

Electronic Supporting Information

Hypervalent Zinc(I) Complexes with an *N,N',N'',N'''*-Macrocycle: C-H Bond Activation Across the Zinc(I)-Zinc(I) Bond

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Table of Contents

1. General Considerations	1
2. Experimental Procedures and Characterization Data.....	2
2.1. Synthesis of [(Me ₄ TACD)Zn–ZnCp*][BAr ^{Me} ₄] (1).....	2
2.2. Reaction of [Me ₄ TACDZn–ZnCp*][BAr ^{Me} ₄] (1) with Acetonitrile.....	5
2.3. Reaction of [Me ₄ TACDZn–ZnCp*][BAr ^{Me} ₄] (1) with Phenylacetylene	9
2.4. Synthesis of [(Me ₄ TACD)Zn–Zn(Me ₄ TACD)][BAr ^{Me} ₄] (4)	13
3. X-ray Crystallography	16
4. Density Functional Theory Calculations.....	19
5. References.....	24

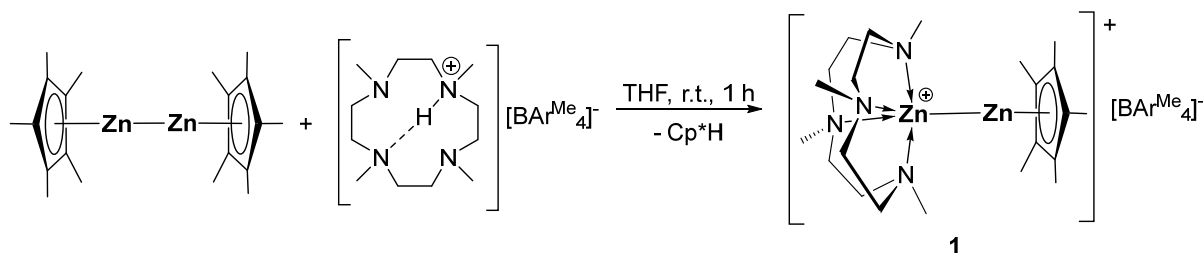
1. General Considerations

All operations were carried out under an inert atmosphere of dry argon using standard Schlenk and glovebox techniques. Glassware was dried in an oven at 130 °C and flame dried under vacuum before use. THF and THF-*d*₈, were distilled under argon from sodium/benzophenone ketyl. *n*-Pentane and *n*-hexane were dried over sodium chunks and distilled under vacuum before use. Hydrogen (99.999%) was purchased from Praxair-Westfalen AG. Solvents used for Schlenk line

operations were vacuum distilled directly into Teflon valve-sealed storage ampoules containing freshly activated 3 Å molecular sieves. All solvents were degassed before use. ZnH_2 ,^{S1} Zn_2Cp^*_2 ,^{S2} ($\text{Cp}^* = \text{C}_5\text{Me}_5$), $[\text{Et}_3\text{NH}][\text{B}(\text{C}_6\text{H}_3-3,5-\text{Me}_2)_4]$,^{S3} $[(\text{Me}_4\text{TACD})\text{H}][\text{B}(\text{C}_6\text{H}_3-3,5-\text{Me}_2)_4]$,^{S3} were prepared according to literature procedures. NMR spectra were recorded on a Bruker Avance II 400 or Bruker Avance III HD 400 NMR spectrometer at 298 K. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to residual solvent signals and reported relative to tetramethylsilane. ^{11}B NMR spectra were referenced externally to $\text{BF}_3(\text{OEt}_2)$. Solid-state IR spectra were in powder form using Shimadzu IR Spirit spectrometer fitted with a Single Reflection ATR accessory. Elemental analysis was performed on an Elementar vario EL instrument.

2. Experimental Procedures and Characterization Data

2.1. Synthesis of $[(\text{Me}_4\text{TACD})\text{Zn}-\text{ZnCp}^*][\text{BAr}^{\text{Me}}_4]$ (**1**)



A solution of $[(\text{Me}_4\text{TACD})\text{H}]^+[\text{BAr}^{\text{Me}}_4]^-$ (200 mg, 0.302 mmol) in THF (10 mL) was added to a Schlenk flask charged with $\text{Zn}_2(\text{C}_5\text{Me}_5)_2$ (133.1 mg, 0.332 mmol) at room temperature and was stirred rapidly for one hours to give colorless reaction mixture. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. Addition of *n*-hexane resulted in the precipitation of a colorless solid. The supernatant was decanted off, the residue was washed with *n*-hexane (2 x 5 ml) and dried *in vacuo* to obtain compound **1** as a colorless solid. yield: 252 mg (0.272 mmol), 90% (based on $[(\text{Me}_4\text{TACD})\text{H}]^+$). Colorless single crystals suitable for X-ray diffraction analysis were obtained by diffusing *n*-pentane to a saturated solution of **1** in THF at $-35\text{ }^\circ\text{C}$. Compound **1** is stable in the solid state at room temperature.

Anal. calcd for $\text{C}_{54}\text{H}_{79}\text{BN}_4\text{Zn}_2$: C, 70.06; H, 8.60; N, 6.05%. Found: C, 70.45; H, 8.90; N, 5.98%.

^1H NMR (400 MHz, THF- d_8 , 299 K) δ 7.00 (br, 8H, 2,6- C_6H_3), 6.38 (s, 4H, 4- C_6H_3), 2.31 – 2.26 (m, br, 8H, NCH_2), 2.21 – 2.14 (m, br, 8H, NCH_2), 2.11 (s, 24H, Ar- CH_3), 2.10 (s, br, 12H, NCH_3), 2.02 (s, 15H, C_5Me_5) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, THF- d_8 , 299 K) δ 165.7 (q, $^1J_{\text{C-B}} = 49.1$ Hz, *ipso*- $\text{C}_6\text{H}_3\text{Me}_2$), 135.2 (q, $^2J_{\text{C-B}} = 1.5$ Hz, *ortho*- $\text{C}_6\text{H}_3\text{Me}_2$), 132.8 (q, $^3J_{\text{C-B}} = 2.8$ Hz, *meta*- $\text{C}_6\text{H}_3\text{Me}_2$), 123.4 (*para*- $\text{C}_6\text{H}_3\text{Me}_2$), 108.4 (C_5Me_5), 53.4 (NCH_2), 45.6 (Ar- CH_3), 22.2 ($\text{C}_6\text{H}_3(\text{CH}_3)_2$), 10.5 (C_5Me_5) ppm.

^{11}B NMR (128 MHz, THF- d_8 , 299 K) δ -7.00 ppm.

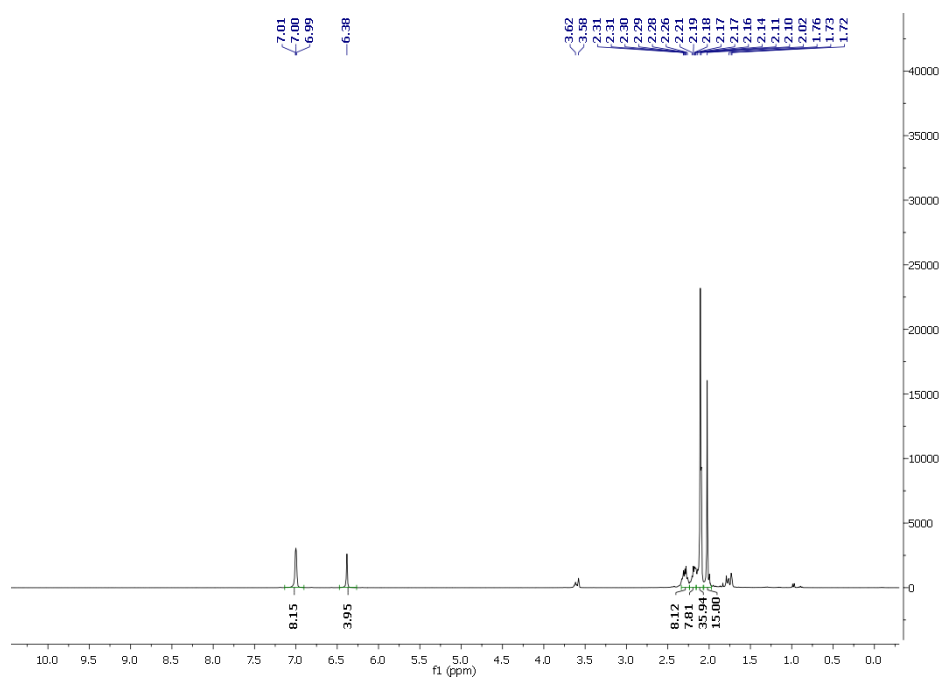


Figure S1. ^1H NMR spectrum (400 MHz, THF- d_8) of compound **1**.

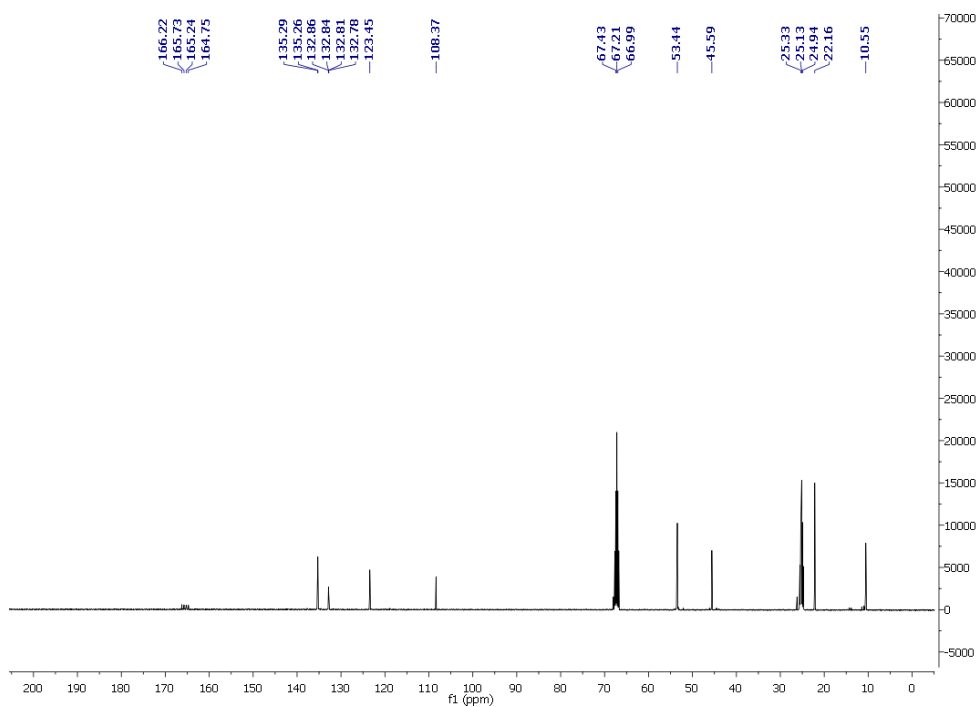


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, $\text{THF-}d_8$) of compound **1**.

