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Synthesis of a Terminal Zinc Hydride Compound, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$, from a Hydroxide Derivative, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$: Interconversions with the Fluoride Complex, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}^\ddagger$

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Abstract: The terminal zinc hydride complex, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$, can be conveniently obtained from the hydroxide derivative, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$, by reaction with H_3NBH_3 . The zinc hydride complex $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ is reactive and the Zn–H bond undergoes (i) insertion of CO_2 to produce the formate complex, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2\text{CH})$, (ii) protolytic cleavage with Me_3SiOH to afford $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOSiMe}_3$, and (iii) metathesis with Me_3SnF to form the zinc fluoride derivative, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$. The fluoride derivative, which may also be formed by the reactions of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$ with $[\text{Me}_3\text{O}][\text{BF}_4]$ or Me_3SnF , can be converted back to $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ upon treatment with either H_3NBH_3 or $(\text{MeO})_3\text{SiH}$.

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Keywords: Zinc, hydride, fluoride, hydroxide, formate.

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‡ Dedicated to Professor Malcolm H. Chisholm on the occasion of his 70th birthday.

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Happy birthday, Malcolm!

INTRODUCTION

Monomeric zinc compounds that feature a terminal hydride ligand constitute a relatively rare class of molecules, but are of interest in view of the ability of zinc hydride compounds to serve as catalysts for organic transformations, such as hydrosilylation of aldehydes, ketones and carbon dioxide,^{1,2,3,4} dehydrocoupling of silanes and alcohols,^{1,5} and hydrogenation of nitriles,³ imines,⁶ and alkenes.⁵ The first monomeric zinc hydride compound, namely the *tris*(3-*tert*-butylpyrazolyl)hydroborato⁷ complex, [Tp^{Bu^t}]ZnH, was synthesized by the reaction of [Tp^{Bu^t}]Tl with ZnH₂,⁸ but several other methods have also been employed for obtaining zinc hydride compounds.⁹ For example, zinc hydride compounds have been obtained by (i) metathesis of zinc fluoride compounds with Et₃SiH,^{10,11} (ii) metathesis of zinc alkoxides or siloxides with silanes,^{2,12,13,14} (iii) the reactions of zinc chloride compounds with CaH₂,¹⁵ K[PrⁱN(H)BH₃],¹⁵ or [(Ph₂p_z)₃AlH]Li(THF),¹⁶ and (iv) hydrogenation of Cp*₂Zn.⁶ Herein, we report another method for synthesizing a terminal zinc hydride complex, namely the metathesis of a zinc hydroxide compound with H₃NBH₃, and also describe aspects of its reactivity, including the formation of a fluoride derivative.

RESULTS AND DISCUSSION

We have previously reported the synthesis of the *tris*(3-*tert*-butyl-5-methylpyrazolyl)hydroborato zinc hydride complex, [Tp^{Bu^t,Me}]ZnH,¹⁷ by the method described above for that of the less substituted derivative, [Tp^{Bu^t}]ZnH. In addition, we also observed that [Tp^{Bu^t,Me}]ZnH is formed upon dissolving the zinc aqua complex, {[Tp^{Bu^t,Me}]Zn(OH₂)}[HOB(C₆F₅)₃], in methanol, a reaction that is accompanied by the release of 3-*tert*-butyl-5-methylpyrazole.¹⁸ The formation of the zinc hydride complex in the latter reaction is of interest since it is generated in a protic environment. Also of note, deuterium labeling studies demonstrated that the source of the zinc hydride ligand is the borohydride group rather than either the H₂O/OH ligands or methanol solvent. Although the formation of [Tp^{Bu^t,Me}]ZnH from

$\{[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\text{OH}_2)\}[\text{HOB}(\text{C}_6\text{F}_5)_3]$ *via* the transfer of hydride from boron is of mechanistic interest, it is of little synthetic utility because it requires sacrificial destruction of a $[\text{Tp}^{\text{Bu}^t, \text{Me}}]$ ligand. It is, therefore, noteworthy that we have discovered a useful method for the synthesis of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ by metathesis involving a borane. Specifically, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ may be conveniently obtained from the hydroxide derivative, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$,¹⁹ by reaction with H_3NBH_3 , as illustrated in Scheme 1. Two advantages of this method are that it does not require the synthesis of either the thallium reagent, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Tl}$, or thermally unstable ZnH_2 .

Scheme 1.

