Organozinc Fluoride and Trifluoromethyl Compounds Supported by the *Bis*(2-pyridylthio)methyl Ligand

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***Abstract**:* The *bis*(2-pyridylthio)methyl ligand, [Bptm], has been employed in the synthesis of {[Bptm]Zn(μ–F)}$_2$, a rare example of an organozinc fluoride compound. The dimeric nature of {[Bptm]Zn(μ–F)}$_2$, which possesses an uncommon [Zn(μ–F)]$_2$ motif, contrasts with the monomeric structures reported for the other halide derivatives, [Bptm]ZnX (X = Cl, Br, I); this difference is supported by density functional theory calculations which indicate that the fluoride derivative favors a dimeric form with bridging fluoride ligands, whereas the other derivatives favor monomeric structures with terminal halide ligands. {[Bptm]Zn(μ–F)}$_2$ reacts with Me_3SiCF_3 to afford the organozinc trifluoromethyl complex, namely [Bptm]ZnCF$_3$. The Zn–CF$_3$ bond in this complex is longer than the Zn–CH$_3$ bond of the previously reported methyl derivative [Bptm]ZnMe, an observation that is precedented in related zinc compounds, but counter to other metal complexes. The infrared frequency corresponding to the asymmetric C–F stretch of [Bptm]ZnCF$_3$ is unusually low for a metal trifluoromethyl species, but is comparable to that for other zinc and cadmium complexes.

INTRODUCTION

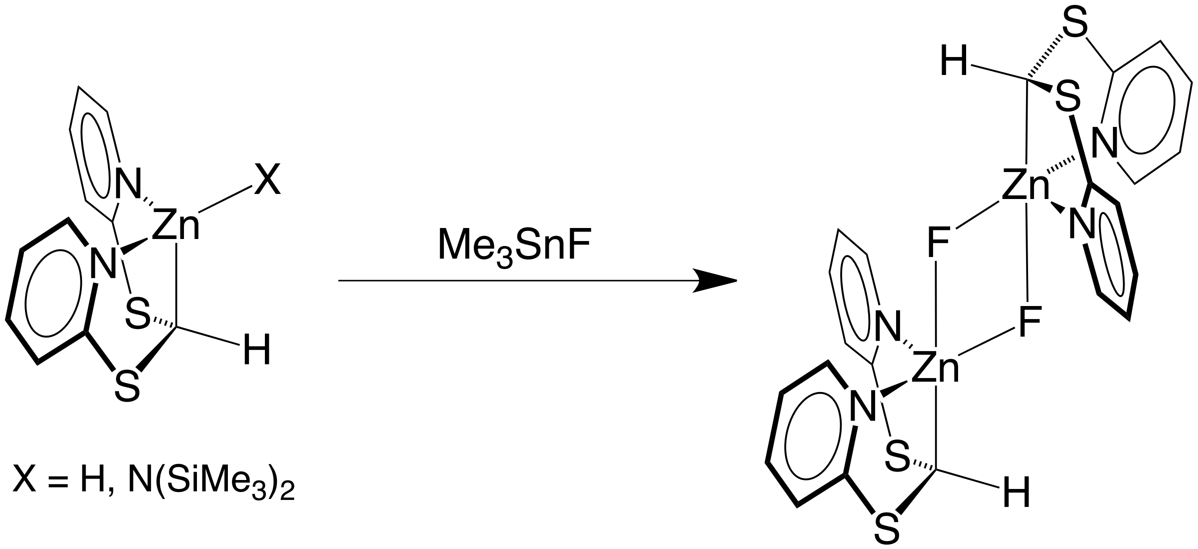
The chemistry of fluorine is often distinctly different from that of the other halogens as a consequence of its small size, high electronegativity and low polarisability.[1] Interest in fluorine chemistry has also risen dramatically over recent years, in part owing to the ubiquity of fluorine compounds in agrochemical[2] and pharmaceutical[3] industries. In addition, metal fluoride compounds, which often exhibit novel structures and reactivity,[4-9] have also attracted attention and have found applications in homogeneous and heterogeneous catalysis,[10] battery construction,[11] and optical materials.[12] Despite such interest, however, fluoride chemistry remains severely underexplored compared to that for the other halides. For example, with respect to zinc, the number of Zn–F bonds in compounds listed in the Cambridge Structural Database (CSD)[13] is only 1.5 % of the total number of zinc-halide interactions.[14,15] Moreover, notwithstanding that organozinc halides have played a prominent role as reagents in organic syntheses,[16] there is only a single mononuclear organozinc fluoride compound listed in the CSD, namely the *tris*(2-pyridylthio)methyl complex, [Tptm]ZnF.[14a,17] Similar to fluoride compounds, trifluoromethyl zinc compounds have also received little attention, especially by comparison to transition metal derivatives.[18] As an illustration, there is only a single structurally characterized compound possessing a Zn–CF_3 bond that is listed in the CSD.[19] Therefore, we describe here the use of the *bis*(2-pyridylthio)methyl ligand to afford rare examples of structurally characterized organozinc fluoride and trifluoromethyl compounds, namely $\{[Bptm]Zn(\mu\text{–}F)\}_2$ and $[Bptm]ZnCF_3$.