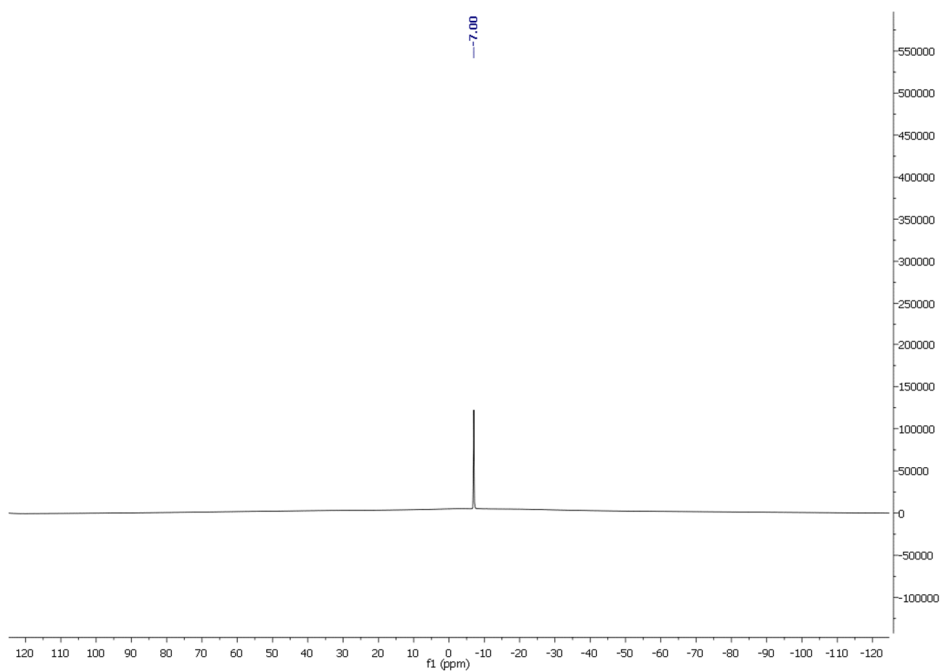


Figure S3. ^{11}B NMR spectrum (128 MHz, $\text{THF-}d_8$) of compound **1**.

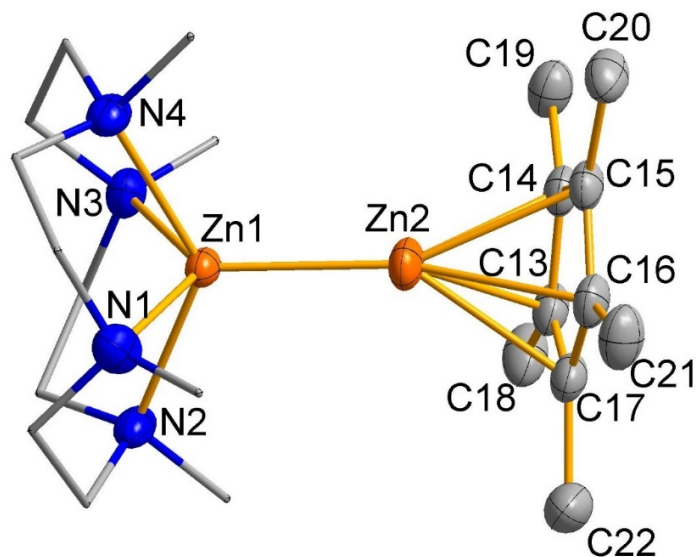
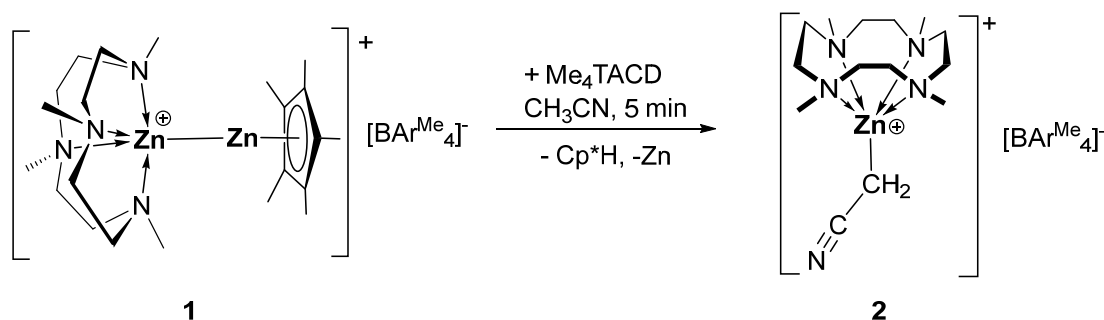


Figure S4. Cationic part of the molecular structure of compound **1**. The anion $[\text{BAr}^{\text{Me}}_4]^-$ and all H atoms are omitted for clarity. Displacement parameters of the Zn and N atoms, as well as of the C atoms of the Cp* ligand are shown with 50% probability; each carbon atom of the methylene unit of the ligand Me₄TACD is shown with one split position. Selected interatomic distances [Å] and angles [°]: Zn1–Zn2 2.3510(3), Zn1–N1 2.2388(17), Zn1–N2 2.2177(15), Zn1–N3 2.2550(15), Zn1–N4 2.2181(15), Zn1–C13 2.3484(18), Zn1–C14 2.3168(18), Zn1–C15 2.2779(17), Zn1–C16 2.2889(18), Zn1–C17 2.3275(18); N1–Zn1–N2 80.40(6), N1–Zn1–N3 130.33(6), N1–Zn1–N4 79.98(6), N1–Zn1–Zn2 115.79(4), N2–Zn1–Zn2 112.12(4), N3–Zn1–Zn2 113.83(4), N4–Zn1–Zn2 117.99(4).

2.2. Reaction of $[\text{Me}_4\text{TACDZn–ZnCp}^*][\text{BAr}^{\text{Me}}_4]$ (**1**) with Acetonitrile



To a Schlenk flask charged with **1** (100 mg, 0.108 mmol), CH₃CN (5 mL, 3.915 g, 95 mmol) and 10 mol% of Me₄TACD was added at room temperature and rapidly stirred for 5 min to give a colorless reaction mixture along with a grey precipitate of zinc metal. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. Addition of diethyl ether resulted in the precipitation of an off-white solid. The supernatant was decanted off, the residue was washed with

diethyl ether (2 x 5 mL) and dried *in vacuo* to give compound **2** as an off-white solid (70 mg, 0.091 mmol); yield: 85% (based on the [(Me₄TACD)Zn] unit in **1**). Single crystals suitable for X-ray diffraction analysis were obtained by diffusing diethyl ether to a saturated solution of **2** in CH₃CN at -35 °C. Compound **2** is stable in the solid state at room temperature.

Anal. calcd for C₄₆H₆₆BN₅Zn: C, 72.20; H, 8.69; N, 9.15%. Found: C, 72.28; H, 8.88; N, 9.10%.

¹H NMR (400 MHz, THF-*d*₈, 299 K) δ 7.01 (br, 8H, 2,6-C₆H₃), 6.38 (s, 4H, 4-C₆H₃), 2.43–2.31 (m, br, 16H, NCH₂), 2.35 (s, 12H, NCH₃), 2.10 (s, 24H, Ar-CH₃), 0.52 (s, 2H, CH₂CN) ppm.

¹³C {¹H} NMR (101 MHz, THF-*d*₈, 299 K) δ 165.7 (q, ¹J_{C-B} = 49.1 Hz, *ipso*-C₆H₃Me₂), 135.3 (q, ²J_{C-B} = 1.5 Hz, *ortho*-C₆H₃Me₂), 132.9 (q, ³J_{C-B} = 2.8 Hz, *meta*-C₆H₃Me₂), 123.5 (*para*-C₆H₃Me₂), 53.6 (NCH₂), 44.3 (Ar-CH₃) 22.1 (C₆H₃(CH₃)₂), -14.3 (CH₂CN) ppm.

¹¹B NMR (128 MHz, THF-*d*₈, 299 K) δ -6.99 ppm.