In addition to H_3NBH_3 serving as a useful reagent to form $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ from the hydroxide compound, H_3NBH_3 also converts the fluoride, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$,¹⁰ to the hydride (Scheme 1). Furthermore, we have also observed that $(\text{MeO})_3\text{SiH}$ transforms $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$ to $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ (Scheme 1), which complements the aforementioned use of Et_3SiH .^{10,11}

In terms of reactivity, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ undergoes insertion of CO_2 into the Zn–H bond to give the formate complex, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2\text{CH})$, as illustrated in Scheme 2. The formation of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2\text{CH})$ is of note in view of the fact that there are relatively few examples of this transformation for monomeric zinc hydride compounds.^{13,20*} The formate moiety of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2\text{CH})$ is characterized by a singlet at 9.00 ppm in the ^1H NMR spectrum, a doublet ($^1\text{J}_{\text{C-H}} = 201$ Hz) at 166.3 ppm in the ^{13}C NMR spectrum, and absorptions at 1651 cm^{-1} [$\nu_{\text{asym}}(\text{CO}_2)$] and 1293 cm^{-1} [$\nu_{\text{sym}}(\text{CO}_2)$] in the IR spectrum (Figure 1). These vibrational frequencies have been confirmed by analysis of the ^{13}C labeled derivative, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2^{13}\text{CH})$, which has absorptions at 1610 cm^{-1} [$\nu_{\text{asym}}(^{13}\text{CO}_2)$] and 1272 cm^{-1} [$\nu_{\text{sym}}(^{13}\text{CO}_2)$] (Figure 1), and are most diagnostic of unidentate coordination, which is a common feature of zinc formate compounds.²¹ Specifically, unidentate coordination of carboxylate ligands is characterized by an increase in $\nu_{\text{asym}}(\text{CO}_2)$ and a decrease in $\nu_{\text{sym}}(\text{CO}_2)$ relative to that for uncoordinated carboxylate,²² which are 1585 cm^{-1} and 1351 cm^{-1} for the formate anion.²³ Furthermore, the difference between [$\nu_{\text{asym}}(\text{CO}_2)$] and [$\nu_{\text{sym}}(\text{CO}_2)$], *i.e.* $\Delta\nu = 358\text{ cm}^{-1}$, is significantly larger than the threshold value of 200 cm^{-1} that has been proposed to be indicative of unidentate coordination.²² The observation of κ^1 -coordination of the formate ligand is also in accord with the $\square\square\square\square$ entate coordination mode that has been determined crystallographically for the nitrate ligand in $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-ONO}_2)$.²⁴

* For other examples of insertion of CO_2 into the Zn–H bond of $[\text{Tp}^{\text{R}, \text{R}'}]\text{ZnH}$ complexes, see references 8 and 11.

Scheme 2.

Figure 1. IR spectrum of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2\text{CH})$ (top) and $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2^{13}\text{CH})$ (bottom). $\nu(\text{CO}_2)$ absorptions are indicated with an asterisk.

In addition to obtaining $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2\text{CH})$ by insertion of CO_2 into the Zn-H bond, the formate compound can also be obtained by protolytic cleavage using HCO_2H (Scheme 3). Other reactivity of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ which involves protolytic cleavage of the Zn-H bond is provided by the reaction with Me_3SiOH to afford the trimethylsiloxide

derivative, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOSiMe}_3$ (Scheme 3).[†] The latter compound is a counterpart of $[\text{Tp}^{\text{Bu}^t}]\text{ZnOSiMe}_3$, which we previously reported,⁸ and several other $[\text{Tp}^{\text{R}, \text{R}'}]\text{ZnOSiMe}_3$ derivatives that Chisholm has synthesized and used as effective initiators for the ring-opening polymerization of lactide.²⁵

$[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ is also susceptible to other classes of metathesis reactions, such as the formation of the zinc fluoride derivative, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$,¹⁰ upon reaction with Me_3SnF ,²⁶ a transformation that is accompanied by release of Me_3SnH (Scheme 3). The formation of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$ from $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ is of particular interest because silane reagents may be used to effect the *reverse* transformation, *i.e.* the formation of zinc hydride derivatives $[\text{Tp}^{\text{R}, \text{R}'}]\text{ZnH}$ from the corresponding fluoride complexes, $[\text{Tp}^{\text{R}, \text{R}'}]\text{ZnF}$ (*vide supra*).^{10,11} Thus, it is evident that the thermodynamics associated with Zn-F/E-H ($\text{E} = \text{Si}, \text{Sn}$) metathesis are strongly influenced by the nature of E ; as such, tin and silicon reagents may be used to interconvert zinc hydride and fluoride complexes (Scheme 1 and Scheme 3). In this regard, we also note that the tin reagent Me_3SnF may be used to obtain the fluoride derivative, $[\kappa^4\text{-Tptm}]\text{ZnF}$, from the hydride, $[\kappa^3\text{-Tptm}]\text{ZnH}$, and that the hydride complex may be regenerated by treatment of the fluoride complex with the silane reagent, PhSiH_3 .²⁷

[†] For the reactivity of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ towards alcohols, see reference 17.

