

Supporting Information

Synthesis, Structure and Reactivity of [Tm^{Bu^t}]ZnH, a Monomeric Terminal Zinc Hydride Compound in a Sulfur-Rich Coordination Environment: Access to a Heterobimetallic Compound

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Received xxxx xx, 2015.

EXPERIMENTAL SECTION

General considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under an argon or nitrogen atmosphere.¹ Solvents were purified and degassed using standard procedures. NMR spectra were measured on Bruker 300 DRX, Bruker 300 DPX, Bruker 400 Avance III, Bruker 400 Cyber-enabled Avance III, and Bruker 500 DMX spectrometers. ¹H NMR spectra are reported in ppm relative to SiMe₄ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity ($\delta = 7.16$ for C₆D₅H).² ¹³C NMR spectra are reported in ppm relative to SiMe₄ ($\delta = 0$) and were referenced internally with respect to the solvent ($\delta = 128.06$ for C₆D₆).² ¹⁹F NMR spectra are reported in ppm relative to CFCl₃ ($\delta = 0$) and were referenced internally with respect to C₆F₆ ($\delta = -164.9$).³ Coupling constants are given in hertz. Infrared spectra were recorded on a Perkin Elmer Spectrum Two spectrometer in attenuated total reflectance (ATR) mode, and are reported in reciprocal centimeters. Mass spectra were obtained on a JEOL JMS-HX110HF tandem mass spectrometer using fast atom bombardment (FAB). [Tm^{Bu^t}]ZnOPh,⁴ CpMo(CO)₃H⁵ and [Tp^{Bu^t,Me}]ZnH⁶ were prepared according to the literature procedures. PhOH (Aldrich), PhSH (Aldrich), 4-fluorothiophenol (Aldrich), PhSeH (TCI), Ph₂S₂ (Aldrich), Ph₂Se₂ (Aldrich), Ph₂Te₂ (Aldrich), HCO₂H (Aldrich), PhSiH₃ (Acros), H₂S (Aldrich), CO₂ (Aldrich), Me₂Zn (Strem Chemicals) and Et₂Zn (Strem Chemicals) were commercially obtained and used without further purification.

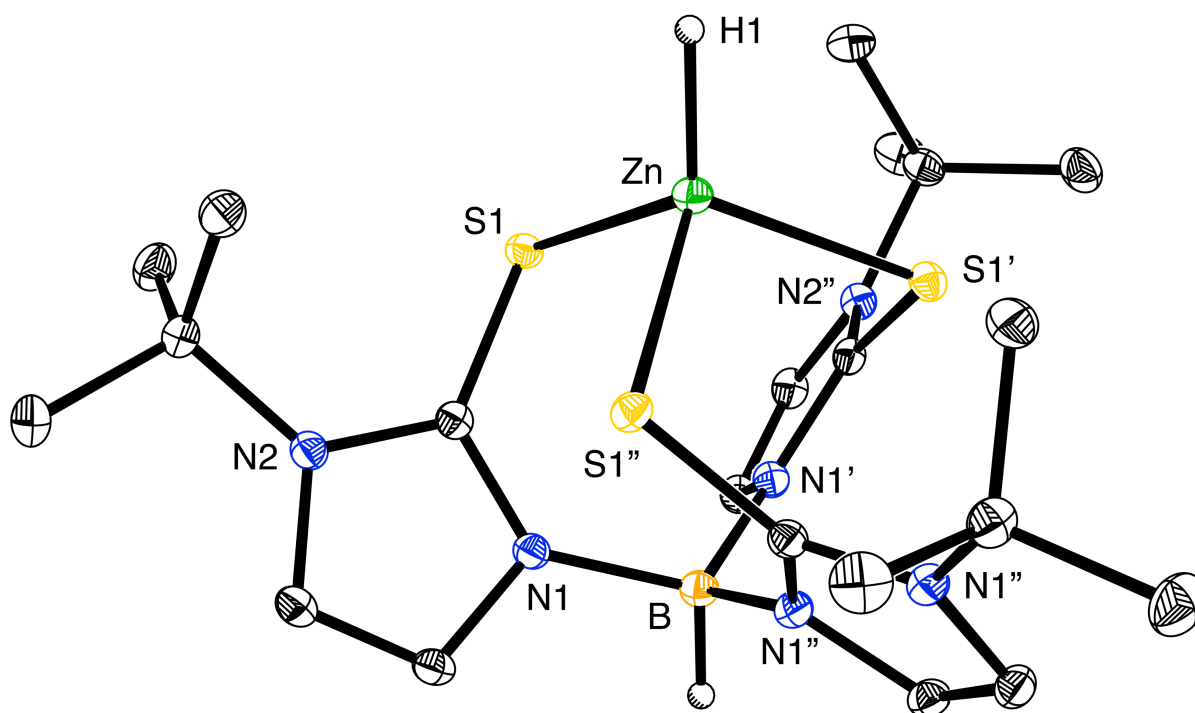
X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2014/7).⁷

Synthesis of [Tm^{Bu^t}]ZnH

A solution of [Tm^{Bu^t}]ZnOPh (162 mg, 0.255 mmol) in C₆H₆ (*ca.* 6 mL) was treated with PhSiH₃ (35 μL, 0.28 mmol). The solution was stirred at room temperature for 1 hour, over which period a cloudy suspension formed. The volatile components were removed *in vacuo*, and the resulting powder was washed twice with a mixture of pentane (3 mL) and Et₂O (2 mL), yielding [Tm^{Bu^t}]ZnH as a white powder (130 mg, 94%). Crystals suitable for X-ray diffraction were obtained from a solution in benzene.