ATIR: ν = 2193 cm⁻¹ (C≡N)

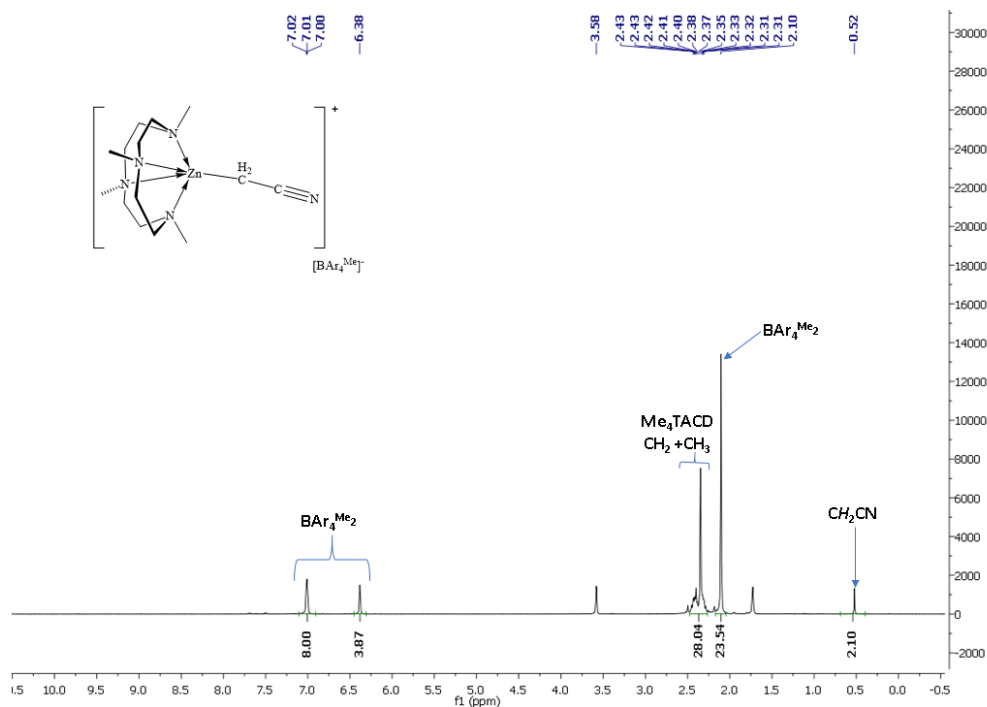


Figure S5. ¹H NMR spectrum (400 MHz, THF-*d*₈) of compound **2**.

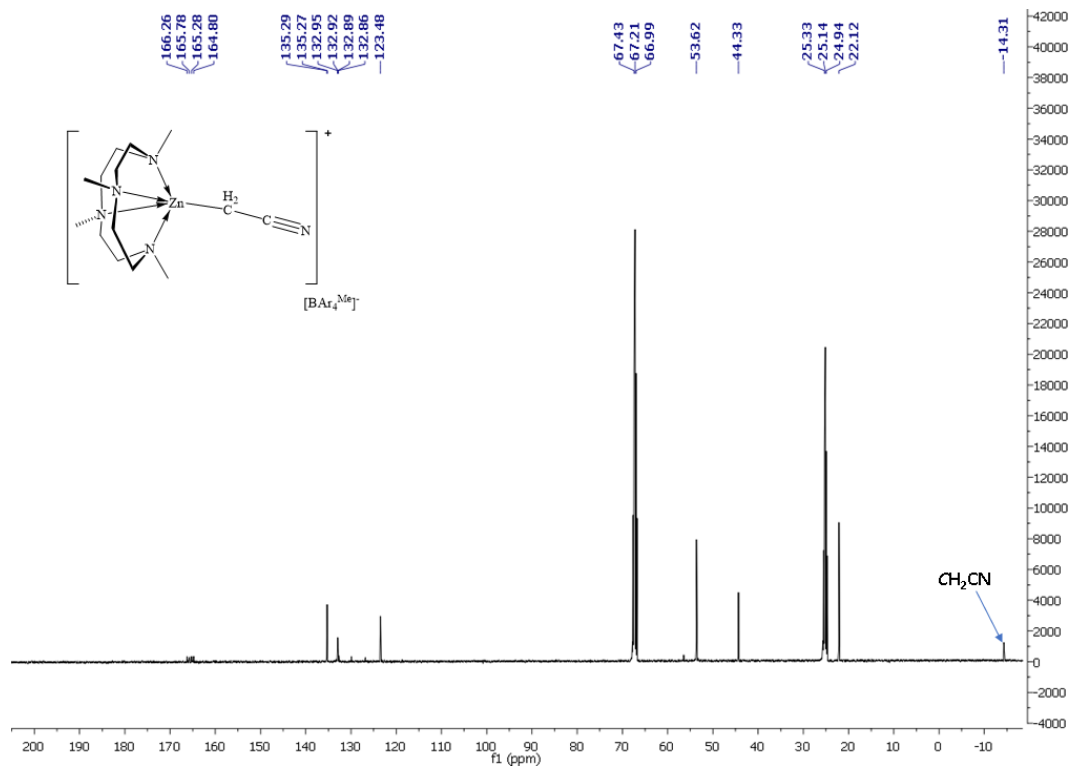


Figure S6. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, THF- d_8) of compound **2**.

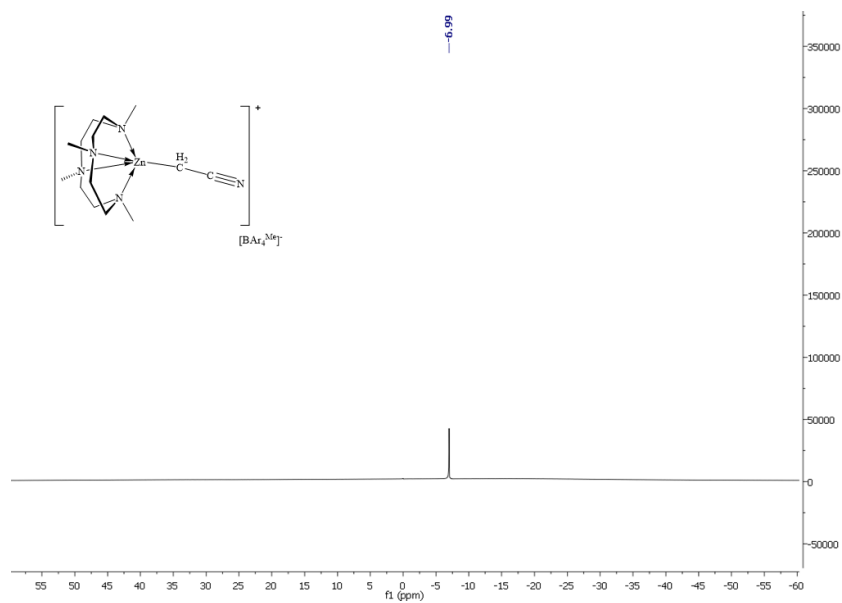


Figure S7. ^{11}B NMR spectrum (128 MHz, THF- d_8) of compound **2**.

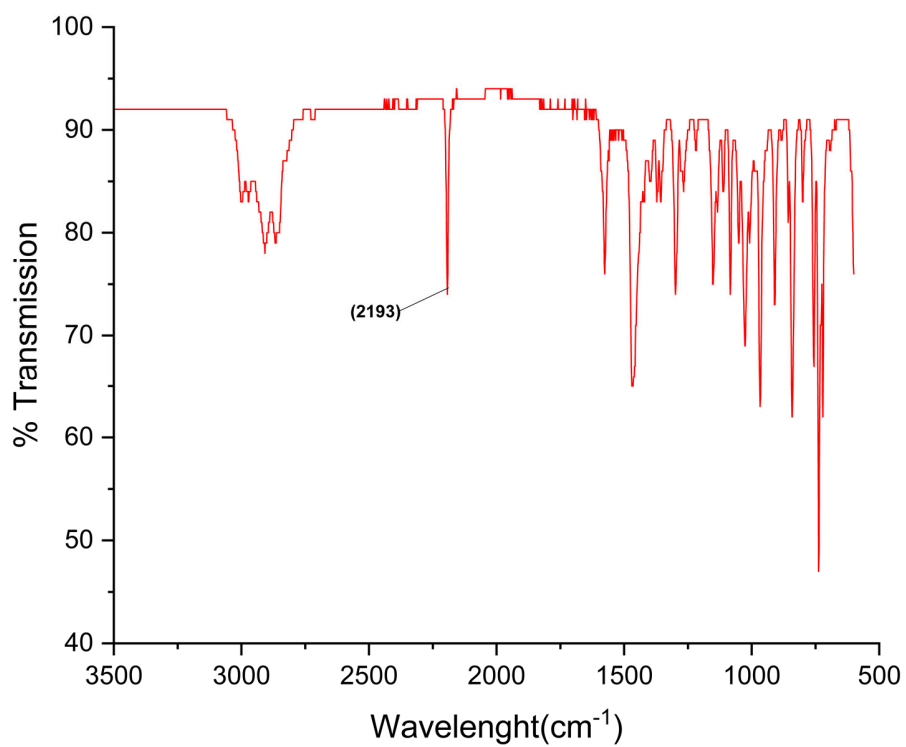


Figure S8. ATIR spectrum of compound **2**.

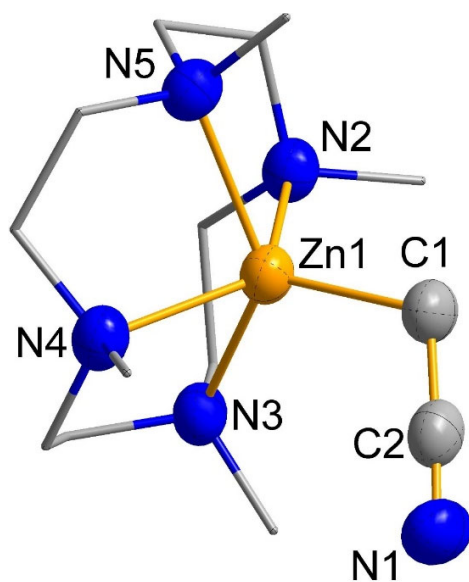
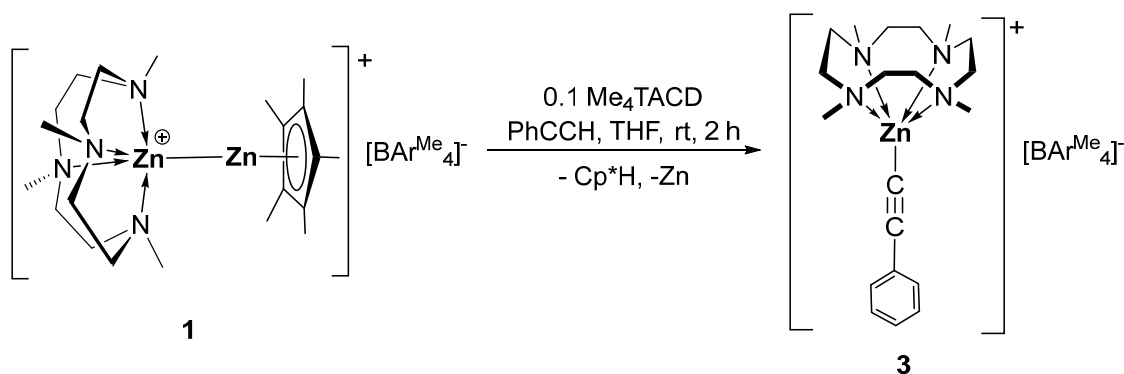