Scheme 3.

Since terminal metal fluoride compounds are not common by comparison to the other halide derivatives,²⁸ we have investigated other methods to generate $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$. Thus, we have observed that $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$ may be generated by the reactions of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$ with either $[\text{Me}_3\text{O}][\text{BF}_4]$ or Me_3SnF (Scheme 4).

Scheme 4.

The molecular structure of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$ has been determined by X-ray diffraction, as illustrated in Figure 2. For comparison, there are very few examples of four-coordinate *tris*(pyrazolyl)hydroborato metal fluoride compounds of the type $[\text{Tp}^{\text{R}, \text{R}'}]\text{MF}$, with $[\text{Tp}]\text{BeF}$,²⁹ $[\text{Tp}^{\text{Bu}^t}]\text{CoF}$,³⁰ and $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{FeF}$ ³¹ being the only examples other than zinc listed in the Cambridge Structural Database.^{32,33}

Figure 2. The molecular structure of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$.

The Zn–F bond length of [Tp^{Bu^t,Me}]ZnF [1.8128(13) Å] is slightly shorter than that in the [Tp^{p-Tol,Me}]ZnF [1.849(4) Å]¹⁰ and {[Tp^{3Py,Me}]ZnF}₂ [1.849(3) Å]³⁴ counterparts, although the latter possesses a five-coordinate trigonal bipyramidal geometry by virtue of an interaction with a pyridyl group of an adjacent molecule. The Zn–F bond length of [Tp^{Bu^t,Me}]ZnF is also considerably shorter than that of the *tris*(mercaptoimidazolyl)hydroborato counterpart, [Tm^{Bu^t}]ZnF [1.916(13) Å],^{35‡} which features an [S₃] coordination environment rather than an [N₃] coordination environment. Several other terminal zinc fluoride compounds have been structurally characterized,^{33,36} such that the current range of bond lengths is 1.81 – 2.04 Å. As is evident from Table 1, the principal difference between the structures of [Tp^{R,R'}]ZnF and [Tm^{Bu^t}]ZnF is that the former compounds exhibit a greater distortion from tetrahedral coordination. For example, the F–Zn–N angles of [Tp^{R,R'}]ZnF range from 120.9° to 124.0°, while the N–Zn–N angles range from 93.8° to 95.1°; in contrast, the F–Zn–S (110.7°) and S–Zn–S (108.2°) angles of [Tm^{Bu^t}]ZnF are much closer to the tetrahedral value. In accord with these differences, the τ_4 four-coordinate geometry indices³⁷ for [Tp^{R,R'}]ZnF range from 0.81 to 0.83 (Table 1) and deviate considerably from the value of 1.00 for that of an idealized tetrahedron.

‡ The value of 1.916(13) Å is that which is listed in the CIF, whereas the paper lists a value of 1.85(1) Å. See reference 35.

Table 1. Comparison of Zinc Coordination Environments in Four-Coordinate Zinc Fluoride Compounds.

	$d(\text{Zn-F})/\text{\AA}$	F-Zn-X°	X-Zn-X°	τ_4	Reference
$[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$	1.8128(13)	120.89(6) - 123.93(7)	93.82(6) - 94.54(7)	0.81	this work
$[\text{Tp}^{p\text{-Tol}, \text{Me}}]\text{ZnF}$	1.849(4)	121.54(11)	95.14(14)	0.83	10
$[\text{Tm}^{\text{Bu}^t}]\text{ZnF}$	1.916(13) [‡]	110.69(12)	108.23(12)	0.98	35

SUMMARY

In summary, the terminal zinc hydride complex, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$, can be conveniently obtained from the hydroxide derivative, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$, by reaction with H_3NBH_3 . The zinc hydride complex $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ is reactive and undergoes insertion of CO_2 into the Zn-H bond to afford the formate complex, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2\text{CH})$. The Zn-H bond also participates in metathesis reactions, as illustrated by its susceptibility towards protolytic cleavage, such that $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ reacts with Me_3SiOH to afford $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOSiMe}_3$. Similarly, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ reacts with Me_3SnF to form the zinc fluoride derivative $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$ and Me_3SnH . The latter transformation is of particular interest because silane reagents, namely, $(\text{MeO})_3\text{SiH}$ and Et_3SiH , effect the *reverse* transformation, *i.e.* the formation of a zinc hydride from the corresponding fluoride.