RESULTS AND DISCUSSION

1. Synthesis and Structural Characterization of $\{[Bptm]Zn(\mu\text{–}F)\}_2$

One factor that has been proposed for the paucity of metal fluoride compounds, compared to the other halide derivatives, is a dearth of suitable reagents to introduce the fluoride ligand.[5a] In this regard, it is pertinent to note that metal fluoride compounds are often obtained (sometimes serendipitously) as a result of decomposition of counterions such as $[BF_4]^-$.[20] One reason for the scarcity of conventional reagents for the synthesis of metal fluoride compounds is presumably a consequence of the thermodynamics and/or kinetics for introducing fluorine being unfavorable compared to corresponding reactions for the other halogens. For example, while we previously reported that the chloride, bromide and iodide complexes, [Tptm]ZnX (X = Cl, Br, I), can be obtained *via* the reactions of [Tptm]Li with ZnX_2, the fluoride complex [Tptm]ZnF is not obtained from ZnF_2 under comparable conditions.[14a] Furthermore, while $[Tptm]ZnOSiMe_3$ reacts with Me_3SiX (X = Cl, Br, I) to afford the corresponding halide derivative, [Tptm]ZnX, the fluoride counterpart [Tptm]ZnF is not obtained upon treatment of $[Tptm]ZnOSiMe_3$ with Me_3SiF.[14a] Therefore, it is noteworthy that we discovered that the tin reagent, Me_3SnF,[21] could be employed to synthesize the fluoride counterpart, [Tptm]ZnF.[14a] As such, we considered that Me_3SnF could also be used as a reagent for other zinc fluoride compounds.

Significantly, [Bptm]ZnH[22] reacts with Me_3SnF at room temperature to yield the fluoride complex, $\{[Bptm]Zn(\mu\text{–}F)\}_2$ (Scheme 1). In addition, $\{[Bptm]Zn(\mu\text{–}F)\}_2$ can also be obtained by the corresponding reaction between $[Bptm]ZnN(SiMe_3)_2$ and Me_3SnF. $\{[Bptm]Zn(\mu\text{–}F)\}_2$ has been characterized both spectroscopically and structurally by using X-ray diffraction. For example, $\{[Bptm]Zn(\mu\text{-}F)\}_2$ exhibits a signal in the ^{19}F NMR spectrum at δ -196.8 ppm,[23] and the molecular structure as determined by using X-ray diffraction is illustrated in Figure 1, with selected bond lengths and angles listed in Table 1.



Scheme 1.

