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Synthesis, Structure, and Reactivity of a Terminal Organozinc Fluoride Compound: Hydrogen Bonding, Halogen Bonding, and Donor−Acceptor Interactions

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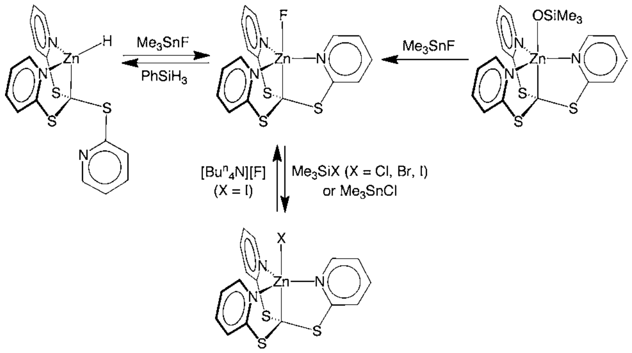
S *Supporting Information*

ABSTRACT: [Tris(2-pyridylthio)methyl]zinc fluoride, [κ^4-Tptm]ZnF, the first example of an organozinc compound that features a terminal fluoride ligand, may be obtained by the reactions of either [Tptm]ZnX (X = H, $OSiMe_3$) with Me_3SnF or [κ^4-Tptm]ZnI with $[Bu^n{}_4N]F$. Not only is the fluoride ligand of [κ^4-Tptm]ZnF susceptible to coordination by $B(C_6F_5)_3$ to give the adduct [κ^4-Tptm]$ZnFB(C_6F_5)_3$, but it is also an effective hydrogen bond and halogen bond acceptor. For example, X-ray diffraction studies demonstrate that [κ^4-Tptm]ZnF forms an adduct with water in which hydrogen bonding between the fluoride ligands and water molecules serves to link pairs of [κ^4-Tptm]ZnF molecules with a $[F\cdots(H\text{-}O\text{-}H)_2\cdots F]$ motif. Furthermore, ^1H and ^{19}F NMR spectroscopic studies provide evidence for hydrogen bonding and halogen bonding interactions with indole and C_6F_5I, respectively.

Although organozinc halides have played a prominent role as reagents in organic syntheses,[1] the chemistry of the fluoride derivatives is virtually nonexistent,[2] despite the fact that metal fluoride compounds are of fundamental interest. For example, metal fluoride compounds often exhibit novel structures[3] and reactivity,[4,5] as illustrated by their involvement in C-F bond formation[6] and cleavage,[7] and their role as catalysts for stereoselective and asymmetric transformations.[8] While one factor responsible for the dearth of organozinc fluoride compounds is that fluorocarbons possess strong C-F bonds, which inhibit the direct reaction with a metal center,[7] it has also been noted that convenient methods for synthesizing metal fluoride compounds are not generally available; indeed, such compounds are often obtained serendipitously as a result of ligand decomposition.[4,9] Therefore, it is significant that we report here the first organozinc compound that features a terminal fluoride ligand and also describe its reactivity, which includes its ability to serve as a Lewis base and as a hydrogen bond and halogen bond acceptor.

We recently employed the tris(2-pyridylthio)methyl ligand, [Tptm], to prepare a variety of organozinc derivatives of the type [Tptm]ZnX.[10,11] However, although the halide complexes [κ^4-Tptm]ZnX (X = Cl, Br, I) can be obtained *via* the reactions of [κ^4-Tptm]Li with ZnX_2,[10a,11] the fluoride counterpart [κ^4-Tptm]ZnF is not obtained from ZnF_2 under comparable conditions. It is, therefore, significant that we have discovered that the fluoride complex [κ^4-Tptm]ZnF can be conveniently obtained by metathesis of either [Tptm]ZnX (X = H, $OSiMe_3$) with Me_3SnF[12] or [κ^4-Tptm]ZnI with $[Bu^n{}_4N]F$, as illustrated in Scheme 1.