EXPERIMENTAL SECTION

General considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under an argon atmosphere.³⁸ 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 SiMe_4 ($\delta = 0$) and

were referenced internally with respect to the protio solvent impurity ($\delta = 7.16$ for $\text{C}_6\text{D}_5\text{H}$).³⁹ ^{13}C NMR spectra are reported in ppm relative to SiMe_4 ($\delta = 0$) and were referenced internally with respect to the solvent ($\delta = 128.06$ for C_6D_6).³⁹ ^{11}B NMR are reported in ppm relative to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ($\delta = 0$) and were obtained by using the $\mathcal{E}/100\%$ value of 32.083974.⁴⁰ ^{19}F NMR chemical shifts are reported in ppm relative to CFCl_3 ($\delta = 0.0$) and were obtained by using the $\mathcal{E}/100\%$ value of 94.094011.⁴⁰ ^{29}Si NMR chemical shifts are reported in ppm relative to SiMe_4 ($\delta = 0.0$) and were obtained by using the $\mathcal{E}/100\%$ value of 19.867187.⁴⁰ 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. $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$ ^{19d} and $\text{Me}_3\text{SnF}^{41}$ were obtained by literature methods and Me_3SiOH (Sigma-Aldrich), $(\text{MeO})_3\text{SiH}$ (Acros) and H_3NBH_3 (Alfa Aesar) were used as received.

X-ray Structure Determination

X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection and refinement parameters are summarized in Table 2. The structure was solved by using direct methods and standard difference map techniques, and was refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2008/4).⁴²

Synthesis of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$

(i) A solution of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$ (154 mg, 0.30 mmol) in benzene (3 mL) was treated with a suspension of NH_3BH_3 (16 mg, 0.52 mmol) in benzene (2 mL). The mixture was stirred for a period of 4 hours and then filtered. The solution was lyophilized to give $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ as a white powder (121 mg, 81% yield) and was identified by comparison of the ^1H NMR spectrum with that of the literature.¹⁷

(ii) A solution of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$ (10 mg, 0.02 mmol) in benzene (0.5 mL) was treated with a suspension of NH_3BH_3 (3 mg, 0.10 mmol) in benzene (0.5 mL). The mixture was

stirred for a period of 16 hours and then filtered. The solution was lyophilized to give $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ as a white powder (6 mg, 62% yield).

(iii) A solution of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$ (10 mg, 0.02 mmol) in benzene (0.7 mL) was treated with $(\text{MeO})_3\text{SiH}$ (3 mg, 0.03 mmol). The mixture was stirred for a period of 12 hours, after which after which period the sample was lyophilized to give $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ as a white powder (7 mg, 73% yield).

Synthesis of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOSiMe}_3$

A solution of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ (10 mg, 0.02 mmol) in benzene (0.7 mL) was treated with Me_3SiOH (5 mg, 0.06 mmol) and heated at 60 °C for three days. After this period, the sample was lyophilized to give $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOSiMe}_3$ (11 mg, 93 % yield) as a white powder. Anal. calcd. for $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOSiMe}_3$: C, 56.1%; H, 8.5%; N, 14.5%. Found: C, 58.0%; H, 7.5%; N, 14.1%. ^1H NMR (C_6D_6): 0.60 [s, 9H of $\text{Si}(\text{CH}_3)_3$], 1.51 [s, 27H of $3(\text{C}(\text{CH}_3)_3)$], 2.08 [s, 9H of $3(\text{CH}_3)$], 4.71 [br, 1H of BH], 5.62 [s, 3H of $3(\text{C}_3\text{N}_2\text{H})$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 5.42 [s, 3C of $\text{Si}(\text{CH}_3)_3$], 12.64 [s, 3C of $3(\text{CH}_5)$], 31.14 [s, 9C of $3(\text{C}(\text{CH}_3)_3)$], 32.03 [s, 3C of $3(\text{C}(\text{CH}_3)_3)$], 102.92 [s, 3C of $3(\text{C}_3\text{N}_2\text{H})$], 143.95 [s, 3C of $3(\text{C}_3\text{N}_2\text{H})$], 163.49 [s, 3C of $3(\text{C}_3\text{N}_2\text{H})$]. $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): -9.7 [br, BH]. $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6): -5.1 [s, $\text{Si}(\text{CH}_3)_3$]. IR Data (ATR, cm^{-1}): 2960 (m), 1541 (m), 1465 (w), 1431 (m), 1383 (w), 1364 (m), 1343 (w), 1238 (m), 1187 (s), 1067 (s), 1036 (vs), 987 (w), 827 (s), 787 (s), 767 (s), 746 (m), 680 (w), 646 (m).