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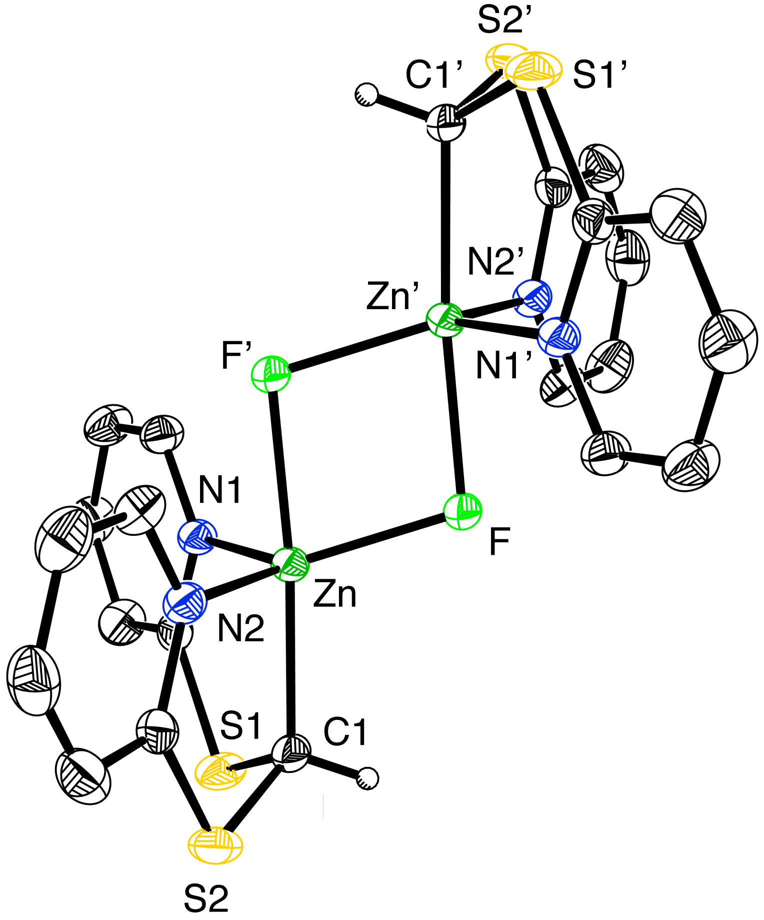


Figure 1. Molecular structure of {[Bptm]Zn(μ-F)}$_2$

Table 1. Selected metrical data for $\{[\text{Bptm}]\text{Zn}(\mu\text{-F})\}_2$

	$\{[\text{Bptm}]\text{Zn}(\mu\text{-F})\}_2$
d(Zn–F) / Å	1.9533(19)
d(Zn–F′) / Å	2.0888(18)
d(Zn–N1) / Å	2.084(3)
d(Zn–N2) / Å	2.102(3)
d(Zn–C1) / Å	2.097(3)
C1—Zn—F / °	107.11(12)
C1—Zn—F′ / °	174.77(12)
N1—Zn—N2 / °	118.94(11)
Zn—F—Zn′ / °	101.95(8)
F—Zn—F′ / °	78.05(8)

The structure of $\{[\text{Bptm}]\text{Zn}(\mu\text{–F})\}_2$ exhibits several interesting features. Firstly, in marked contrast to the other halide derivatives, [Bptm]ZnX (X = Cl, Br, I),[22] the fluoride complex $\{[\text{Bptm}]\text{Zn}(\mu\text{–F})\}_2$ is a dimer with bridging fluoride ligands.[4] Secondly, the dinuclear nature of $\{[\text{Bptm}]\text{Zn}(\mu\text{–F})\}_2$ is also distinct from the [Tptm]ZnF counterpart that is monomeric with a terminal fluoride ligand.[14a] Thirdly, the $[\text{Zn}(\mu\text{–F})]_2$ motif is not common, with there being only four discrete dinuclear compounds with this motif listed in the CSD (Table 2).

Table 2. Comparison of structural parameters in complexes that possess a $[Zn(\mu\text{-}F)]_2$ moiety.

	d(Zn–F)/Å	**Zn–F–Zn/°**	**Ref**
$\{[Bptm]Zn(\mu\text{-}F)\}_2$	1.9533(19), 2.0888(18)	101.95(8)	This work
$[\{HC(CMeNAr)_2\}Zn(\mu\text{-}F)]_2{}^a$	1.9473(12), 2.0034(11)	97.72(5)	15a
$[(C_{38}H_{36}N_8)\{Zn(\mu\text{-}F)\}_2](BF_4)_2$	1.938(2), 2.063(2)	104.53(11)	15b
$[Zn_4(L^{Et})_2F_4](BF_4)_4{}^b$	1.9860(15), 2.0581(14)	101.26(6)	15c
	1.9485(15), 2.1027(14)	104.17(6)	
$[Zn_2(\mu\text{-}F)_2({}^iPr\text{-}bpa)_2](BF_4)_2{}^c$	1.9313(11), 2.0462(12)	98.51(5)	15d

(a) Ar = 2,6-$Me_2C_6H_3$.

(b) L^{Et} = 4,6-bis[*N*,*N*-bis(2′pyridylethyl)aminomethyl]-2-phenylpyrimidine.