Figure S9. Cationic part of the molecular structure of compound **2**. The anion [BAr^{Me}₄]⁻ and all H atoms are omitted for clarity. Displacement parameters of the Zn and N atoms, as well as the carbon atoms of the

CH₂CN ligand are shown at 50% probability; Selected interatomic distances [Å] and angles [°]: Zn1–N2 2.180(2), Zn1–N3 2.191(2), Zn1–N4 2.194(2), Zn1–N5 2.234(2), Zn1–C1 2.025(3); N2–Zn1–N3 80.47(9), N2–Zn1–N4 132.30(9), N2–Zn1–N5 80.50(9), N2–Zn1–C1 113.36(11), N3–Zn1–C1 116.93(11), N4–Zn1–C1 114.25(11), N5–Zn1–C1 110.33(11), Zn1–C1–C2 114.1(2).

2.3. Reaction of [Me₄TACDZn–ZnCp*][BAr^{Me}₄] (1) with Phenylacetylene



To a Schlenk flask charged with **1** (100 mg, 0.102 mmol), phenylacetylene (12.1 mg, 0.112 mmol) and 10 mol% of Me₄TACD was added at room temperature and stirred rapidly for 2 h to give a colorless reaction mixture along with some grey ppt of zinc metal. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. Addition of diethyl ether resulted in the precipitation of an off-white solid. The supernatant was decanted off, the residue was washed with diethyl ether (2 x 5 mL) and dried *in vacuo* to give compound **3** as an off-white solid (80 mg, 0.097 mmol); yield: 90% (based on the [(Me₄TACD)Zn] unit in **1**). Single crystals suitable for X-ray diffraction analysis were obtained by diffusing THF to a saturated solution of **3** in CH₂Cl₂ at -35 °C. Compound **3** is stable in the solid state at room temperature.

Anal. calcd for C₅₂H₆₉BN₄Zn: C, 75.58; H, 8.42; N, 6.72%. Found: C, 75.40; H, 8.50; N, 6.76%.

¹H NMR (400 MHz, THF-*d*₈, 299 K) δ 7.23–7.26 (m, 2H, *Ph*), 7.12–7.18 (m, 3H, *Ph*), 7.02 (br, 8H, 2,6-*C*₆*H*₃), 6.38 (s, 4H, 4-*C*₆*H*₃), 2.45–2.33 (m, br, 16H, NCH₂), 2.42 (s, 12H, NCH₃), 2.10 (s, 24H, Ar-CH₃) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{THF-}d_8$, 299 K) δ 165.7 (q, $^1J_{\text{C-B}} = 49.1$ Hz, *ipso*- $\text{C}_6\text{H}_3\text{Me}_2$), 135.3 (*ortho*- $\text{C}_6\text{H}_3\text{Me}_2$), 132.8 (q, $^3J_{\text{C-B}} = 2.8$ Hz, *meta*- $\text{C}_6\text{H}_3\text{Me}_2$), 132.0, 128.4, 127.5, 126.8 (*Ph*) 123.4 (*para*- $\text{C}_6\text{H}_3\text{Me}_2$), 109.0, 107.8 ($\text{C}\equiv\text{C}$), 53.5 (NCH_2), 44.6 (Ar-CH_3) 22.1 ($\text{C}_6\text{H}_3(\text{CH}_3)_2$) ppm.

^{11}B NMR (128 MHz, $\text{THF-}d_8$, 299 K) δ -6.97 ppm.

ATIR: $\nu = 1575, 1470$ cm^{-1} ($\text{C}=\text{C}$).

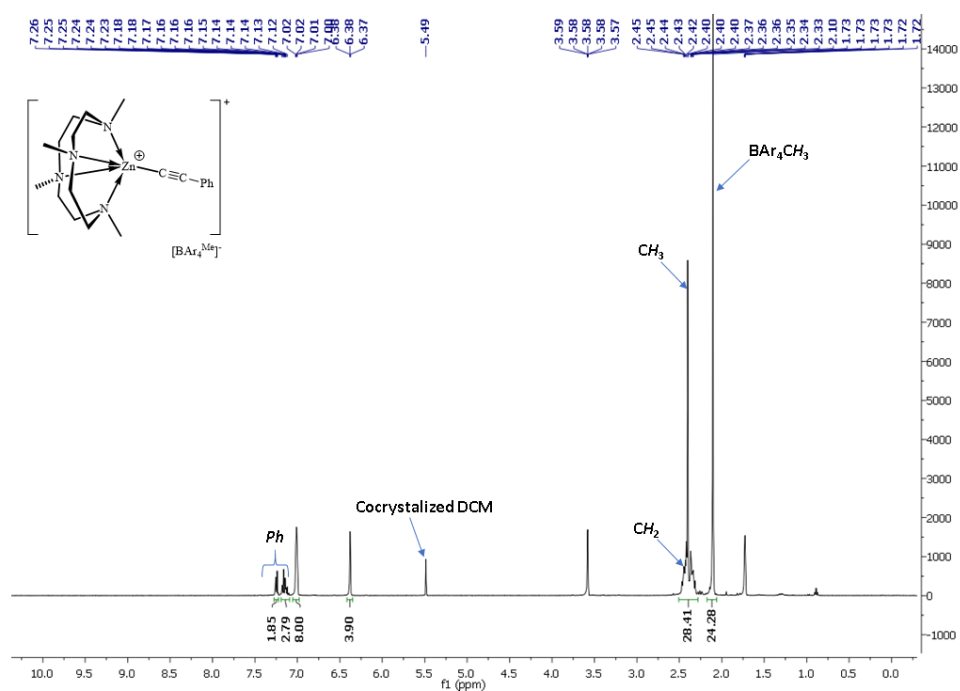


Figure S10. ^1H NMR spectrum (400 MHz, $\text{THF-}d_8$) of compound **3**.

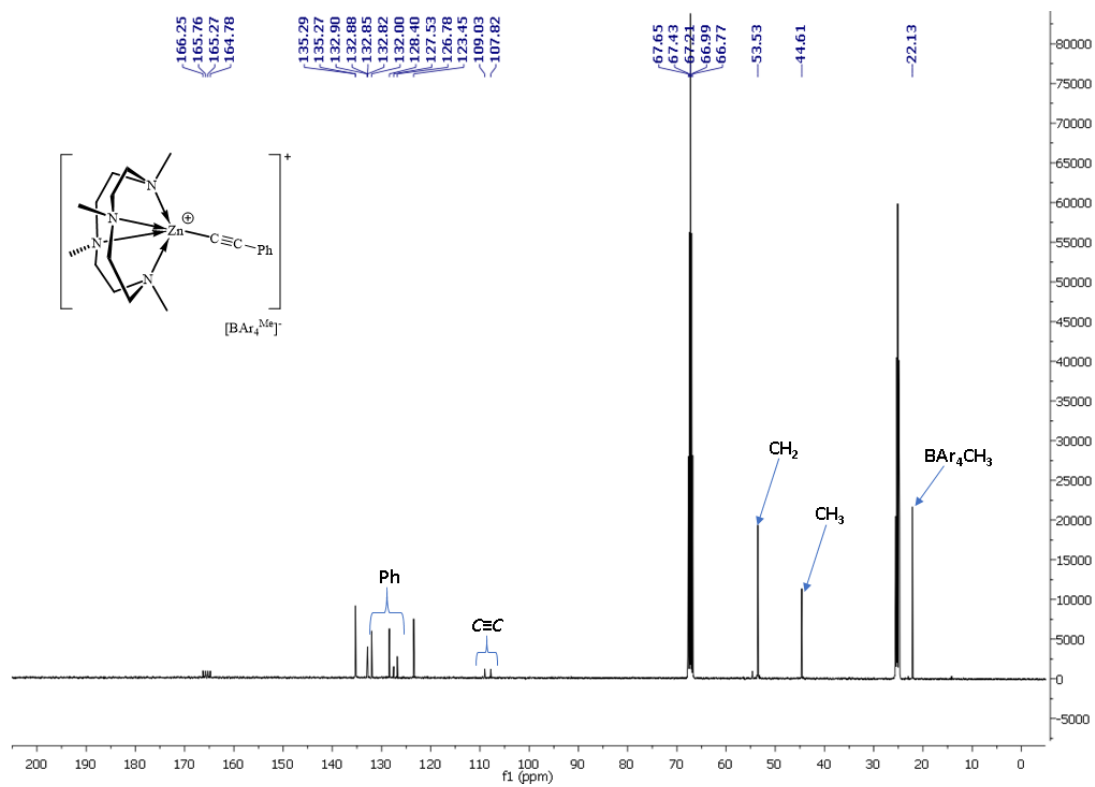


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, $\text{THF}-d_8$) of compound 3.

