)	C(2)	C(1)	120.8(2)
B(6)	B(5)	B(1)	59.6(2)	C(3)	N(1)	C(4)	117.0(2)
B(6)	B(5)	B(10)	59.73(19)	C(3)	N(1)	Mo(1)	133.35(19)
B(6)	B(5)	B(4)	107.2(3)	C(3)	N(2)	C(7)	123.0(3)
B(6)	C(1)	B(10)	61.92(18)	C(3B')	C(2B')	C(1B')	103.0(7)
B(6)	C(1)	B(2)	61.75(19)	C(4)	N(1)	Mo(1)	108.73(17)
B(6)	C(1)	B(7)	112.1(2)	C(4A')	O(1A')	C(1A')	105.4(11)
B(6)	C(1)	Mo(1)#1	111.01(18)	C(4B)	C(3B)	C(2B)	103.5(7)
B(7)	B(2)	B(1)	109.0(3)	C(6)	C(4)	C(5)	111.7(3)
B(7)	B(2)	B(3)	60.7(2)	C(8)	C(7)	C(9)	112.4(3)
B(7)	B(2)	B(6)	108.0(2)	Mo(1)#1	Mo(1)	C(1)#1	96.92(7)
B(7)	C(1)	B(10)	111.8(2)	Mo(1)#1	Mo(1)	N(1)	109.90(6)
B(7)	C(1)	Mo(1)#1	123.25(19)	Mo(1)#1	Mo(1)	O(1)	92.22(6)
B(7)	C(2)	B(9)	113.9(2)	Mo(1)#1	Mo(1)	O(2)#1	91.88(6)
B(8)	B(3)	B(1)	107.9(3)	N(1)	C(3)	C(2)	121.1(2)
B(8)	B(3)	B(2)	107.5(2)	N(1)	C(3)	N(2)	125.1(3)
B(8)	B(3)	B(4)	60.3(2)	N(1)	C(4)	C(5)	111.6(3)
B(8)	B(3)	B(7)	60.4(2)	N(1)	C(4)	C(6)	109.0(3)
B(8)	B(4)	B(5)	107.5(2)	N(2)	C(3)	C(2)	113.8(2)
B(8)	B(9)	B(10)	107.4(2)	N(2)	C(7)	C(8)	110.7(3)
B(8)	C(2)	B(7)	63.01(19)	N(2)	C(7)	C(9)	107.8(3)
B(8)	C(2)	B(9)	62.22(19)	O(1)	C(10)	C(11)	118.9(3)
B(9)	B(10)	B(5)	59.17(19)	O(1)	C(10)	O(2)	121.9(3)
B(9)	B(4)	B(1)	107.7(3)	O(1)	Mo(1)	C(1)#1	90.93(9)
B(9)	B(4)	B(3)	107.9(2)	O(1)	Mo(1)	N(1)	91.68(8)
B(9)	B(4)	B(5)	59.4(2)	O(1)	Mo(1)	O(2)#1	175.71(8)
B(9)	B(4)	B(8)	60.2(2)	O(1A)	C(1A)	C(2A)	102.8(7)
B(9)	B(5)	B(1)	107.3(3)	O(1A)	C(4A)	C(3A)	105.0(7)
B(9)	B(5)	B(10)	60.33(19)	O(1A')	C(4A')	C(3A')	105.6(10)
B(9)	B(5)	B(4)	59.6(2)	O(1B)	C(1B)	C(2B)	104.1(9)
B(9)	B(5)	B(6)	107.7(2)	O(1B)	C(4B)	C(3B)	107.5(9)
B(9)	B(8)	B(4)	59.4(2)	O(1B')	C(1B')	C(2B')	107.5(8)
B(9)	B(8)	B(7)	108.0(2)	O(1B')	C(4B')	C(3B')	106.5(8)
C(1)	B(10)	B(5)	106.0(2)	O(2)	C(10)	C(11)	119.2(3)
C(1)	B(10)	B(6)	58.50(18)	O(2)#1	Mo(1)	C(1)#1	89.86(9)
C(1)	B(10)	B(9)	106.5(2)	O(2)#1	Mo(1)	N(1)	85.71(8)