Synthesis of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$

(i) A solution of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ (50 mg, 0.10 mmol) in benzene (3 mL) was treated with Me_3SnF (30 mg, 0.16 mmol) and the mixture was heated at 60 °C for three days. After this period, the mixture was filtered and the solution was lyophilized to give $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$ as a white powder (49 mg, 95 % yield) which was identified by comparison of the ^1H NMR spectrum with that of an authentic sample that was structurally determined by X-ray diffraction.

(ii) A solution of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$ (2 mg, 0.004 mmol) in C_6D_6 (0.7 mL) was treated with Me_3SnF (4 mg, 0.02 mmol). The reaction was monitored by ^1H NMR spectroscopy which demonstrated the formation of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$ over a period of 2 hours at room temperature.

(iii) A solution of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$ (30 mg, 0.06 mmol) in benzene (1 mL) was treated with $[\text{Me}_3\text{O}][\text{BF}_4]$ (9 mg, 0.06 mmol). The mixture was filtered after a period of 2.5 hours and the solution obtained was lyophilized. The solid obtained was washed with pentane to give $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$ as a white powder (21 mg, 70% yield). Crystals suitable for X-ray diffraction were obtained by evaporation of a solution in benzene.

Synthesis of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2\text{CH})$

(i) A solution of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ (15 mg, 0.03 mmol) in C_6D_6 (1.5 mL) in an NMR tube equipped with a J. Young valve was treated with CO_2 (1 atm.). The mixture was heated at 60°C for a period of 12 hours, after which period the sample was lyophilized to give $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2\text{CH})$ as a white powder (15 mg, 92 % yield). ^1H NMR (C_6D_6): 1.51 [s, 27H of $3(\text{C}(\text{CH}_3)_3)$], 2.08 [s, 9H of $3(\text{CH}_3)$], 4.71 [br, 1H of BH], 5.66 [s, 3H of $3(\text{C}_3\text{N}_2\text{H})$], 9.00 [s, 1H of ZnO_2CH]. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 12.7 [s, 3C of $3(\text{CH}_5)$], 30.7 [s, 9C of $3(\text{C}(\text{CH}_3)_3)$], 32.1 [s, 3C of $3(\text{C}(\text{CH}_3)_3)$], 103.7 [s, 3C of $3(\text{C}_3\text{N}_2\text{H})$], 144.5 [s, 3C of $3(\text{C}_3\text{N}_2\text{H})$], 164.2 [s, 3C of $3(\text{C}_3\text{N}_2\text{H})$], 166.3 [s, 1C of ZnO_2CH]. $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): -9.4 [br, BH]. Anal. calcd. for $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2\text{CH})$: C, 56.3%; H, 7.7%; N, 15.7%. Found: C, 56.6%; H, 8.0%; N, 15.6%. IR Data (ATR, cm^{-1}): 2959 (m), 2865 (w), 2557 (w), 2202 (w), 1676 (w), 1651 (vs) [$\nu_{\text{asym}}(\text{CO}_2)$], 1542 (m), 1476 (m), 1465 (w), 1424 (m), 1385 (w), 1363 (m), 1337 (m), 1293 (s) [$\nu_{\text{sym}}(\text{CO}_2)$], 1243 (w), 1187 (s), 1129 (w), 1068 (s), 1032 (w), 991 (w), 870 (w), 857 (w), 843 (w), 806 (m), 789 (m), 767 (s), 730 (w), 680 (w), 647 (m), 521 (w), 498 (w), 452 (w), 431 (w), 409 (w).

(ii) A solution of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ (5 mg, 0.01 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with $^{13}\text{CO}_2$ (1 atm.). The mixture was heated at 60°C for a period of 20 hours, after which period the sample was lyophilized

to give $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2\text{CH})$ as a white powder. IR Data (ATR, cm^{-1}): 1610 cm^{-1} $[\nu_{\text{asym}}(^{13}\text{CO}_2)]$ and 1272 cm^{-1} $[\nu_{\text{sym}}(^{13}\text{CO}_2)]$.

(iii) A solution of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ (5 mg, 0.010 mmol) in C_6D_6 (0.7 mL) was treated with formic acid (10 μL , 0.27 mmol). The sample was monitored by ^1H NMR spectroscopy which demonstrated the formation of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Zn}(\kappa^1\text{-O}_2\text{CH})$ after a period of 10 minutes.

Table 2. Crystal, intensity collection, and refinement data.