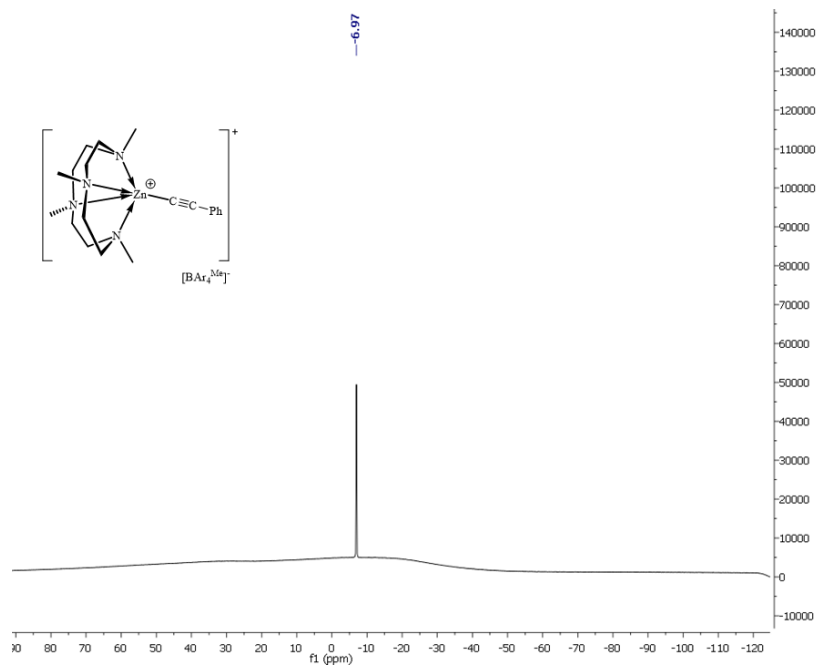


Figure S12. ^{11}B NMR spectrum (128 MHz, $\text{THF}-d_8$) of compound 3.

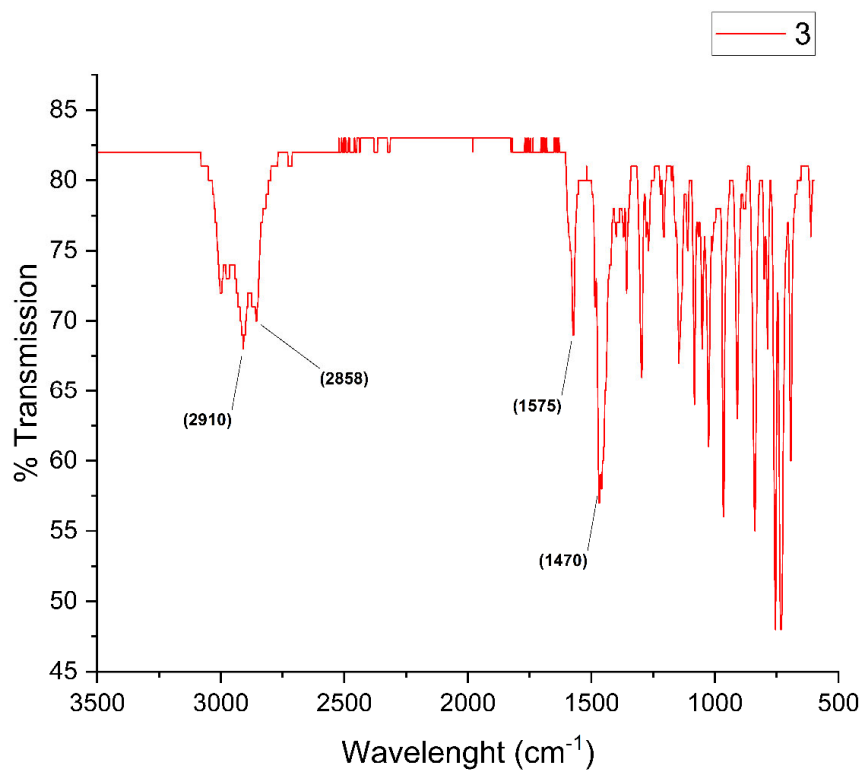


Figure S13. AT IR spectrum of compound **3**.

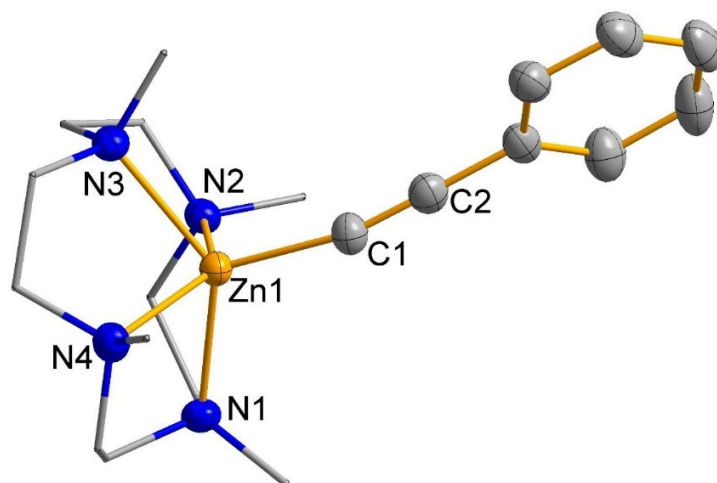
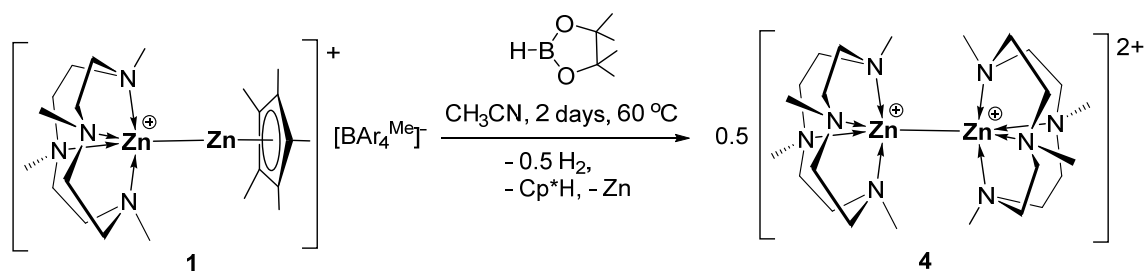


Figure S14. Cationic part of the molecular structure of compound **3**. The anion part $[\text{BAr}^{\text{Me}}_4]$ and all H atoms are omitted for clarity. Displacement parameters of the Zn and N atoms, as well as the carbon atoms

of the phenylacetylide ligand are shown at 50% probability; Selected interatomic distances [\AA] and angles [$^\circ$]: Zn1–N1 2.2217(14), Zn1–N2 2.1983 (14), Zn1–N3 2.2026(14), Zn1–N4 2.1846(14), Zn1–C1 1.9534(17); N1–Zn1–N2 80.38(5), N1–Zn1–N3 132.90(5), N1–Zn1–N4 80.77(6), N1–Zn1–C1 116.51(6), N2–Zn1–C1 108.33(6), N3–Zn1–C1 110.41(6), N4–Zn1–C1 118.50(6), Zn1–C1–C2 166.01(16).

2.4. Synthesis of $[(\text{Me}_4\text{TACD})\text{Zn}–\text{Zn}(\text{Me}_4\text{TACD})][\text{BAr}^{\text{Me}}_4]$ (**4**)



A solution of **1** (100 mg, 0.108 mmol) in CH_3CN (5 mL) was added to a Schlenk flask charged with HBpin (68 mg, 0.54 mmol) at room temperature and the reaction mixture was heated at 60°C for 2 days to give a colorless reaction mixture with grey precipitate of zinc metal. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. Addition of *n*-hexane resulted in the precipitation of a colorless solid. The supernatant was decanted off, the residue was washed with *n*-hexane (2 x 5 ml) and dried *in vacuo* to obtain compound **4** as a colorless solid; yield: 46 mg (0.32mmol), 30%. Colorless single crystals suitable for X-ray diffraction analysis were obtained by diffusing diethyl ether to a saturated solution of **4** in CH_3CN at -35°C . Compound **4** is stable in the solid state at room temperature.

Anal. calcd for $\text{C}_{88}\text{H}_{126}\text{B}_2\text{N}_8\text{Zn}_2$: C, 72.97; H, 8.77; N, 7.74%. Found: C, 71.88; H, 7.98; N, 7.90%.

^1H NMR (400 MHz, $\text{THF}-d_8$, 299 K) δ 6.99 (br, 16H, 2,6- C_6H_3), 6.38 (s, 8H, 4- C_6H_3), 2.43 – 2.51 (m, br, 16H, NCH_2), 2.33 – 2.39 (m, br, 16H, NCH_2), 2.20 (s, br, 24 H, NCH_3), 2.10 (s, 48 H, Ar- CH_3) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{THF}-d_8$, 299 K) δ 165.7 (q, $^1J_{\text{C-B}} = 49.1$ Hz, *ipso*- $\text{C}_6\text{H}_3\text{Me}_2$), 135.3 (q, $^2J_{\text{C-B}} = 1.5$ Hz, *ortho*- $\text{C}_6\text{H}_3\text{Me}_2$), 132.8 (q, $^3J_{\text{C-B}} = 2.8$ Hz, *meta*- $\text{C}_6\text{H}_3\text{Me}_2$), 123.4 (*para*- $\text{C}_6\text{H}_3\text{Me}_2$), 53.7 (NCH_2), 44.6 (Ar- CH_3) 22.1 ($\text{C}_6\text{H}_3(\text{CH}_3)_2$) ppm.

^{11}B NMR (128 MHz, $\text{THF}-d_8$, 299 K) δ -7.00 ppm.