3. Computational Details

The effective bond order (EBO) [S6] was calculated on compound **4** and also on $[Mo_2Cl_8]^{4-}$ molecule. The calculations on $[Mo_2Cl_8]^{4-}$ system were performed imposing D_{4h} symmetry. Initially both systems were optimized employing the Amsterdam Density Functional (ADF) package. [S7] The scalar relativistic effects were incorporated through a two-component Hamiltonian with the zeroth-order regular approximation (ZORA). [S8, S9] The BP86 generalized gradient approximation exchange-correlation functional was used with the standard Slater-type orbital (STO) basis set and the triple-ξ quality double plus polarization function for all the atoms (TZ2P). [S10-S12] To accurately analyze systems containing transition metals, the correlation effects should be considered. In this context, the single-reference formalism cannot properly describe their electronic structure and a more accurate treatment is needed. The complete active space self-consistent field (CASSCF) approximation is a robust method frequently used to study properties of multireference systems. [S13, S14]
All the correlated calculations were performed employing the ORCA 4.4 program. [S15] The Stuttgart-Dresden effective core potential (ECP), def-SD, was used along with def2-TZVPP for Mo atom. [S16] This basis set def2-TZVPP was also employed for all the other atoms. The active space was selected in order to include the *d* orbitals from the metal and those with possible contributions of *p* orbitals oft he ligands. For both systems, a CAS(8,8)SCF was employed, including the bonding σ_{z^2}, $\pi_{d_{yz}}, \pi_{d_{xz}}$ and $\delta_{d_{x^2-y^2}}$ orbitals and their anti-bonding counterparts. The calculations were performed on their ground states and the fractional occupation numbers were obtained for the active orbitals. The EBO was determined using the equation S1, in which η_b and η_{ab} are the occupation numbers of the bonding and anti-bonding molecular pairs derived from the CASSCF wave function.

$$EBO = \sum(\eta_b - \eta_{ab})/2 \qquad \text{(S1)}$$

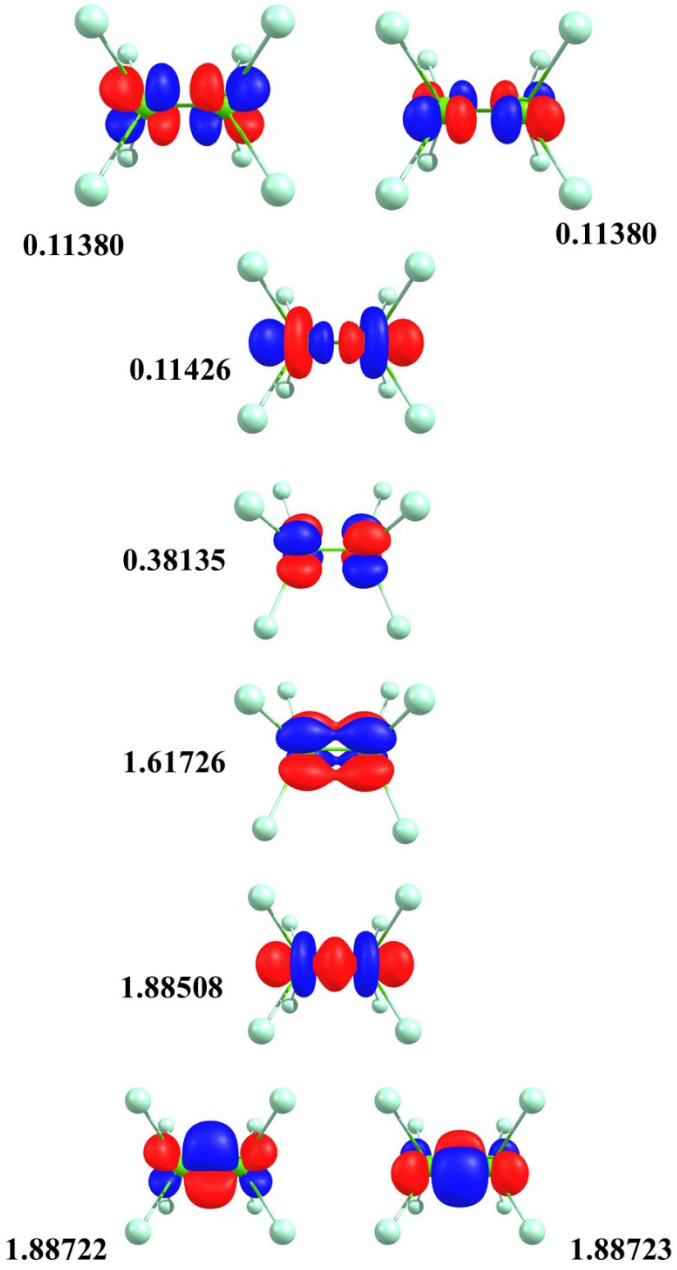

Figure S4. Molecular orbitals included in the active space obtained from the CAS(8,8)SCF calculation with their fractional occupations.

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