	[Tp^{But,Me}]ZnF
lattice	Monoclinic
formula	C ₂₄ H ₄₀ BFN ₆ Zn
formula weight	507.80
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	9.4178(15)
<i>b</i> /Å	30.408(5)
<i>c</i> /Å	9.4614(15)
α /°	90
β /°	100.763(2)
γ /°	90
<i>V</i> /Å ³	2661.9(7)
<i>Z</i>	4
temperature (K)	150(2)
radiation (λ , Å)	0.71073
ρ (calcd.) g cm ⁻³	1.267
μ (Mo K α), mm ⁻¹	0.952
θ max, deg.	30.95
no. of data collected	46073
no. of data	9362
no. of parameters	314
R_1 [$I > 2\sigma(I)$]	0.0494
wR_2 [$I > 2\sigma(I)$]	0.1023
R_1 [all data]	0.0892
wR_2 [all data]	0.1153
GOF	1.027
R_{int}	0.0646

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APPENDIX A. Supplementary Data

Crystallographic data in CIF format (CCDC #1417144). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.xxxxxx>.

REFERENCES

- (1) (a) Sattler, W.; Parkin, G. *J. Am. Chem. Soc.* **2012**, *134*, 17462-17465.
 (b) Sattler, W.; Ruccolo, S.; Rostami Chaijan, M.; Nasr Allah, T.; Parkin, G. *Organometallics* DOI: 10.1021/acs.organomet.5b00506.
- (2) Mou, Z.; Xie, H.; Wang, M.; Liu, N.; Yao, C.; Li, L.; Liu, J.; Li, S.; Cui, D. *Organometallics* **2015**, *34*, 3944–3949.
- (3) Boone, C.; Korobkov, I.; Nikonov, G. I. *ACS Catal.* **2013**, *3*, 2336-2340.
- (4) Mimoun, H. *J. Org. Chem.* **1999**, *64*, 2582-2589.
- (5) Rit, A.; Spaniol, T. P.; Okuda, J. *Chem. Asian J.* **2014**, *9*, 612–619.
- (6) Jochmann, P.; Stephan, D. W. *Angew. Chem. Int. Ed. Engl.* **2013**, *52*, 9831–9835.
- (7) For reviews articles concerned with *tris*(pyrazolyl)hydroborato ligands, see:
 (a) *Scorpionates – The Coordination Chemistry of Polypyrazolylborate Ligands*, S. Trofimenko, Imperial College Press, London, 1999.
 (b) *Scorpionates II: Chelating Borate Ligands*, C. Pettinari, Imperial College Press, London, 2008.
 (c) Parkin, G. *Chem. Rev.* **2004**, *104*, 699-767.
 (d) Parkin, G. *Chem. Commun.* **2000**, 1971-1985.
 (e) Parkin, G. *Met. Ions Biol. Syst.*, Vol. 38, Chapter 14, pp 411-460; A. Sigel and H. Sigel, eds., M. Dekker, New York, 2001.
 (f) Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291-393.
 (g) Santini, C.; Pellei, M.; Lobbia, G. G.; Papini, G. *Mini-Rev. Org. Chem.* **2010**, *7*, 84-124.
 (h) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419-531.
- (8) (a) Han, R.; Gorrell, I. B.; Looney, A. G.; Parkin, G. *J. Chem. Soc. Chem. Commun.* **1991**, 717-719.

- (b) Looney, A.; Han, R.; Gorrell, I. B.; Cornebise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274-288.
- (9) Intemann, J.; Sirsch, P.; Harder, S. *Chem. Eur. J.* **2014**, *20*, 11204-11213.
- (10) Kläui, W.; Schilde, U.; Schmidt, M. *Inorg. Chem.* **1997**, *36*, 1598-1601.
- (11) Rombach, M.; Brombacher, H.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **2002**, 153-159.
- (12) Mukherjee, D.; Ellern, A.; Sadow, A. D. *J. Am. Chem. Soc.* **2010**, *132*, 7582-7583.
- (13) Sattler, W.; Parkin, G. *J. Am. Chem. Soc.* **2011**, *133*, 9708-9711.
- (14) Brown, N. J.; Harris, J. E.; Yin, X.; Silverwood, I.; White, A. J. P.; Kazarian, S. G.; Hellgardt, K.; Shaffer, M. S. P.; Williams, C. K. *Organometallics* **2014**, *33*, 1112-1119.
- (15) Spielmann, J.; Piesik, D.; Wittkamp, B.; Jansen, G.; Harder, S. *Chem. Commun.* **2009**, 3455-3456.
- (16) Snyder, C. J.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **2011**, 9210-9212.
- (17) Bergquist, C.; Parkin, G. *Inorg. Chem.* **1999**, *38*, 422-423.
- (18) Bergquist, C.; Koutcher, L.; Vaught, A. L.; Parkin, G. *Inorg. Chem.* **2002**, *41*, 625-627.
- (19) (a) Alsfasser, R.; Trofimenko, S.; Looney, A.; Parkin, G.; Vahrenkamp, H. *Inorg. Chem.* **1991**, *30*, 4098-4100.
- (b) Alsfasser, R.; Ruf, M.; Trofimenko, S.; Vahrenkamp, H. *Chem. Ber. Recl.* **1993**, *126*, 703-710.
- (c) Looney, A.; Han, R.; McNeill, K.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4690-4697.
- (d) Sattler, W.; Parkin, G. *Chem.Sci.* **2012**, *3*, 2015-2019.
- (20) For CO₂ insertion reactions of other zinc hydride complexes, see.
- (a) Merz, K.; Moreno, M.; Löffler, E.; Khodeir, L.; Rittermeier, A.; Fink, K.; Kotsis, K.; Muhler, M.; Driess, M. *Chem. Commun.* **2008**, 73-75.