Scheme 1. Synthesis of [κ^4-Tptm]ZnF



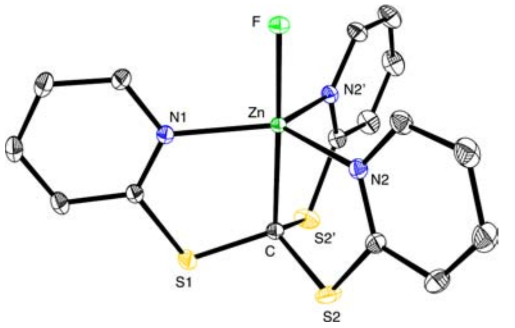


Figure 1. Molecular structure of [κ^4-Tptm]ZnF.

The molecular structure of [κ^4-Tptm]ZnF has been determined by X-ray diffraction (Figure 1), thereby revealing a well-defined monomeric trigonal bipyramidal geometry with an atrane motif[13] and axial carbon and fluorine atoms. The observation that [κ^4-Tptm]ZnF possesses a terminal fluoride ligand is not only of interest because of the propensity of the fluoride ligand to bridge two zinc centers,[14] but also because the hydroxide counterpart, $\{[\kappa^3\text{-Tptm}]Zn(\mu\text{-OH})\}_2$, exists as a hydroxide-bridged dimer in which the [Tptm] ligands coordinate in a κ^3-manner by using only two of the three pyridine donors.[10b]

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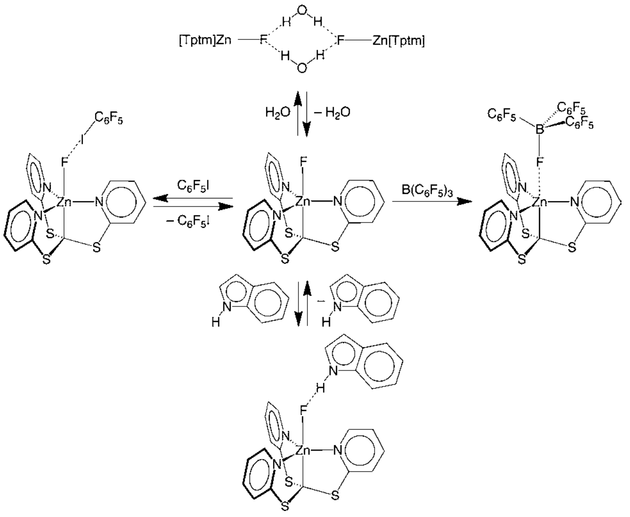
Scheme 2. Reactivity of [κ^4-Tptm]ZnF



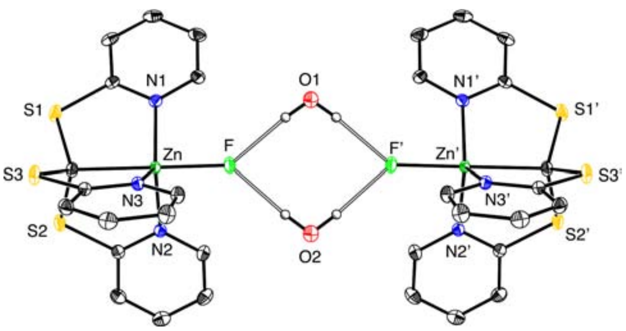


Figure 2. Molecular structure of [κ^4-Tptm]ZnF·H_2O.

The Zn-F bond length in [κ^4-Tptm]ZnF [1.944(1) Å] is within the range observed for the few other zinc compounds that feature terminal fluoride ligands (1.85−2.04 Å),[15,16] but is distinctly longer than that in the related neutral tris(pyrazolyl)-hydroborato complex, namely [$Tp^{p\text{-Tol,Me}}$]ZnF [1.849(4) Å],[15a] which also contains an N_3 donor array. The difference in Zn-F bond lengths reflects the fact that [$Tp^{p\text{-Tol,Me}}$]ZnF has an approximately tetrahedral geometry with a conventional 2-center-2-electron Zn-F bond, while [κ^4-Tptm]ZnF possesses a trigonal bipyramidal structure in which the Zn-F bond is a component of a 3-center-4-electron interaction[17] involving the bridgehead carbon atom of the [κ^4-Tptm] ligand. In this regard, the Zn-C bond length [2.221(2) Å] is also longer than the mean value of 2.01 Å for compounds listed in the CSD.