Analysis calcd. for [Tm^{Bu^t}]ZnH•0.5(benzene): C, 49.5%; H, 6.6%; N, 14.4%. Found: C, 50.2%; H, 6.4%; N, 13.9%. ¹H NMR (C₆D₆): 1.50 [s, 27H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 5.78 [s, 1H, ZnH], 6.39 [d, ³J_{H-H} = 2, 3H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 6.70 [d, ³J_{H-H} = 2, 3H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], [BH, not observed]. ¹³C{¹H} NMR (C₆D₆): 28.8 [9C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 59.2 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 116.4 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 122.5 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 159.5 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 1716 (m), 1564 (w), 1477 (w), 1412 (m), 1396 (m), 1356 (vs), 1302 (m), 1254 (w), 1228 (w), 1190 (s), 1170 (s), 1129 (w), 1062 (m), 1028 (w), 926 (w), 820 (m), 755 (m), 724 (s), 686 (m), 674 (s), 587 (m), 550 (m), 501 (m), 469 (s). FAB-MS: *m/z* = 541.6 [M – H]⁺, M = [Tm^{Bu^t}]ZnH.



Molecular Structure of [Tm^{Bu^t}]ZnH}

Reaction of [Tm^{Bu^t}]ZnH with H₂S}

A solution of [Tm^{Bu^t}]ZnH (5 mg, 0.009 mmol) in C₆D₆ (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with H₂S (1 atm). The sample was monitored by ¹H NMR spectroscopy, thereby demonstrating the immediate formation of [Tm^{Bu^t}]ZnSH as identified by comparison of the ¹H NMR spectrum to that of an authentic sample.⁴}}

Reactivity of [Tm^{Bu^t}]ZnH towards ArEH}

(a) PhOH

A solution of [Tm^{Bu^t}]ZnH (8.8 mg, 0.016 mmol) in C₆D₆ (ca. 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with PhOH (2.3 mg, 0.024 mmol). The sample was monitored by ¹H NMR spectroscopy, thereby demonstrating the rapid}

conversion to $[\text{Tm}^{\text{Bu}^t}]\text{ZnOPh}$, as identified by comparison with the data for an authentic sample.⁴