- (b) Schulz, S.; Eisenmann, T.; Schmidt, S.; Blaser, D.; Westphal, U.; Boese, R. *Chem. Commun.* **2010**, 46, 7226-7228.
- (c) Rit, A.; Spaniol, T. P.; Maron, L.; Okuda, J. *Angew. Chem. Int. Edit.* **2013**, 52, 4664-4667.
- (d) Ermert, D. M.; Ghiviriga, I.; Catalano, V. J.; Shearer, J.; Murray, L. J. *Angew. Chem. Int. Edit.* **2015**, 54, 7047-7050.
- (e) Brown, N. J.; Harris, J. E.; Yin, X.; Silverwood, I.; White, A. J. P.; Kazarian, S. G.; Hellgardt, K.; Shaffer, M. S. P.; Williams, C. K. *Organometallics* **2014**, 33, 1112-1119.
- (21) See, for example, references 5, 13 and
- (a) Mukherjee, D.; Lampland, N. L.; Yan, K.; Dunne, J. F.; Ellern, A.; Sadow, A. D. *Chem. Commun.* **2013**, 49, 4334-4336.
- (b) Cheng, M.-L.; Li, H.-X.; Liu, L.-L.; Wang, H.-H.; Zhang, Y.; Lang, J.-P. *Dalton Trans.* **2009**, 2012-2019.
- (c) Chang, S.; Sommer, R. D.; Rheingold, A. L.; Goldberg, D. P. *Chem. Commun.* **2001**, 2396-2397.
- (22) (a) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, 33, 227-250.
- (b) Deacon, G. B.; Huber, F.; Phillips, R. J. *Inorg. Chim. Acta* **1985**, 104, 41-45.
- (c) Manhas, B. S.; Trikha, A. K. *J. Indian Chem. Soc.* **1982**, 59, 315-319.
- (23) Ito, K.; Bernstein, H. J. *Can. J. Chem.* **1956**, 34, 170-178.
- (24) Sattler, W.; Parkin, G. *Polyhedron* **2012**, 32, 41-48.
- (25) (a) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C.; Iyer, S. S.; Pacold, M.; Phomphrai, K. *J. Am. Chem. Soc.* **2000**, 122, 11845-11854.
- (b) Chisholm, M. H.; Gallucci, J. C.; Yaman, G. *Dalton Trans.* **2009**, 368-374.
- (c) Chisholm, M. H. *Inorg. Chim. Acta* **2009**, 362, 4284-4290.
- (26) For the use of Me₃SnF as a fluorinating agent, see:
- (a) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, 97, 3425-3468.