Spectroscopically, [κ^4-Tptm]ZnF is characterized by a ^{19}F NMR signal at δ −217.9 ppm, a value that is within the range for other zinc complexes with terminal fluoride ligands (δ −162 to −219 ppm).[15]

In terms of reactivity, the fluoride ligand of [κ^4-Tptm]ZnF is an effective hydrogen bond acceptor. For example, the fluoride complex may be isolated as the aqua adduct [κ^4-Tptm]ZnF·H_2O (Scheme 2), in which hydrogen bonding between the fluoride ligands and two water molecules serves to link pairs of [κ^4-Tptm]ZnF molecules with a [F···(H-O-H)$_2$···F] motif, as illustrated in Figure 2.[18−20] This hydrogen bonding motif, in which two water molecules bridge two metal fluoride ligands, is uncommon[21] and observed in extended structures, some of which feature hydrogen bonding interactions involving additional water molecules.[21a,b] [κ^4-Tptm]ZnF·H_2O, however, possesses a discrete dinuclear [F···(H-O-H)$_2$···F] core that does not exhibit any additional intermolecular hydrogen bonding interactions with other water molecules, and the closest nonbonded contacts for the oxygen atoms are with C-H bonds of the benzene of crystallization.[22]

The formation of the aqua complex [κ^4-Tptm]ZnF·H_2O is reversible, such that it may be converted to the anhydrous form by either treatment with KH or by exposing the sample to vacuum. Nevertheless, despite this reversibility, ^{19}F NMR spectroscopy provides evidence that hydrogen bonding interactions between [κ^4-Tptm]ZnF and water do persist in solution. For example, the ^{19}F NMR signal for [κ^4-Tptm]ZnF in benzene shifts progressively from δ −217.9 to −205.5 ppm upon addition of water.

Hydrogen bonding involving [κ^4-Tptm]ZnF is not restricted to interactions with water. For example, ^1H and ^{19}F NMR spectroscopic studies provide evidence for hydrogen bonding of [κ^4-Tptm]ZnF to indole (Scheme 2).[23] We have analyzed the NMR spectroscopic data in detail since there is relatively little quantitative thermodynamic data pertaining to hydrogen bonding interactions involving fluoride ligands.[23a,24,25] In this regard, Job plots[26] based on the ^1H and ^{19}F NMR spectroscopic data demonstrate that the interaction involves formation of a 1:1 adduct in benzene. Furthermore, analysis of the variation of the ^{19}F NMR chemical shift as a function of indole concentration provides a value of $K = 85 \pm 7\ M^{-1}$ at 27 °C for formation of the adduct, comparable to that for $(Et_3P)_2Ni(C_5NF_4)F$ (57.9 M^{-1}).[23a,27,28]

^{19}F NMR spectroscopy also demonstrates that the fluoride ligand of [κ^4-Tptm]ZnF can serve as an acceptor for a halogen bond (Scheme 2).[29] Specifically, the ^{19}F NMR spectroscopic signal of [κ^4-Tptm]ZnF shifts downfield in the presence of C_6F_5I and analysis of the concentration dependence indicates that the binding constant is $9.0 \pm 0.5\ M^{-1}$ in benzene,[30] approximately an order of magnitude smaller than that for the hydrogen bonding interaction with indole. For comparison, the only other study of this type pertaining to halogen bonding involving metal fluorides is for Ni, Pd and Pt complexes of the type *trans*-$(R_3P)_2M(Ar)F$,[23a,30a] for which the equilibrium constants range from 2.4 to 5.2 M^{-1}.[27,30a]