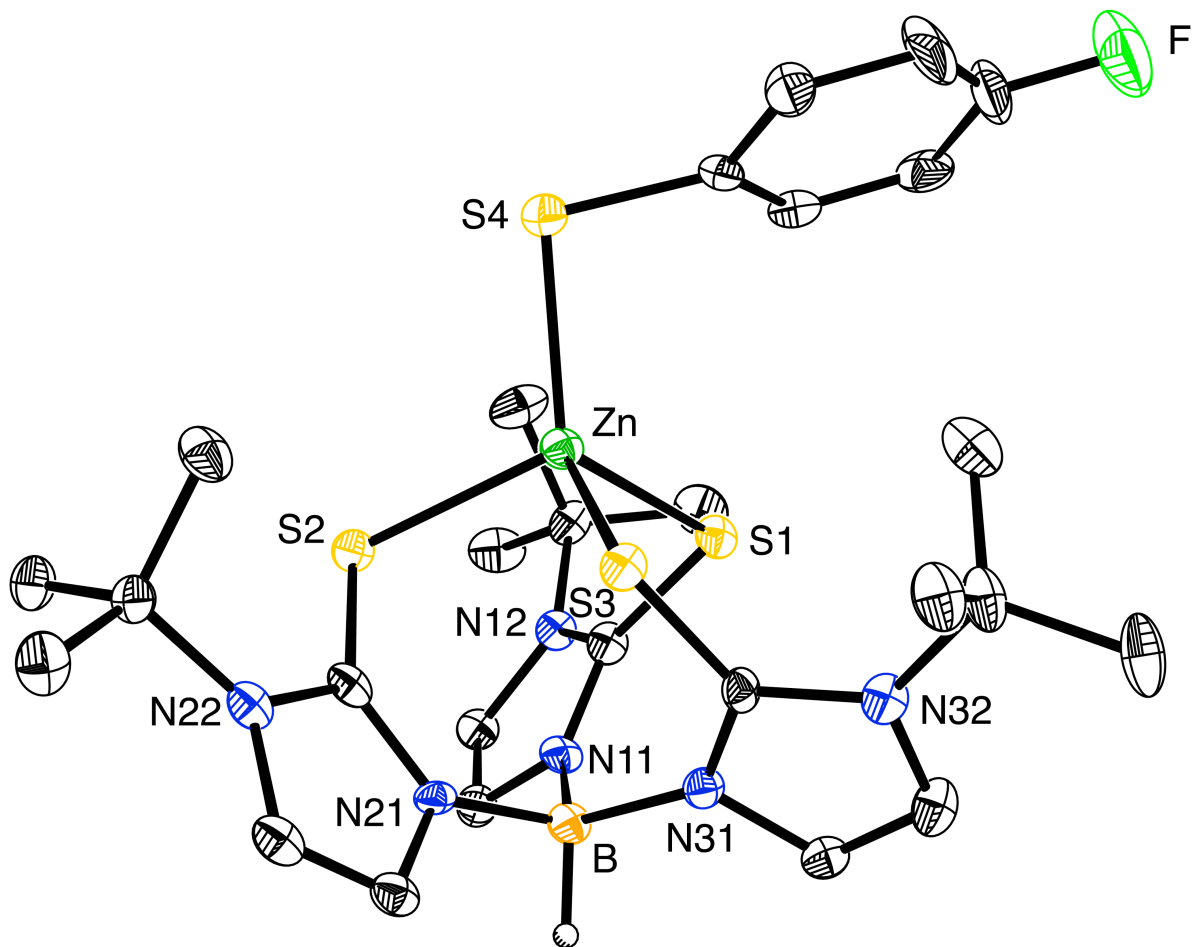
(b) PhSH

A solution of $[\text{Tm}^{\text{Bu}^t}]\text{ZnH}$ (10 mg, 0.018 mmol) in C_6D_6 (*ca.* 0.7 mL) in an NMR tube equipped with a J. Young valve was prepared in a glove box. The sample was removed from the glove box treated with PhSH (2.3 μL , 0.022 mmol) and then degassed *via* one freeze-pump-thaw cycle. The sample was monitored by ^1H NMR spectroscopy, thereby demonstrating the rapid conversion to $[\text{Tm}^{\text{Bu}^t}]\text{ZnSPh}$ as identified by comparison with the data for an authentic sample.⁴

(c) *p*- $\text{FC}_6\text{H}_4\text{SH}$

A solution of $[\text{Tm}^{\text{Bu}^t}]\text{ZnH}$ (8 mg, 0.015 mmol) in C_6D_6 (*ca.* 0.7 mL) in an NMR tube equipped with a septum was treated with *p*- $\text{FC}_6\text{H}_4\text{SH}$ (1.6 μL , 0.015 mmol). The sample was monitored by ^1H NMR spectroscopy, thereby demonstrating the rapid conversion to $[\text{Tm}^{\text{Bu}^t}]\text{ZnS}(\text{C}_6\text{H}_4\text{-4-F})$. The volatile components were removed by lyophilization to give a white powder, which was dissolved in Et_2O (*ca.* 1 mL). The solution was allowed to evaporate at room temperature to yield $[\text{Tm}^{\text{Bu}^t}]\text{ZnS}(\text{C}_6\text{H}_4\text{-4-F})$ (7 mg, 71%) as a microcrystalline powder. Analysis calcd. for $[\text{Tm}^{\text{Bu}^t}]\text{ZnS}(\text{C}_6\text{H}_4\text{-4-F})\cdot(\text{benzene})$: C, 53.0%; H, 5.9%; N, 11.2%. Found: C, 52.7%; H, 5.8%; N, 11.3%. Crystals of $[\text{Tm}^{\text{Bu}^t}]\text{ZnS}(\text{C}_6\text{H}_4\text{-4-F})$ suitable for X-ray diffraction were obtained *via* slow diffusion of pentane into a solution in benzene. ^1H NMR (C_6D_6): 1.41 [s, 27H, $\text{HB}\{\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}\}_3$], 6.37 [d, $^3J_{\text{H-H}} = 2$, 3H, $\text{HB}\{\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}\}_3$], 6.62 [d, $^3J_{\text{H-H}} = 2$, 3H, $\text{HB}\{\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}\}_3$], 6.77 [m, 2H, $\text{CdS}(\text{C}_6\text{H}_4\text{-4-F})$], 7.86 [m, 2H, $\text{CdS}(\text{C}_6\text{H}_4\text{-4-F})$], [BH, not observed]. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 28.7 [9C, $\text{HB}\{\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}\}_3$], 59.4 [3C, $\text{HB}\{\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}\}_3$], 114.7 [d, $^2J_{\text{C-F}} = 21$, 2C, $\text{CdS}(\text{C}_6\text{H}_4\text{-4-F})$], 117.0 [3C, $\text{HB}\{\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}\}_3$], 122.9 [3C, $\text{HB}\{\text{C}_2\text{N}_2\text{H}_2[\text{C}(\text{CH}_3)_3]\text{CS}\}_3$], 135.7 [d, $^3J_{\text{C-F}} = 7$, 2C, $\text{CdS}(\text{C}_6\text{H}_4\text{-4-F})$], 139.9 [d, $^4J_{\text{C-F}} = 3$, 1C, $\text{CdS}(\text{C}_6\text{H}_4\text{-4-F})$], 157.2 [3C,

HB{C₂N₂H₂[C(CH₃)₃]CS₃}, 160.6 [d, ¹J_{C-F} = 240, 1C, CdS(C₆H₄-4-F)]. ¹⁹F NMR (C₆D₆): 125.31 (multiplet). IR data (ATR, cm⁻¹): 3180 (w), 3147 (w), 2976 (w), 2928 (w), 2417 (w), 2233 (w), 1860 (w), 1687 (w), 1565 (m), 1480 (s), 1420 (m), 1398 (w), 1362 (vs), 1310 (m), 1259 (w), 1221 (m), 1194 (vs), 1174 (vs), 1130 (m), 1087 (m), 1071 (m), 1031 (w), 1014 (w), 928 (w), 816 (s), 759 (s), 732 (vs), 688 (s), 626 (s), 590 (m), 554 (m), 494 (s), 458 (w).