(c) ^{i}Pr-bpa = isopropyl-bis(2-picolyl)amine.

The Zn–F bond lengths of centrosymmetric $\{[Bptm]Zn(\mu\text{–}F)\}_2$ [1.9533(19) Å and 2.0888(18) Å] are slightly different, which is in accord with that observed in other structurally characterized examples of compounds that possess a $[Zn(\mu\text{-}F)]_2$ moiety (Table 2). Of these interactions, the longer Zn–F bond corresponds to the fluorine that is trans to the carbon atom. Interestingly, the shorter Zn–F bond is only slightly longer than the terminal Zn–F bond in the terminal fluoride counterpart, [Tptm]ZnF [1.944(1) Å]. With respect to these Zn–F bond lengths, it is pertinent to note that the average values for terminal and μ_2–bridging complexes listed in the CSD are 2.008 Å and 2.017 Å, respectively.

In addition to the Zn–F bond lengths, it is also relevant to compare the Zn–C and Zn–N bond lengths of $\{[Bptm]Zn(\mu\text{-}F)\}_2$ with those of [Tptm]ZnF (Table 3). The most significant difference is that the Zn–C bond length of $\{[Bptm]Zn(\mu\text{-}F)\}_2$ is 0.12 Å shorter than that in [Tptm]ZnF. This difference may be accounted by the fact that trigonal bipyramidal carbatrane motifs such as [Tptm]ZnX, [Titm]ZnX and $[Titm^{Pr^iBenz}]$ZnX possess 3c-4e hypervalent C–Zn–X interactions, such that the coordination of the atrane is flexible.[24]

Table 3. Comparison of Zn–X bond lengths in $\{[\text{Bptm}]\text{Zn}(\mu\text{-F})\}_2$ and [Tptm]ZnF

	***d*(Zn–F)/Å**	***d*(Zn–C1)/Å**	***d*(Zn–N)/Å**
$\{[\text{Bptm}]\text{Zn}(\mu\text{-F})\}_2$	1.9533(19)	2.097(3)	2.084(3)
	2.0888(18)		2.102(3)
[Tptm]ZnF	1.9443(10)	2.2207(16)	2.0782(10)
			2.0782(10)
			2.0911(14)

In view of the fact that the structure of fluoride complex $\{[\text{Bptm}]\text{Zn}(\mu\text{-F})\}_2$ is distinct from the monomeric structures of the other halide derivatives, the structures of both monomeric and dimeric forms of the complete series of halide derivatives were evaluated by using density functional theory (DFT) calculations. The geometry optimized structures of [Bptm]ZnX and $\{[\text{Bptm}]\text{Zn}(\mu\text{-X})\}_2$ (X = F, Cl, Br, I) are illustrated in Figure 2 and Figure 3, respectively.