- (b) Roesky, H. W. *Inorg. Chem.* **1999**, 38, 5934-5943.
- (c) Herzog, A.; Liu, F.-Q.; Roesky, H. W.; Demsar, A.; Keller, K.; Noltemeyer, M.; Pauer, F. *Organometallics* **1994**, 13, 1251-1256.
- (27) Sattler, W.; Ruccolo, S.; Parkin, G. *J. Am. Chem. Soc.* **2013**, 135, 18714-18717.
- (28) (a) Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, 91, 553-573.
- (b) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, 97, 3425-3468.
- (c) Roesky, H. W. *Inorg. Chem.* **1999**, 38, 5934-5943.
- (d) Roesky, H. W.; Haiduc, I. *J. Chem. Soc. Dalton Trans.* **1999**, 2249-2264.
- (29) Naglav, D.; Bläser, D.; Wölper, C.; Schulz, S. *Inorg. Chem.* **2014**, 53, 1241-1249.
- (30) Gorrell, I. B.; Parkin, G. *Inorg. Chem.* **1990**, 29, 2452-2456.
- (31) Jové, F. A.; Pariya, C.; Scoblete, M.; Yap, G. P. A.; Theopold, K. H. *Chem. Eur. J.* **2011**, 17, 1310-1318.
- (32) For other [Tp^{R,R'}] metal fluoride compounds with non-four-coordinate geometries, see:
- (a) Adams, C. J.; Anderson, K. M.; Connelly, N. G.; Harding, D. J.; Hayward, O. D.; Orpen, A. G.; Patron, E.; Rieger, P. H. *Dalton Trans.* **2009**, 530-543.
- (b) Jones, P.; Amoroso, A. *Inorg. Chem.* **1997**, 36, 10-18.
- (c) Amoroso, A. J.; Thompson, A. M. C.; Jeffery, J. C.; Jones, P. L.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc. Chem. Commun.* **1994**, 2751-2752.
- (d) Etienne, M.; Carfagna, C.; Lorente, P.; Mathieu, R.; de Montauzon, D. *Organometallics* **1999**, 18, 3075-3086.
- (e) Liu, W.; Welch, K.; Trindle, C. O.; Sabat, M.; Myers, W. H.; Harman, W. D. *Organometallics* **2007**, 26, 2589-2597.
- (f) Hillier, A. C.; Maunder, G. H.; Liu, S. Y.; Eberspacher, T. A.; Metz, M. V.; McDonald, R.; Domingos, Â.; Marques, N.; Day, V. W.; Sella, A.; Takats, J. *Inorg. Chem.* **2001**, 40, 5106-5116.

- (g) Lee, E.; Kamlet, A. S.; Powers, D. C.; Neumann, C. N.; Boursalian, G. B.; Furuya, T.; Choi, D. C.; Hooker, J. M.; Ritter, T. *Science* **2011**, 334, 639–642.
- (33) Cambridge Structural Database (Version 5.36). *3D Search and Research Using the Cambridge Structural Database*, Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, 8 (1), pp 1 & 31-37.
- (34) Weis, K.; Vahrenkamp, H. *Inorg. Chem.* **1997**, 36, 5592-5596.
- (35) Tesmer, M.; Shu, M.; Vahrenkamp, H. *Inorg. Chem.* **2001**, 40, 4022-4029.
- (36) (a) Hahn, F. E.; Jocher, C.; Lügger, T.; Pape, T. *Z. Anorg. Allg. Chem.* **2003**, 629, 2341-2347.
- (b) Ambrosi, G.; Formica, M.; Fusi, V.; Giorgi, L.; Macedi, E.; Micheloni, M.; Paoli, P.; Pontellini, R.; Rossi, P. *Chem. Eur. J.* **2011**, 17, 1670-1682.
- (37) $\tau_4 = [360 - (\alpha + \beta)]/141$, where $\alpha + \beta$ is the sum of the two largest angles. See: Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955-964.
- (38) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. in *Experimental Organometallic Chemistry*, Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 2, pp 6-23. (b) Burger, B. J.; Bercaw, J. E. (b) Burger, B.J.; Bercaw, J. E. in *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98.
- (c) Shriver, D. F.; Drezdson, M. A.; *The Manipulation of Air-Sensitive Compounds*, 2nd Edition; Wiley-Interscience: New York, 1986.
- (39) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, 29, 2176-2179.
- (40) (a) Harris, R. K.; Becker, E. D.; De Menezes, S. M. C.; Goodfellow, R.; Granger, P. *Pure Appl. Chem.* **2001**, 73, 1795-1818.
- (b) Harris, R. K.; Becker, E. D.; De Menezes, S. M. C.; Granger, P.; Hoffman, R. E.; Zilm, K. W. *Pure Appl. Chem.* **2008**, 80, 59-84.

- 1
2
3
4
5
6 (41) Krause, E. *Ber. Dtsch. Chem. Ges.* **1918**, 51, 1447-1456.
7
8 (42) (a) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining, and
9 Displaying Crystal Structures from Diffraction Data; University of Göttingen,
10 Göttingen, Federal Republic of Germany, 1981.
11
12
13
14 (b) Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112-122.
15
16
17
18
19
20
21
22
23
24
25
26
27
28
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Graphical Pictogram

Graphical Abstract

The terminal zinc hydride complex, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$, can be conveniently obtained from the hydroxide and fluoride derivatives, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$ and $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$, by reaction with H_3NBH_3 , while treatment of the zinc hydride with Me_3SnF regenerates $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$.