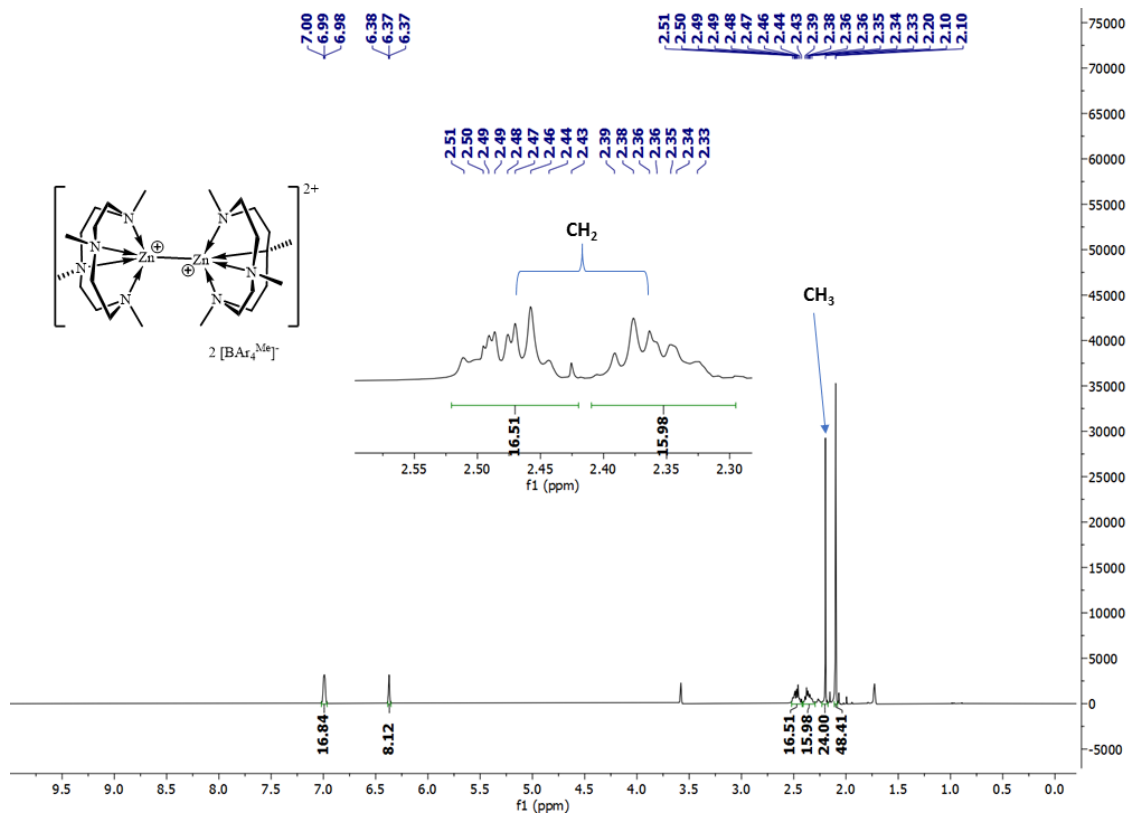


Figure S15. ^1H NMR spectrum (400 MHz, $\text{THF-}d_8$) of compound 4.

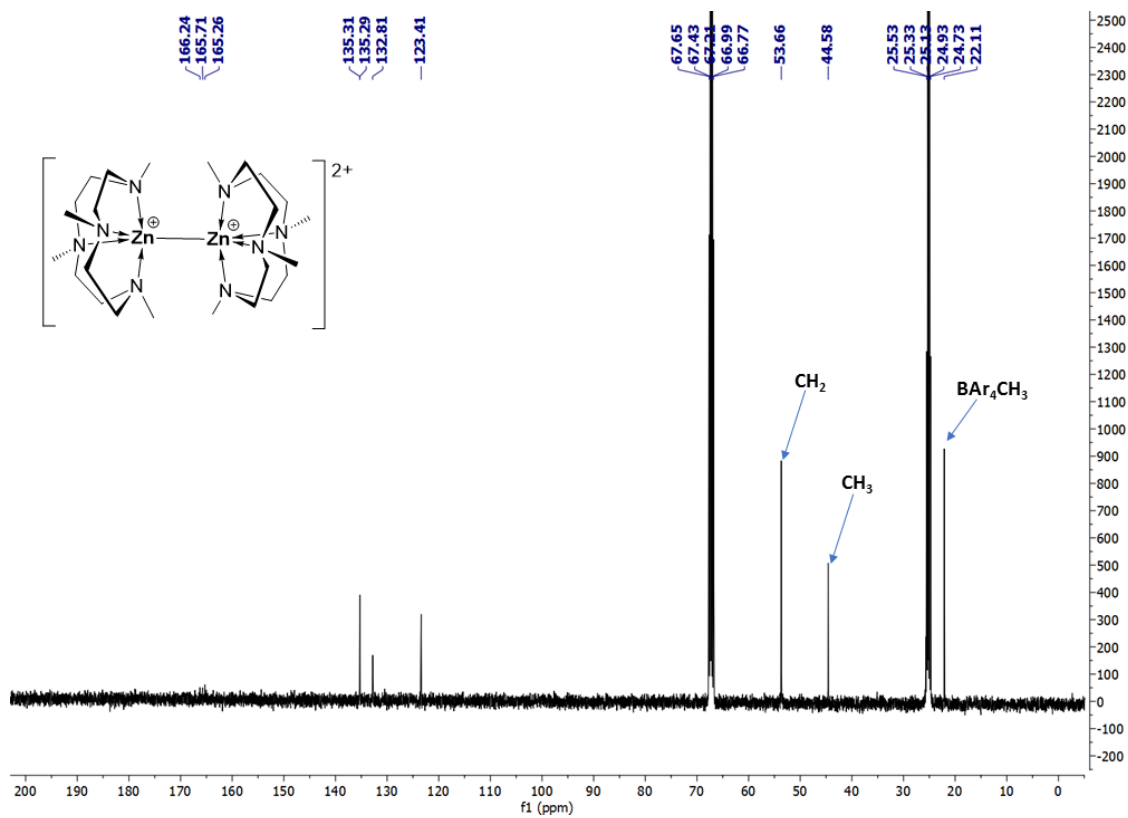


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, THF- d_8) of compound 4.

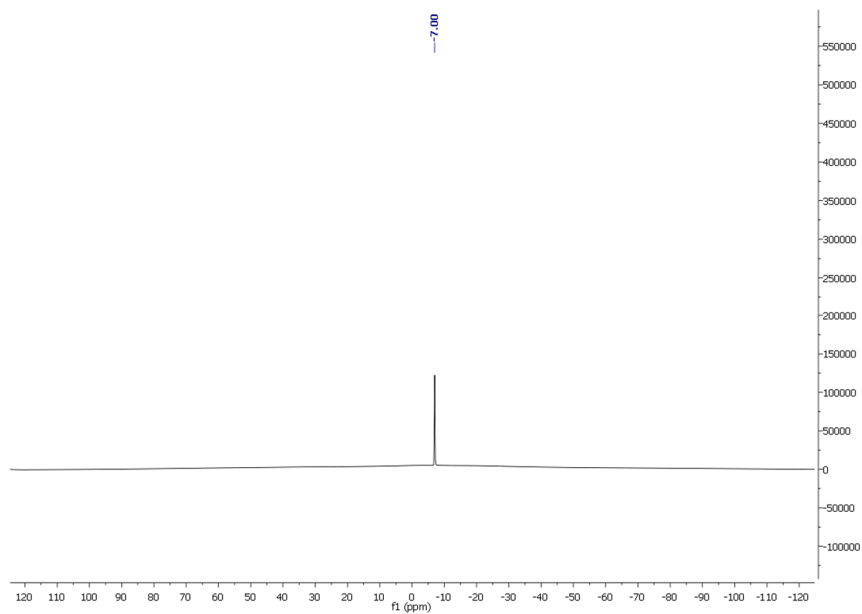


Figure S17. ^{11}B NMR spectrum (128 MHz, THF- d_8) of compound 4.

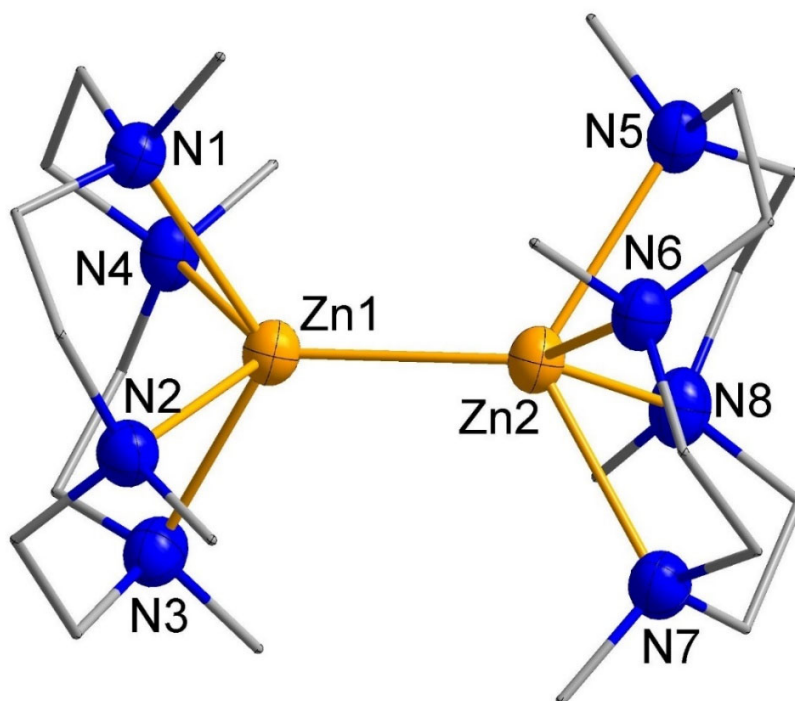


Figure S18. Cationic part of the molecular structure of compound **4**. The anion [BAr^{Me}₄] and all H atoms are omitted for clarity. Displacement parameters of the Zn and N atoms are shown at 50% probability; Selected interatomic distances [Å] and angles [°]: Zn1–N1 2.378(3), Zn1–N2 2.337(3), Zn1–N3 2.390(3), Zn1–N4 2.326(3), Zn1–Zn2 2.4860(6), Zn2–N5 2.480(3), Zn2–N6 2.291(3), Zn2–N7 2.463(3), Zn2–N8 2.278(3); N1–Zn1–N2 76.31(11), N1–Zn1–N3 120.82(11), N1–Zn1–N4 75.92(11), N1–Zn1–Zn2 120.99(8), N2–Zn1–Zn2 119.19(8), N3–Zn1–Zn2 118.18(8), N4–Zn1–Zn2 119.86(8).