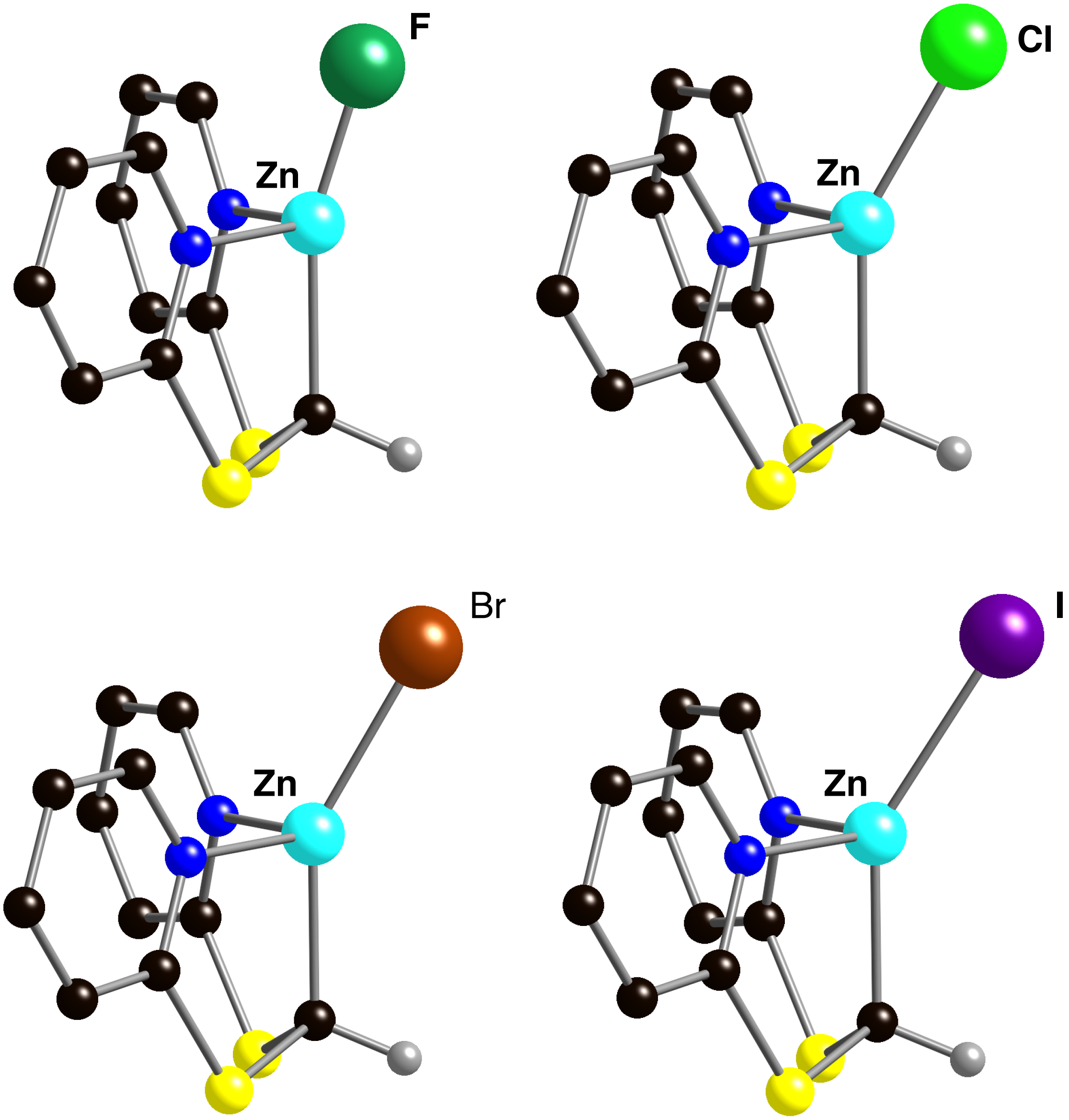


Figure 2. DFT Geometry optimized structures of [Bptm]ZnX (X = F, Cl, Br, I)