Molecular Structure of [Tm^{Bu^t}]ZnS(C₆H₄-4-F)

(d) PhSeH

A solution of [Tm^{Bu^t}]ZnH (10 mg, 0.018 mmol) in C₆D₆ (ca. 0.7 mL) in an NMR tube equipped with a septum was treated with PhSeH (2 μL, 0.019 mmol). The sample was

monitored by ^1H NMR spectroscopy, thereby demonstrating the rapid conversion to $[\text{Tm}^{\text{Bu}^t}]\text{ZnSePh}$, as identified by comparison with the data for an authentic sample.⁴

Reactivity of $[\text{Tm}^{\text{Bu}^t}]\text{ZnH}$ towards Ph_2E_2

(a) Ph_2S_2

A solution of $[\text{Tm}^{\text{Bu}^t}]\text{ZnH}$ (10 mg, 0.018 mmol) in C_6D_6 (*ca.* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Ph_2S_2 (2 mg, 0.009 mmol). The sample was monitored by ^1H NMR spectroscopy, thereby demonstrating the rapid conversion to $[\text{Tm}^{\text{Bu}^t}]\text{ZnSPh}$, as identified by comparison with the data for an authentic sample.⁴ The conversion is quantitative in the presence of excess Ph_2S_2 .

(b) Ph_2Se_2

A solution of $[\text{Tm}^{\text{Bu}^t}]\text{ZnH}$ (6 mg, 0.011 mmol) in C_6D_6 (*ca.* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Ph_2Se_2 (2 mg, 0.006 mmol). The sample was monitored by ^1H NMR spectroscopy, thereby demonstrating the rapid conversion to $[\text{Tm}^{\text{Bu}^t}]\text{ZnSePh}$, as identified by comparison with the data for an authentic sample.⁴ The conversion is quantitative in the presence of excess Ph_2Se_2 .

(c) Ph_2Te_2

A solution of $[\text{Tm}^{\text{Bu}^t}]\text{ZnH}$ (6 mg, 0.011 mmol) in C_6D_6 (*ca.* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Ph_2Te_2 (2 mg, 0.005 mmol). The sample was monitored by ^1H NMR spectroscopy, thereby demonstrating the rapid conversion to $[\text{Tm}^{\text{Bu}^t}]\text{ZnTePh}$, as identified by comparison with the data for an authentic sample.⁴ The conversion is quantitative in the presence of excess Ph_2Te_2 .

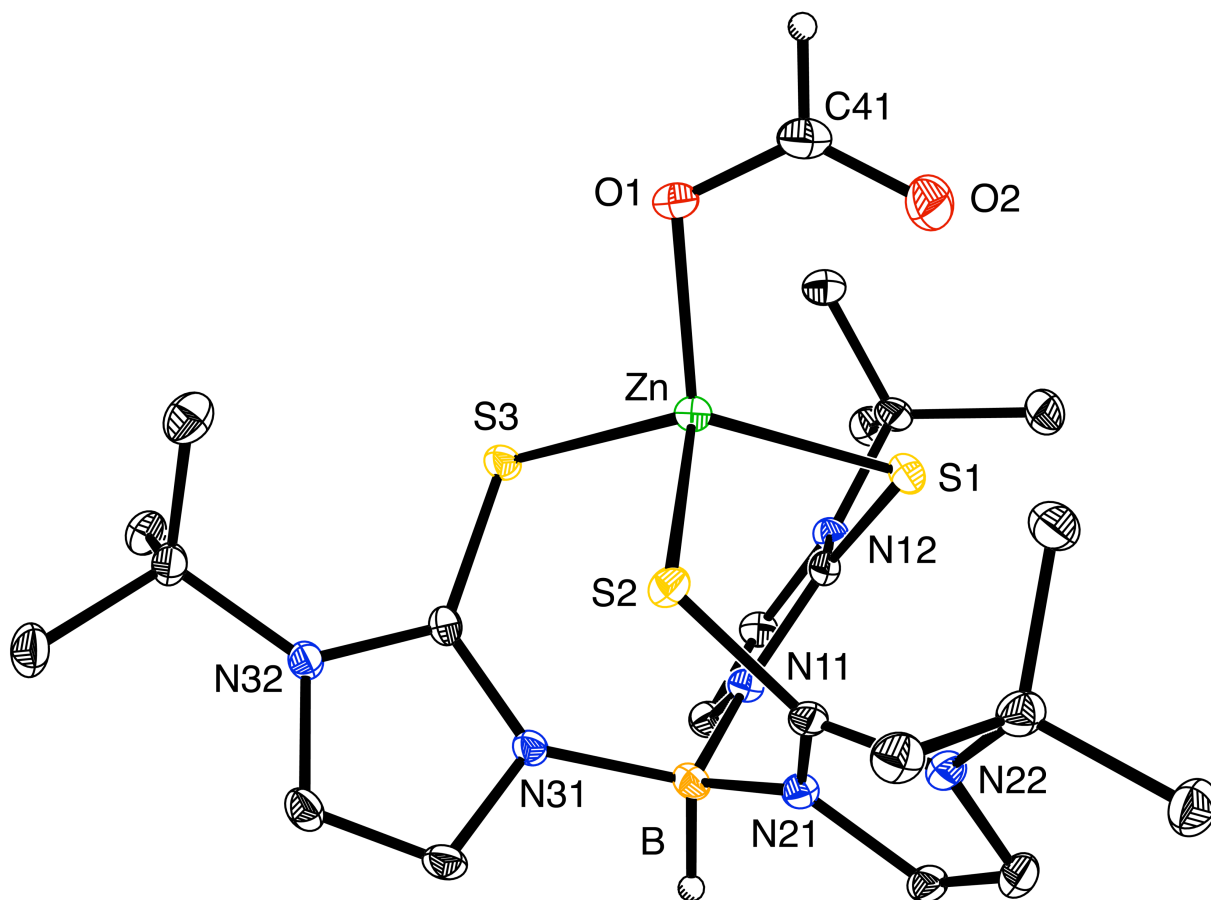
Synthesis of [Tm^{Bu^t}]Zn(κ^1 -O₂CH)