3. X-ray Crystallography

X-ray diffraction data of **1-4** were collected at 100 K on a Eulerian 4-circle diffractometer STOE STADIVARI in ω -scan mode with Cu-K α radiation. All structures were solved by intrinsic phasing using SHELXT^{S4} and all refinements were carried out against F^2 with SHELXL^{S5} as implemented in the program system Olex2.^{S6} All crystals contain co-crystallized solvent molecules in the lattice (**1**: acetonitrile and n-pentane; **2**: acetonitrile; **3**: THF; **4**: acetonitrile and diethyl ether). In the refinement of **1**, positional disorder was resolved for the CH₂ groups of the Me₄TACD ligand,

affecting the carbon atoms C1–C8. Distance restraints as well as similarity restraints for the displacement parameters were used in the refinement of the Me₄TACD ligand. All atoms C59–C63 of the co-crystallized and disordered molecule pentane were refined with split positions. The atoms N7, C57 C58 of a co-crystallized acetonitrile molecule are disordered around a center of inversion at Wyckoff position *2a*. In **3**, the solvent molecule THF is also found disordered around an inversion center at Wyckoff position *2a*. In **4**, co-crystallized molecules of diethyl ether (involving atom positions O2–O4 and C105–C116) and acetonitrile (involving atoms N14 and C103, C104) are disordered. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions with isotropic displacement parameters.

Refinement results are given in Table S1. Graphical representations were performed with the program DIAMOND.^{S7} CCDC-2378377 (**1**), CCDC-2378378 (**2**), CCDC-2378379 (**3**), and CCDC-2378380 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data of **1-4**.

	1	2	3	4
formula	C ₁₂₄ H ₁₉₁ B ₂ N ₁₁ Zn ₄	C ₅₀ H ₇₂ BN ₇ Zn	C ₁₀₈ H ₁₄₆ B ₂ N ₈ OZn ₂	C ₂₁₈ H ₃₃₉ B ₄ N ₂₇ O ₅ Zn ₄
moiety formula	2(C ₃₂ H ₃₆ B), 2(C ₂₂ H ₄₃ N ₄ Zn ₂), 3(C ₂ H ₃ N), 2(C ₅ H ₁₂)	C ₃₂ H ₃₆ B, C ₁₄ H ₃₀ N ₅ Zn, 2(C ₂ H ₃ N)	2(C ₃₂ H ₃₆ B), 2(C ₂₀ H ₃₃ N ₄ Zn), C ₄ H ₈ O	4(C ₃₂ H ₃₆ B), 2(C ₂₄ H ₅₆ N ₈ Zn ₂), 5(C ₄ H ₁₀ O), 11(C ₂ H ₃ N)
<i>F</i> _w / g mol ⁻¹	2118.97	847.32	1724.68	3722.86
cryst. color, habit	colorless, block	colorless, needle	yellow, block	colorless, block
crystal size / mm	0.22 × 0.27 × 0.35	0.05 × 0.15 × 0.35	0.09 × 0.10 × 0.25	0.14 × 0.16 × 0.20
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> ₂₁ / <i>n</i>	<i>P</i> ₂₁ / <i>n</i>	<i>P</i> ₂₁ / <i>c</i>	<i>Pbca</i>
<i>a</i> /Å	12.5774(2)	9.1732(17)	11.617(2)	24.2793(3)
<i>b</i> /Å	14.25140(10)	21.9001(4)	23.399(3)	19.2350(5)

$c/\text{\AA}$	34.1633(5)	23.9707(5)	18.517(3)	47.6175(10)
$\beta/^\circ$	98.0970(10)	98.7183(15)	105.899(14)	90
$V/\text{\AA}^3$	6062.57(14)	4731.15(16)	4840.9(13)	22238.0(8)
Z	2	4	2	4
d_{calc} / $\text{Mg}\cdot\text{m}^{-3}$	1.161	1.190	1.183	1.112
$\mu(\text{CuK}\alpha)$ / mm^{-1}	1.267	1.022	0.998	0.923
$F(000)$	2284	1824	1856	8064
θ range / $^\circ$	4.72, 71.08	2.75, 64.98	3.96, 70.87	2.60, 70.86
index ranges	$-15 \leq h \leq 15,$ $-13 \leq k \leq 17,$ $-35 \leq l \leq 41$	$-10 \leq h \leq 8,$ $-21 \leq k \leq 25,$ $-28 \leq l \leq 27$	$-14 \leq h \leq 14,$ $-28 \leq k \leq 21,$ $-22 \leq l \leq 16$	$-29 \leq h \leq 23,$ $-20 \leq k \leq 23,$ $-51 \leq l \leq 58$
refln.	98964	63205	58053	270691
independent reflections [R_{int}, R_σ]	11668 [$R_{\text{int}} = 0.0146,$ $R_\sigma = 0.0064$]	8046 [$R_{\text{int}} = 0.0617$ $R_\sigma = 0.0340$]	9198 [$R_{\text{int}} = 0.0433,$ $R_\sigma = 0.0335$]	21322 [$R_{\text{int}} = 0.0716,$ $R_\sigma = 0.0293$]
observed reflections [$I > 2\sigma(I)$]	11331	6061	7236	15720
data/ restr./ param.	11668/253/787	8046/0/546	9198/0/580	21322/110/1280
$R1, wR2$ [$I > 2\sigma(I)$]	0.0400, 0.1155	0.0521, 0.1390	0.0336, 0.0849	0.0762, 0.2227
$R1, wR2$ (all data)	0.0407, 0.1161	0.0698, 0.1505	0.0460, 0.0893	0.1009, 0.2496
GooF on F^2	1.043	1.026	0.980	1.021
largest diff. peak, hole / $\text{e}\cdot\text{\AA}^{-3}$	0.98, -0.63	0.48, -0.33	0.43, -0.36	1.34, -0.64
CCDC Number	2378377	2378378	2378379	2378380

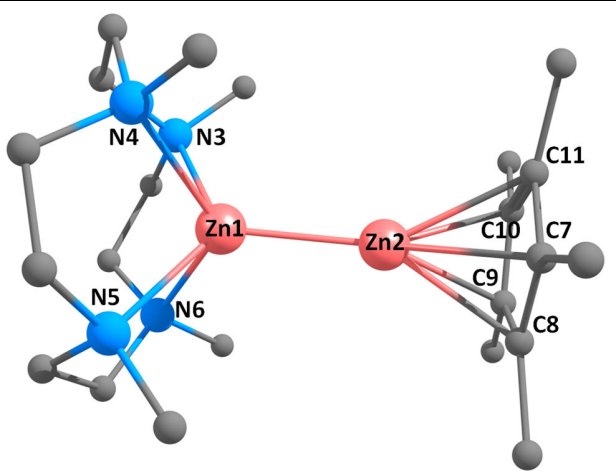
4. Density Functional Theory Calculations

Computational details

All DFT calculations were performed using the Gaussian09 suite of programs.^{S8} A hybrid DFT functional (B3PW91) along with SDD basis sets with additional polarization functions for Zn atoms and 6-31G** basis sets for the rest of the atoms was employed for the computation.^{S9-S10} Dispersion corrections were included in our calculations by employing the D3 version of Grimme's dispersion with Becke-Johnson damping.^{S11} To account for solvation effects, an SMD model using tetrahydrofuran solvent has been included in the calculations.^{S12}

Table S2. Comparison of bond distances (Å) between selected atoms obtained from DFT optimization and experimentally by X-ray diffraction for complex **1**.

Atom Labels	DFT		X-ray
	No dispersion	Dispersion	
Zn1-Zn2	2.36	2.32	2.35
Zn1-N3	2.33	2.27	2.24
Zn1-N4	2.34	2.28	2.22
Zn1-N5	2.34	2.28	2.25
Zn1-N6	2.34	2.27	2.22
Zn2-C7	2.29	2.35	2.35
Zn2-C8	2.29	2.30	2.32
Zn2-C9	2.28	2.23	2.28
Zn2-C10	2.29	2.23	2.29
Zn2-C11	2.29	2.30	2.33



The figure shows the molecular structure of complex 1. It features two zinc atoms, Zn1 and Zn2, coordinated to a bidentate nitrogen ligand (N3, N4, N5, N6) and a terdentate carbon ligand (C7, C8, C9, C10, C11). The Zn1 atom is coordinated to N3, N4, and N5. The Zn2 atom is coordinated to N6, C7, C8, C9, and C10. The Zn1-Zn2 distance is 2.35 Å. The Zn1-N3, Zn1-N4, Zn1-N5, Zn1-N6, Zn2-C7, Zn2-C8, Zn2-C9, Zn2-C10, and Zn2-C11 distances are also indicated in the table.

Table 3. Computed MOs for complex **1** (dispersion). (a) HOMO-2 (b) HOMO-1 (c) HOMO (d) LUMO.