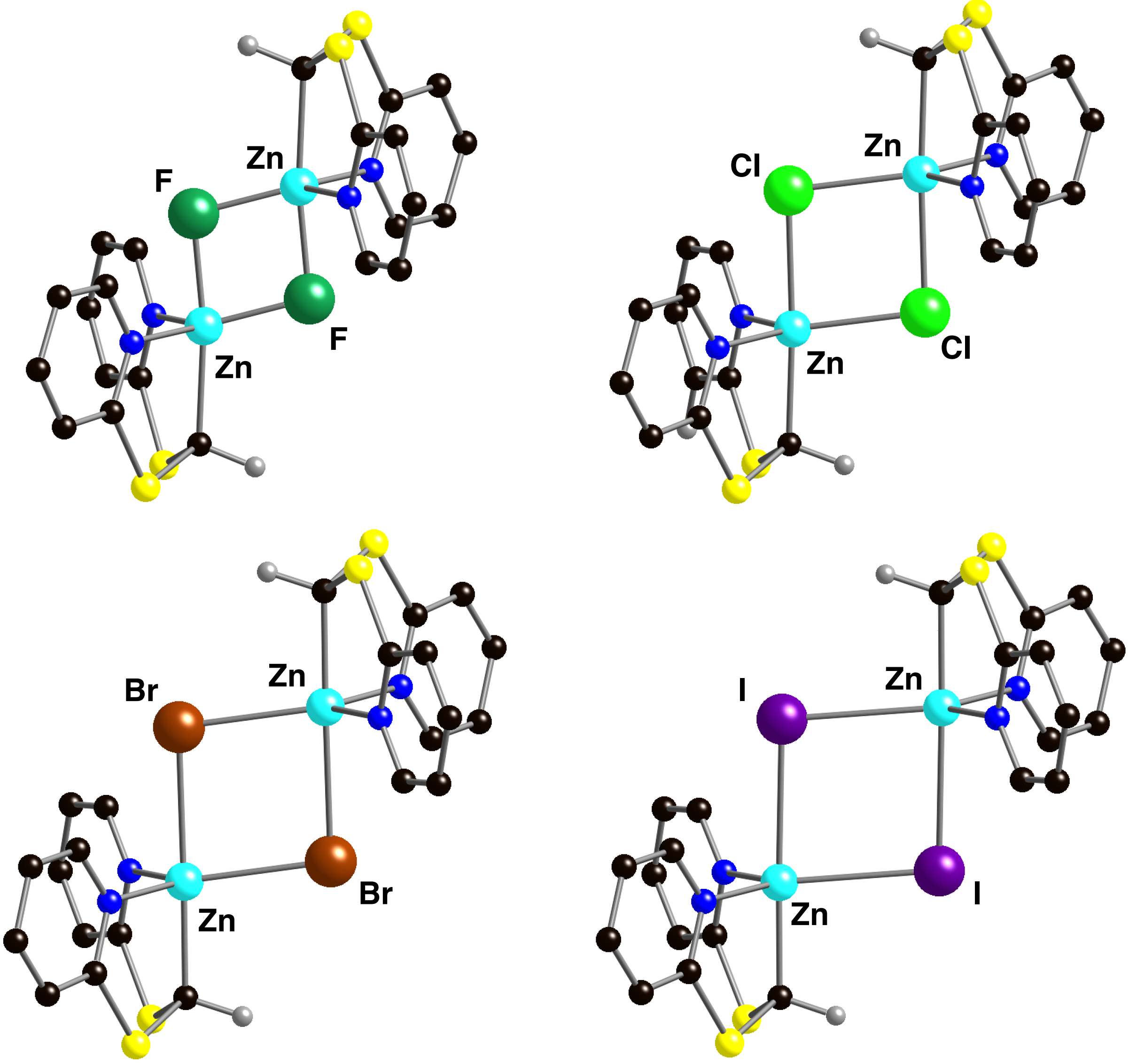


Figure 3. DFT Geometry optimized structures of {[Bptm]Zn(μ-X)}$_2$ (X = F, Cl, Br, I)

The Zn–X bond lengths for geometry optimized [Bptm]ZnX and {[Bptm]Zn(μ-X)}$_2$ are summarized in Table 4. In each case, the Zn–X bond lengths for the dinuclear structure are longer than the corresponding terminal Zn–X bond, but the most interesting aspect is that the difference in Zn–X bond length between the dimer and the monomer increases considerably in the sequence Zn–F < Zn–Cl < Zn–Br < Zn–I.

Table 4. Zn–X bond lengths for geometry optimized [Bptm]ZnX and {[Bptm]Zn(μ-X)}$_2$

	[Bptm]ZnX	**{[Bptm]Zn(μ-X)}$_2$**	**Δ/Å**
F	1.836	1.991 2.067	0.155 0.231
Cl	2.266	2.488 2.585	0.222 0.319
Br	2.460	2.713 2.837	0.259 0.377
I	2.647	2.972 3.042	0.325 0.395

Correspondingly, the energies associated with dimerization of [Bptm]ZnX to form [Bptm]Zn(μ-X)}$_2$ (Table 5) indicate that there is a much greater preference for the fluoride derivative to exist in its dimeric form compared to the other halide derivatives. In this regard, the preferential formation of a dimeric fluoride derivative and monomeric chloride, bromide, and iodide derivatives is precedented for other metal halide series, including magnesium,[25] aluminum,[26] and gallium.[27]