(a) From HCO₂H

A solution of [Tm^{Bu^t}]ZnH (25 mg, 0.046 mmol) in benzene (*ca.* 0.7 mL) was treated with formic acid (1.8 μ L, 0.048 mmol), resulting in immediate effervescence. The volatile components were removed by lyophilization to yield [Tm^{Bu^t}]Zn(κ^1 -O₂CH) as a white powder (24 mg, 89%). Crystals of [Tm^{Bu^t}]Zn(κ^1 -O₂CH) suitable for X-ray diffraction were obtained *via* slow diffusion of pentane into a solution in benzene. Analysis calcd. for [Tm^{Bu^t}]Zn(κ^1 -O₂CH)•(benzene): C, 50.5%; H, 6.2%; N, 12.6%. Found: C, 49.7%; H, 6.9%; N, 12.0%. ¹H NMR (C₆D₆): 1.48 [s, 27H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 6.37 [d, ³J_{H-H} = 2, 3H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 6.64 [d, ³J_{H-H} = 2, 3H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 9.15 [s, 1 H, O₂CH], [BH, not observed]. ¹³C{¹H} NMR (C₆D₆): 28.9 [9C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 59.6 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 117.1 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 123.0 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 157.5 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 167.4 [1C of O₂CH]. IR data (ATR, cm⁻¹): 3144 (w), 2977 (w), 2926(w), 2801 (w), 2420 (w), 1630 (s), 1567 (w), 1480 (w), 1419 (m), 1398 (m), 1362 (vs), 1305 (m), 1229 (w), 1193 (vs), 1174 (vs), 1133 (w), 1071 (w), 1031 (w), 929 (w), 821 (m), 760 (m), 728 (s), 685 (s), 590 (m), 553 (m), 495 (m), 456 (w). FAB-MS: *m/z* = 541.5 [M - O₂CH]⁺, M = [Tm^{Bu^t}]ZnO₂CH.

(b) From CO₂

A solution of [Tm^{Bu^t}]ZnH (11 mg, 0.020 mmol) in C₆D₆ (*ca.* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with CO₂ (*ca.* 1.3 atm). The reaction was monitored by ¹H NMR spectroscopy, thereby demonstrating the rapid formation of [Tm^{Bu^t}]Zn(κ^1 -O₂CH).

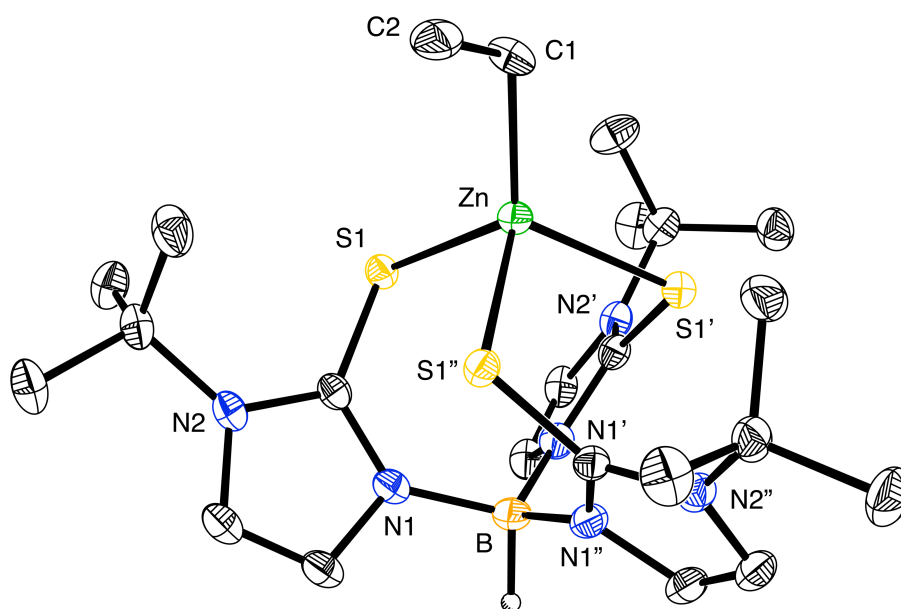


Molecular Structure of $[\text{Tm}^{\text{Bu}^t}]^-\text{Zn}(\kappa^1\text{-O}_2\text{CH})$

Synthesis of $[\text{Tm}^{\text{Bu}^t}]\text{ZnEt}$

A solution of $[\text{Tm}^{\text{Bu}^t}]\text{ZnH}$ (10 mg, 0.018 mmol) in C_6D_6 (ca. 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Et_2Zn (25 μL of a 0.9 M solution in C_6D_6 , 0.023 mmol), thereby resulting in the formation of $[\text{Tm}^{\text{Bu}^t}]\text{ZnEt}$ accompanied by a dark gray precipitate. The mixture was filtered after one hour and the volatile components were removed by lyophilization, yielding $[\text{Tm}^{\text{Bu}^t}]\text{ZnEt}$ as a white powder (6 mg, 57%). Crystals of $[\text{Tm}^{\text{Bu}^t}]\text{ZnEt}$ suitable for X-ray diffraction were obtained *via* slow diffusion of pentane into a solution in benzene. Analysis calcd. for $[\text{Tm}^{\text{Bu}^t}]\text{ZnEt}$: C, 48.3%; H, 6.9%; N, 14.7%. Found: C, 48.0%; H, 7.1%; N, 14.3%. ^1H NMR (C_6D_6 , room temperature): 1.069 [A component of ABX_3 multiplet, $^2J_{\text{H-H}} = 13$, $^3J_{\text{H-H}} = 8$, 1H of ZnCH_2CH_3], 1.085 [B component of ABX_3 multiplet, $^2J_{\text{H-H}} = 13$, $^3J_{\text{H-H}} = 8$, 1H of