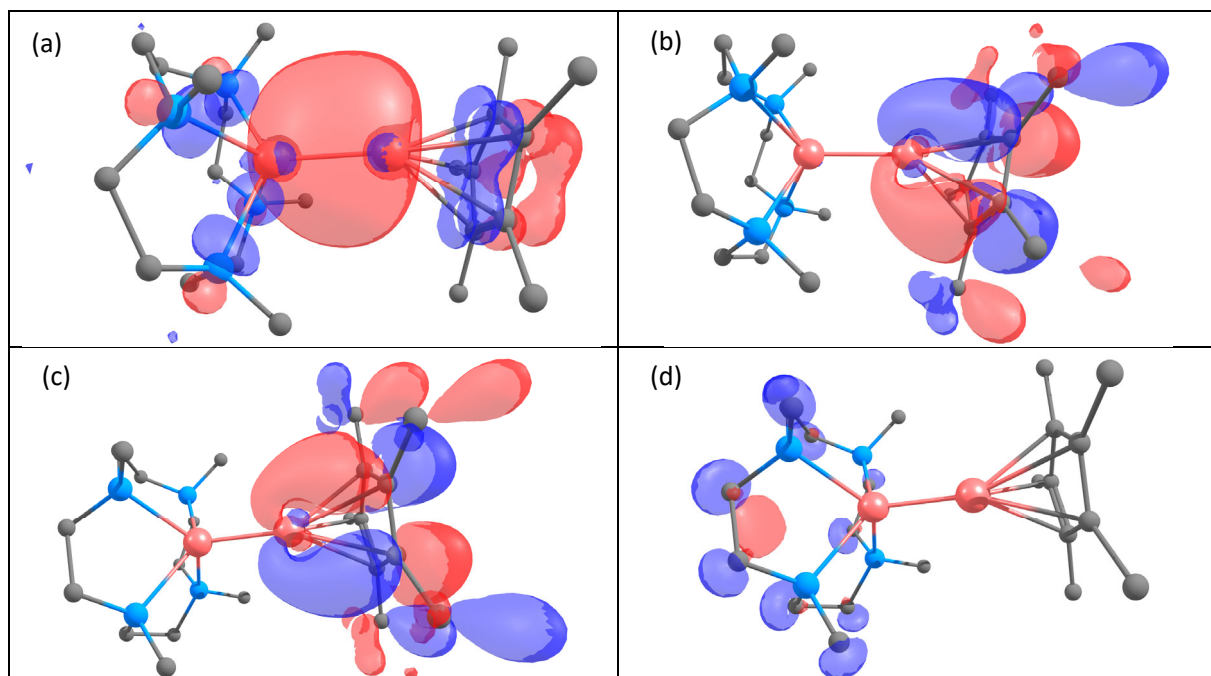
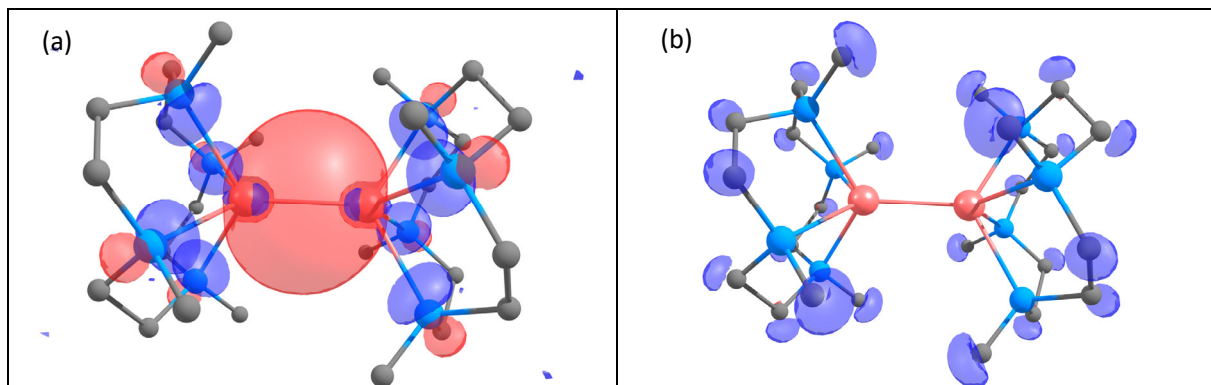


Table S4. Comparison of bond distances (Å) between selected atoms in DFT optimized and X-ray structures for complex **4**.

Atom Labels	DFT	X-ray
	(Dispersion)	
Zn1-Zn2	2.47	2.49
Zn1-N3	2.38	2.33
Zn1-N4	2.38	2.39
Zn1-N5	2.38	2.34
Zn1-N6	2.37	2.38
Zn2-N7	2.38	2.28
Zn2-N8	2.38	2.46
Zn2-N9	2.38	2.29
Zn2-N10	2.38	2.48

Table S5. Computed MOs for complex **4** (dispersion). (a) HOMO; (b) LUMO.



Optimized geometries

1					
Zn	0.919742000	-0.006907000	0.006145000	H	3.432046000 2.994729000 -1.290458000
Zn	-1.441511000	-0.020759000	0.011511000	H	0.548943000 2.913407000 -1.323723000
N	2.018451000	0.020741000	2.065413000	H	1.459301000 4.113335000 -0.372925000
N	1.990541000	2.073213000	-0.020011000	H	0.198557000 3.098499000 0.386682000
N	1.994070000	-0.015161000	-2.070872000	H	3.364721000 1.292812000 -3.057672000
N	2.023928000	-2.065709000	0.015061000	H	1.756967000 1.934638000 -2.771780000
C	-3.367447000	0.855540000	-0.872054000	H	3.894914000 -0.598674000 -1.423100000
C	-3.379300000	-0.562213000	-1.080768000	H	3.455719000 -1.262699000 -2.992055000
C	-3.391719000	-1.198751000	0.203375000	H	0.573996000 -1.340194000 -2.914397000
C	-3.388212000	-0.174722000	1.204952000	H	1.472123000 -0.374983000 -4.111974000
C	-3.374567000	1.095067000	0.539628000	H	0.198220000 0.365139000 -3.098708000
C	3.068431000	1.047973000	1.972814000	H	3.412973000 -3.031824000 -1.289507000
C	2.595884000	-1.312337000	2.310496000	H	1.802735000 -2.771287000 -1.935470000
C	1.044558000	0.350783000	3.118795000	H	3.913166000 -1.390464000 0.603606000
C	2.562286000	2.324561000	1.314300000	H	3.495186000 -2.965750000 1.266894000
C	3.042667000	1.993488000	-1.045535000	H	0.610500000 -2.927155000 1.335875000
C	1.002752000	3.112778000	-0.351735000	H	1.528290000 -4.113773000 0.375841000
C	2.546750000	1.327303000	-2.322015000	H	0.243517000 -3.118585000 -0.370176000
C	3.061456000	-1.024837000	-1.991000000	H	-3.001123000 2.843467000 -1.645257000
C	1.013279000	-0.361391000	-3.112353000	H	-4.525740000 2.132606000 -2.165337000
C	2.583717000	-2.309019000	-1.326097000	H	-3.013843000 1.581519000 -2.879992000
C	3.087193000	-1.970513000	1.027945000	H	-3.050241000 -0.679169000 -3.215776000
C	1.056342000	-3.120283000	0.359036000	H	-4.560404000 -1.404183000 -2.674485000
C	-3.476033000	1.902989000	-1.941439000	H	-3.038045000 -2.244751000 -2.398986000
C	-3.506613000	-1.255772000	-2.405471000	H	-3.078483000 -3.268922000 -0.341658000
C	-3.535710000	-2.671527000	0.453087000	H	-4.592825000 -2.962968000 0.502589000
C	-3.526930000	-0.391569000	2.683336000	H	-3.077455000 -2.974981000 1.399380000
C	-3.492599000	2.435477000	1.203742000	H	-3.059486000 0.411192000 3.261940000
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H	3.471200000	1.291763000	2.969014000	H	-4.583028000 -0.425256000 2.980655000
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H	1.821112000	-1.931902000	2.769795000	H	-3.032676000 3.230044000 0.608185000
H	0.586256000	1.321871000	2.925550000	H	-3.022651000 2.447448000 2.191995000
H	1.515278000	0.373277000	4.112760000		
H	0.241784000	-0.389355000	3.115759000	1-disp	
H	3.379246000	3.060718000	1.268509000	Zn	0.938874000 0.003743000 -0.122985000
H	1.780872000	2.773686000	1.932850000	Zn	-1.364053000 0.007000000 -0.370589000
H	3.883053000	1.427031000	-0.631352000	N	2.218678000 -1.337203000 -1.426888000
				N	1.659544000 -1.545911000 1.393113000

N	1.623810000	1.335989000	1.598750000	H	-3.356938000	-1.029894000	-3.127982000
N	2.185381000	1.542425000	-1.227731000	H	-4.750162000	-1.725079000	-2.302163000
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C	-3.209769000	1.140522000	0.414433000	H	-2.674761000	-2.773227000	1.678164000
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C	-3.211959000	-1.170019000	0.336875000				
C	3.117389000	-2.073296000	-0.527806000	4-disp			
C	2.979722000	-0.501005000	-2.367896000	Zn	1.234270000	-0.001082000	0.000771000
C	1.312927000	-2.244558000	-2.144587000	Zn	-1.234108000	-0.000460000	-0.000565000
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C	2.549820000	-0.838529000	2.321040000	N	2.413614000	-0.054687000	-2.061678000
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C	0.514992000	2.243165000	1.920690000	N	-2.418001000	1.316235000	-1.587686000
C	2.574110000	2.608930000	-0.291920000	N	-2.412647000	1.588740000	1.317558000
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5. References

- S1 F. Ritter, L. J. Morris, K. N. McCabe, T. P. Spaniol, L. Maron, and J. Okuda, *Inorg. Chem.*, 2021, **60**, 15583-15592.
- S2 I. Resa, E. Carmona, E. Gutierrez-Puebla, and A. Monge, *Science*, 2004, **305**, 1136-1138.
- S3 D. Schuhknecht, C. Lhotzky, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem. Int. Ed.* 2017, **56**, 12367-12371.
- S4 G. M. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3–8.
- S5 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112–122.
- S6 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
- S7 K. Brandenburg, Diamond Version 4.6.0, Crystal Impact GbR, Bonn, 2019.
- S8 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, M. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.
- S10 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- S11 A. Hollwarth, M. Bohme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Kohler, R. Stegmann, A. Veldkamp and G. Frenking, *J. Chem. Phys.*, **1993**, *208*, 237–240; A. Bergner,

- M. Dolg, W. Kuechle, H. Stoll and H. Preuss, *Mol. Phys.*, 1993, **80**, 1431–1441; F. Schautz, H.-J. Flad and M. Dolg, *Theor. Chem. Acc.*, 1998, **99**, 231–240.
- S12 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comp. Chem.*, 2011, **32**, 1456–1465.