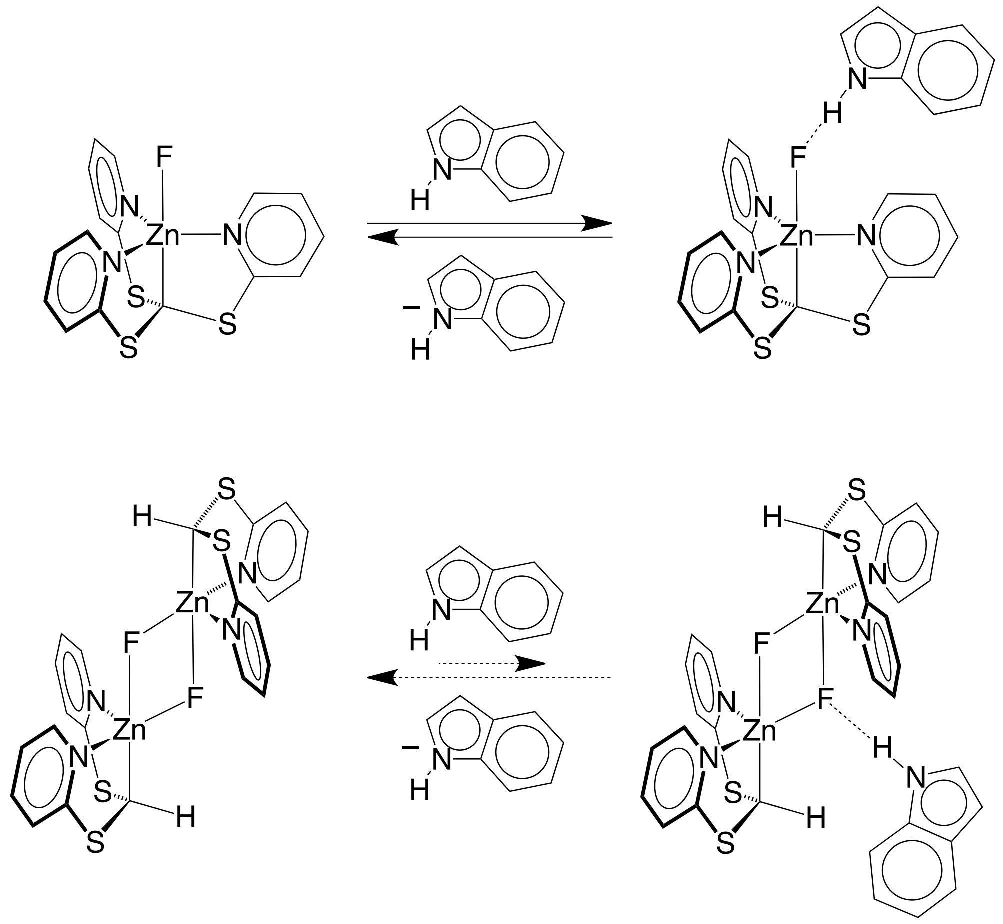
Table 5. Δ*G* for association of [Bptm]ZnX to form {[Bptm]Zn(μ-X)}$_2$ at 25˚C

X	**Δ*G*/kcal mol^{-1} *a***
F	–30.5
Cl	4.3
Br	8.7
I	17.5

(a) Δ*G* = *G*[{[Bptm]Zn(μ-X)}$_2$] – 2G[[Bptm]ZnX]

A simple rationalization for the preference of fluoride to serve as a bridging ligand is a consequence of the Zn–F bond being the most polar,[28] since it is wellestablished that a bond with greater polarity is more likely to form aggregated molecules.[4,29] Therefore, it is not surprising that {[Bptm]Zn(μ-F)}$_2$ is dimeric in the solid state, while the other [Bptm]ZnX (X = Cl, Br, I) derivatives are monomeric.

The different structures of {[Bptm]Zn(μ-F)}$_2$ and [Tptm]ZnF provide a means to compare the properties of bridging and terminal fluoride ligands in two closely related compounds. In this regard, metal fluoride compounds are known to participate in hydrogen bonding interactions,[30] and we previously demonstrated that [Tptm]ZnF exhibits hydrogen bonding interactions with indole (Scheme 2).[14a] Therefore, we examined the ability of {[Bptm]Zn(μ-F)}$_2$ to serve as a hydrogen bond acceptor for indole. Significantly, a solution of a mixture of {[Bptm]Zn(μ-F)}$_2$ and indole exhibits little perturbation in the ^{1}H NMR spectroscopic signals, which indicates that hydrogen bonding interactions with the bridging fluoride ligand are negligible compared to that of the terminal fluoride complex, [Tptm]ZnF (Scheme 2).[31] This observation is in accord with structural studies on terminal and bridging fluoride compounds which indicate that bridging fluoride ligands show a lower tendency to participate in hydrogen bonding interactions. For example, analysis of metal fluoride compounds that are listed in the CSD indicates that whereas 54 % of terminal metal fluoride ligands participate in hydrogen bonding interactions, only 16 % of μ$_2$–bridging fluoride ligands exhibit such interactions.[32]