ZnCH₂CH₃], 1.53 [s, 27H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 1.99 [X₃ component of ABX₃ multiplet, t, ³J_{H-H} = 8, 3H, ZnCH₂CH₃], 4.72 [broad s, 1H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 6.41 [d, ³J_{H-H} = 2, 3H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 6.70 [d, ³J_{H-H} = 2, 3H, HB{C₂N₂H₂[C(CH₃)₃]CS₃]. ¹H NMR (C₇D₈, 340 K) 0.78 [q, ³J_{H-H} = 8, 2H of ZnCH₂CH₃], 1.55 [s, 27H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 1.73 [t, ³J_{H-H} = 8, 3H, ZnCH₂CH₃], 4.52 [broad m, 1H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 6.46 [d, ³J_{H-H} = 2, 3H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 6.60 [d, ³J_{H-H} = 2, 3H, HB{C₂N₂H₂[C(CH₃)₃]CS₃]. ¹³C{¹H} NMR (C₆D₆): 5.4 [1C of ZnCH₂CH₃], 14.9 [1C of ZnCH₂CH₃], 28.8 [9C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 59.0 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 116.3 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 122.5 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 159.6 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}. IR Data (ATR, cm⁻¹): 3134 (w), 2976 (w), 2925 (w), 2878 (w), 2415 (w), 2294 (w), 2237 (w), 1566 (w), 1481 (w), 1417 (m), 1396 (w), 1360 (vs), 1299 (m), 1255 (w), 1228 (w), 1193 (vs), 1174 (vs), 1133 (w), 1069 (m), 1029 (w), 980 (w), 929 (w), 908 (w), 821 (m), 757 (m), 725 (s), 686 (s), 634 (w), 588 (m), 554 (m), 495 (m), 457 (w).



Molecular Structure of [Tm^{But}]ZnEt

(only one configuration of the disordered ethyl group is shown)

Reactivity of [Tm^{But}]ZnH towards Me₂Zn

A solution of [Tm^{But}]ZnH (5 mg, 0.009 mmol) in C₆D₆ (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Me₂Zn (7 mg, 0.073 mmol), resulting in the deposition of a white precipitate. The mixture was lyophilized to afford [Tm^{But}]ZnMe as a white powder as identified by comparison of the ¹H NMR spectrum to that of an authentic sample.⁴

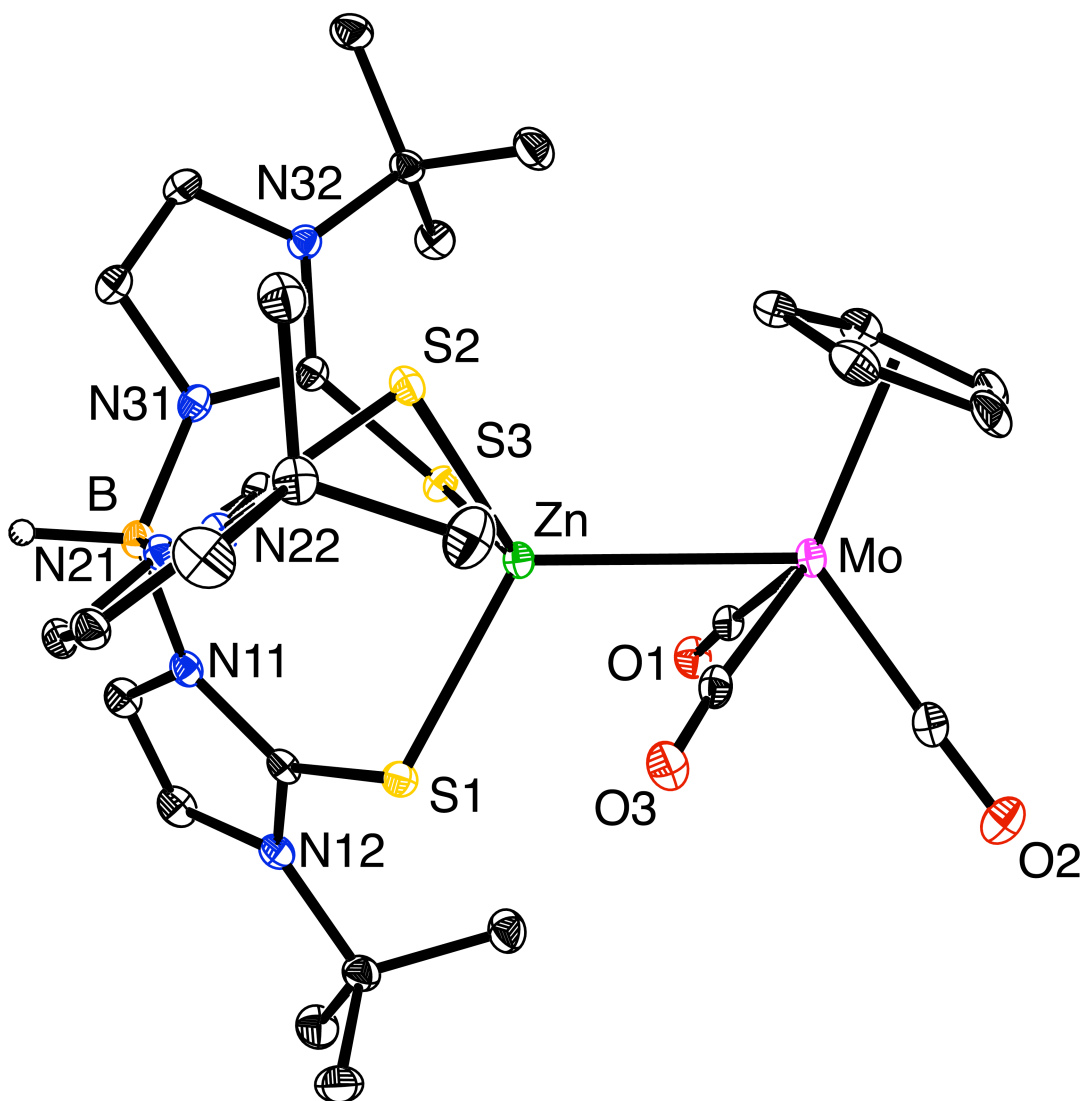
Reactivity of [Tm^{But}]ZnH towards Me₂Cd