Consistent with its ability to serve as an acceptor for hydrogen bonding and halogen bonding interactions, the Lewis basicity of the fluoride ligand is exemplified by its coordination to the Lewis acid, $B(C_6F_5)_3$ (Scheme 2). Specifically, [κ^4-Tptm]ZnF binds $B(C_6F_5)_3$ to give [κ^4-Tptm]ZnFB$(C_6F_5)_3$, which has been structurally characterized by X-ray diffraction (Figure 3). The formation of [κ^4-Tptm]ZnFB$(C_6F_5)_3$ is significant because, despite the fact that $B(C_6F_5)_3$ is a well-known Lewis acid,[31,32] compounds that feature M-F-B$(C_6F_5)_3$ interactions are very rare.[33,34] The molecular structures of [κ^4-Tptm]ZnF and [κ^4-Tptm]ZnFB$(C_6F_5)_3$ thus provide the first comparison of a pair of M-F and M-FB$(C_6F_5)_3$ compounds, thereby enabling an evaluation of the binding of F^- and $[(C_6F_5)_3BF]^-$ to the same metal center.

In this regard, the Zn-F bond of the adduct [κ^4-Tptm]ZnFB$(C_6F_5)_3$ [2.262(3) Å] is significantly longer, by 0.32 Å (*i.e.* 16.5%), than that in the terminal fluoride complex [κ^4-Tptm]ZnF [1.9443(10) Å]. In contrast, the B-F bond of the adduct [κ^4-Tptm]ZnFB$(C_6F_5)_3$ [1.476(6) Å] is only 0.04 Å (*i.e.* 2.9%) longer than the average value for the $[(C_6F_5)_3BF]^-$ anion [1.434 Å] in non-metal-containing salts.[34d,e,35] Another indication of the magnitude of the interaction between boron and the fluoride ligand is provided by the sum of the C-B-C bond

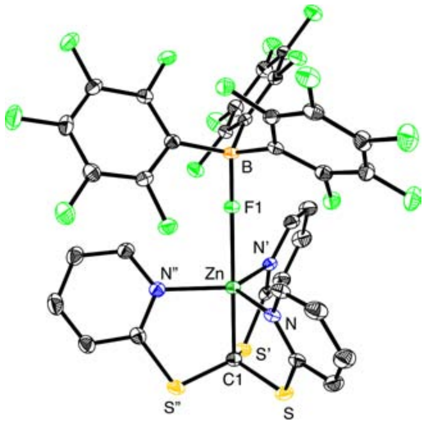


Figure 3. Molecular structure of [κ^4-Tptm]ZnFB(C_6F_5)$_3$.

angles,[32a,36,37] which indicates that the value for [κ^4-Tptm]ZnFB(C_6F_5)$_3$ (337.1°) is comparable to the average value for the [(C_6F_5)$_3$BF]$^-$ anion (334.5°) in non-metal-containing salts.[34d,e] Therefore, on the basis of both the bond length and geometrical changes that are associated with adduct formation, it is evident that the transfer to boron is largely complete. As such, the observation implies that the Lewis acidity of B(C_6F_5)$_3$ is greater than that of {[κ^4-Tptm]Zn}$^+$ with respect to its tendency to coordinate to fluorine in this system.