A solution of [Tm^{But}]ZnH (5 mg, 0.09 mmol) in C₆D₆ (ca. 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Me₂Cd (100 μL of a 0.111 M solution in C₆D₆, 0.011 mmol) resulting in the formation of a dark precipitate. The sample was monitored by ¹H NMR spectroscopy, thereby demonstrating the formation of, inter alia, [Tm^{But}]CdMe.⁸

Synthesis of [Tm^{But}]ZnMoCp(CO)₃

A solution of [Tm^{But}]ZnH (12 mg, 0.022 mmol) in C₆D₆ (ca. 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with CpMo(CO)₃H (12 mg, 0.049 mmol), resulting in immediate evolution of H₂. The mixture was filtered and the volatile components were removed from the filtrate by lyophilization to yield [Tm^{But}]ZnMoCp(CO)₃ as a pale pink powder (10 mg, 58%). Crystals of [Tm^{But}]ZnMoCp(CO)₃ suitable for X-ray diffraction were obtained *via* slow diffusion of pentane into a solution in benzene. Analysis calcd. for [Tm^{But}]ZnMoCp(CO)₃•(benzene): C, 48.5%; H, 5.2%; N, 9.7%. Found: C, 48.2%; H, 5.0%; N, 9.4%. ¹H NMR (CD₂Cl₂): 1.78 [s, 27H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 5.19 [s, 5H, MoCp], 6.84 [d, ³J_{H-H} = 2, 3H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 7.05 [d, ³J_{H-H} = 2, 3H, HB{C₂N₂H₂[C(CH₃)₃]CS₃}]. ¹³C{¹H} NMR (CD₂Cl₂): 29.3 [9C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 59.8 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}], 88.8 [5C of MoCp], 117.1 [3C,

HB{C₂N₂H₂[C(CH₃)₃]CS₃}, 123.5 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}, 157.0 [3C, HB{C₂N₂H₂[C(CH₃)₃]CS₃}, 3C of CO not observed. IR Data for [Tm^{Bu^t}]ZnMoCp(CO)₃ (ATR, cm⁻¹): 3186 (w), 3153 (w), 2978 (w), 2925 (w), 2419 (w), 1938 (s), 1835 (vs), 1568 (m), 1478 (m), 1420 (m), 1397 (m), 1360 (vs), 1307 (m), 1258 (w), 1229 (w), 1195 (s), 1174 (s), 1136 (w), 1105 (w), 1072 (w), 1059 (w), 1036 (w), 1010 (w), 1001 (w), 926 (w), 853 (w), 837 (w), 822 (m), 801 (m), 760 (m), 737 (m), 724 (m), 680 (vs), 598 (s), 555 (m), 515 (m), 490 (m), 457 (w). FAB-MS: m/z = 541.2 [M - MoCp(CO)₃]⁺, M = [Tm^{Bu^t}]ZnMoCp(CO)₃.



Molecular Structure of [Tm^{Bu^t}]ZnMoCp(CO)₃

Comparison of the Reactivity of [Tm^{Bu^t}]ZnH and [Tp^{Bu^t,Me}]ZnH towards CO₂

A solution of [Tm^{Bu^t}]ZnH (5.0 mg, 0.009 mmol) and [Tp^{Bu^t,Me}]ZnH (4.5 mg, 0.009 mmol) in C₆D₆ (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with CO₂ (1 atm). The reaction was monitored by ¹H NMR spectroscopy, thereby demonstrating the immediate formation of [Tm^{Bu^t}]Zn(κ¹-O₂CH), while [Tp^{Bu^t,Me}]ZnH remained unreacted. The mixture was allowed to stand overnight at room temperature, after which period *ca.* 35 % of [Tp^{Bu^t,Me}]ZnH had converted to [Tp^{Bu^t,Me}]Zn(κ¹-O₂CH). The mixture was then heated at 60 °C for one day, thereby resulting in complete conversion of [Tp^{Bu^t,Me}]ZnH to [Tp^{Bu^t,Me}]Zn(κ¹-O₂CH).

Table 1. Crystal, intensity collection and refinement data.

| | [Tm ^{Bu^t}]ZnH•0.5(C ₆ H ₆) | [Tm ^{Bu^t}]ZnS(C ₆ H ₄ -4-F) |
|--|--|--|
| lattice | Rhombohedral | Monoclinic |
| formula | C ₂₄ H ₃₈ BN ₆ S ₃ Zn | C ₂₇ H ₃₈ BFN ₆ S ₄ Zn |
| formula weight | 1165.93 | 670.05 |
| space group | <i>R</i> -3 | <i>P</i> 2 ₁ / <i>n</i> |
| <i>a</i> /Å | 13.3984(11) | 13.199(5) |
| <i>b</i> /Å | 13.3984(11) | 17.979(6) |
| <i>c</i> /Å | 27.542(2) | 13.504(5) |
| α /° | 90 | 90 |
| β /° | 90 | 92.785(5) |
| γ /° | 120 | 90 |
| <i>V</i> /Å ³ | 4281.9(6) | 3200.9(19) |
| <i>Z</i> | 6 | 4 |
| temperature (K) | 130(2) | 130(2) |
| radiation (λ , Å) | 0.71073 | 0.71073 |
| ρ (calcd.), g cm ⁻³ | 1.356 | 1.390 |
| μ (Mo K α), mm ⁻¹ | 1.104 | 1.062 |
| θ max, deg. | 32.771 | 25.679 |
| no. of data collected | 22244 | 35664 |
| no. of data used | 3358 | 6078 |
| no. of parameters | 113 | 373 |
| R_1 [$I > 2\sigma(I)$] | 0.0373 | 0.0680 |
| wR_2 [$I > 2\sigma(I)$] | 0.0739 | 0.1182 |
| R_1 [all data] | 0.0651 | 0.1651 |
| wR_2 [all data] | 0.0799 | 0.1524 |
| GOF | 1.005 | 1.006 |
| R_{int} | 0.0755 | 0.2396 |

Table 1 (continued). Crystal, intensity collection and refinement data.

| | [Tm ^{Bu^t}]Zn- (κ ¹ -O ₂ CH)•2(C ₆ H ₆) | [Tm ^{Bu^t}]ZnEt•3(C ₆ H ₆) |
|---|---|---|
| lattice | Monoclinic | Rhombohedral |
| formula | C ₃₄ H ₄₇ BN ₆ O ₂ S ₃ Zn | C ₄₁ H ₅₇ BN ₆ S ₃ Zn |
| formula weight | 744.13 | 806.28 |
| space group | <i>P</i> 2/ ₁ | <i>R</i> -3 |
| <i>a</i> /Å | 10.3568(8) | 13.4730(14) |
| <i>b</i> /Å | 19.5721(15) | 13.4730(14) |
| <i>c</i> /Å | 10.5278(11) | 67.359(7) |
| α/° | 90 | 90 |
| β/° | 119.4240(1) | 90 |
| γ/° | 90 | 120 |
| <i>V</i> /Å ³ | 1858.8(3) | 10589(2) |
| <i>Z</i> | 2 | 12 |
| temperature (K) | 130(2) | 130(2) |
| radiation (λ, Å) | 0.71073 | 0.71073 |
| ρ (calcd.), g cm ⁻³ | 1.330 | 1.517 |
| μ (Mo Kα), mm ⁻¹ | 0.868 | 0.916 |
| θ max, deg. | 30.974 | 28.276 |
| no. of data collected | 30599 | 37365 |
| no. of data used | 11621 | 2775 |
| no. of parameters | 442 | 121 |
| <i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] | 0.0467 | 0.0411 |
| <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] | 0.0785 | 0.1274 |
| <i>R</i> ₁ [all data] | 0.0694 | 0.0496 |
| <i>wR</i> ₂ [all data] | 0.0858 | 0.1322 |
| GOF | 1.007 | 1.037 |
| <i>R</i> _{int} | 0.0576 | 0.0538 |

Table 1 (continued). Crystal, intensity collection and refinement data.

| [Tm^{Bu^t}]ZnMoCp(CO)₃ •2(C₆H₆) | |
|---|--|
| lattice | Triclinic |
| formula | C ₄₁ H ₅₁ BMoN ₆ O ₃ S ₃ Zn |
| formula weight | 944.17 |
| space group | <i>P</i> -1 |
| <i>a</i> /Å | 10.2866(10) |
| <i>b</i> /Å | 12.0489(12) |
| <i>c</i> /Å | 19.2260(19) |
| α /° | 92.6350(10) |
| β /° | 93.9040(10) |
| γ /° | 114.8880(10) |
| <i>V</i> /Å ³ | 2149.3(4) |
| <i>Z</i> | 2 |
| temperature (K) | 296(2) |
| radiation (λ , Å) | 0.71073 |
| ρ (calcd.), g cm ⁻³ | 1.459 |
| μ (Mo K α), mm ⁻¹ | 1.040 |
| θ max, deg. | 30.722 |
| no. of data collected | 35130 |
| no. of data used | 13225 |
| no. of parameters | 518 |
| R_1 [$I > 2\sigma(I)$] | 0.0398 |
| wR_2 [$I > 2\sigma(I)$] | 0.0871 |
| R_1 [all data] | 0.0607 |
| wR_2 [all data] | 0.0965 |
| GOF | 1.033 |
| R_{int} | 0.0504 |

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