Spectroscopically, the [BF] moiety of [κ^4-Tptm]ZnFB(C_6F_5)$_3$ is characterized by broad ^{11}B and ^{19}F NMR signals at 2.17 and −198.6 ppm, respectively. These chemical shifts are very distinct from the respective values for B(C_6F_5)$_3$ (61.5 ppm)[33] and [κ^4-Tptm]ZnF (−217.9 ppm), but are comparable to those associated with the [(C_6F_5)$_3$BF]$^-$ anion.[38] On this basis, it is pertinent to consider the possibility that [κ^4-Tptm]ZnFB(C_6F_5)$_3$ exists as a dissociated pair of ions, {[κ^4-Tptm]Zn}$^+$ and [FB(C_6F_5)$_3$]$^-$, in solution. However, measurement of the translational self-diffusion coefficient by using pulsed gradient spin-echo (PGSE) diffusion NMR spectroscopic experiments[39] indicates that [κ^4-Tptm]ZnFB(C_6F_5)$_3$ remains intact in benzene solution. Specifically, the diffusion constant for [κ^4-Tptm]ZnFB(C_6F_5)$_3$, as measured by ^{1}H PGSE NMR spectroscopic experiments, indicates that the size of the molecule is distinctly larger than those of [κ^4-Tptm]ZnF and [Tptm]ZnOSiPh$_3$. Furthermore, ^{19}F PGSE experiments indicate that the {FB(C_6F_5)$_3$} moiety of [κ^4-Tptm]ZnFB(C_6F_5)$_3$ has a comparable diffusion constant to that of {[κ^4-Tptm]Zn}, thereby providing additional evidence that two entities are intact.

^{19}F NMR spectroscopic studies also indicate that [κ^4-Tptm]ZnFB(C_6F_5)$_3$ does not exist in solution with an appreciable equilibrium concentration of [κ^4-Tptm]ZnF and B(C_6F_5)$_3$,[40] and so it is evident that the interaction between [κ^4-Tptm]ZnF and B(C_6F_5)$_3$ is more exoergic than the hydrogen bonding and halogen bonding interactions with indole and C_6F_5I, respectively. It is also pertinent to note that the chloride derivative, [κ^4-Tptm]ZnCl, does not exhibit detectable interactions with either indole, C_6F_5I, or B(C_6F_5)$_3$, thereby underscoring the uniqueness of the fluoride ligand in this system.

The reactivity of [κ^4-Tptm]ZnF is not limited to reactions that merely involve coordination to the fluoride ligand. For example, [κ^4-Tptm]ZnF also undergoes metathesis reactions with silyl reagents, as illustrated by the reactions with PhSiH$_3$ to form the hydride complex [κ^3-Tptm]ZnH, and with Me$_3$SiX (X = Cl, Br, I) to form [κ^4-Tptm]ZnX. The occurrence of these reactions is in accord with the silaphilicity of fluorine[41] that results from the formation of products that feature strong Si-F bonds.[42] In addition to the transfer of fluorine from zinc to silicon, [κ^4-Tptm]ZnF reacts with the tin reagent Me$_3$SnCl to give [κ^4-Tptm]ZnCl and Me$_3$SnF. The occurrence of the latter reaction is in accord with the observation that, unlike [Tptm]ZnX (X = H, OSiMe$_3$), the chloride complex [κ^4-Tptm]ZnCl is not a suitable precursor for formation of [κ^4-Tptm]ZnF *via* reaction with Me$_3$SnF. In this regard, it is evident that the thermodynamics for fluoride exchange in this zinc system is in a different direction than in other systems, *e.g.* Cp*TiX$_3$, where the metal chloride derivative may be converted to the metal fluoride derivative by treatment with Me$_3$SnF.[12]

In summary, the terminal zinc fluoride complex [κ^4-Tptm]ZnF can be obtained by several methods, including metathesis of [Tptm]ZnX (X = H, OSiMe$_3$) with Me$_3$SnF. The fluoride ligand of [κ^4-Tptm]ZnF is not only susceptible to coordination by Lewis acidic B(C_6F_5)$_3$, but is also an effective hydrogen bond and halogen acceptor, as illustrated by the interactions with H$_2$O, indole and C_6F_5I. The fluoride ligand also exhibits a pronounced silaphilicity, such that it reacts with PhSiH$_3$ and Me$_3$SiX (X = Cl, Br, I) to give [κ^3-Tptm]ZnH and [κ^4-Tptm]ZnX, respectively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, computational data, and crystallographic data in CIF format. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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