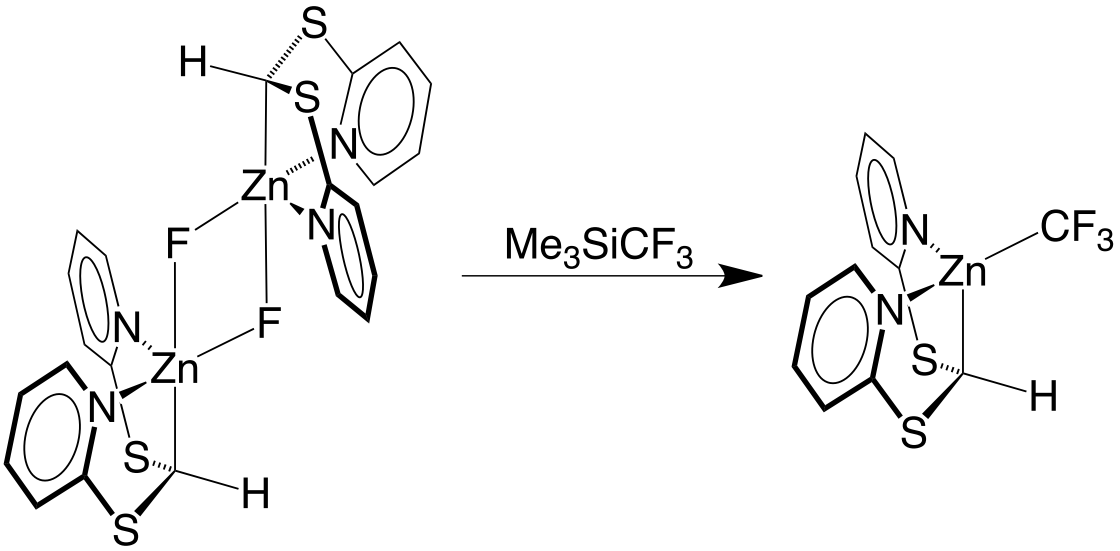
Scheme 2.

2. Synthesis and Structural Characterization of [Bptm]ZnCF$_3$

Trifluoromethyl groups are widespread in pharmaceuticals[33] and agrochemicals[34] and the formation of organic trifluoromethyl compounds often utilize trifluoromethyl-metal complexes as CF$_3$ sources.[18d,35-38] In this regard, trifluoromethyl zinc complexes have been employed for the trifluoromethylation of azinium salts,[39] aromatic compounds,[40,41] alkynes,[42] alkenes,[43] carboxamides,[44] sulfonamides,[44] cycloalkanone oximes,[45] and arylcyclopropanes.[46,47]

Despite this interest in trifluoromethyl zinc chemistry, however, trifluoromethyl zinc complexes are largely restricted to Zn(CF$_3$)$_2$ and CF$_3$ZnX derivatives, and their adducts. For example, the first report of zinc-trifluoromethyl complexes pertained to the use of NMR spectroscopy to identify the formation of Zn(CF$_3$)$_2$ and MeZnCF$_3$ upon the reaction of Me_2Zn with $Hg(CF_3)_2$.[48] Adducts of $Zn(CF_3)_2$, *e.g.* $py_2Zn(CF_3)_2$,[49,50] $(glyme)Zn(CF_3)_2$,[50] $(diglyme)Zn(CF_3)_2$,[50] $(dmpu)_2Zn(CF_3)_2$,[40] $(bpy)Zn(CF_3)_2$,[41] $(DMF)Zn(CF_3)_2$,[41] and $(tmeda)Zn(CF_3)_2$[40] have also been synthesized *via* the reactions of R_2Zn (R = Me, Et) with CF_3I in the presence of the corresponding ligand. Furthermore, halide derivatives, *e.g.* $(DMF)_2Zn(CF_3)Br$[51,52,53] and $(MeCN)_2Zn(CF_3)Br$,[51,53] have been synthesized *via* the reactions of Zn dust with CF_3Br.[54] In addition to these chemical methods, $L_2Zn(CF_3)_2$ and $L_2Zn(CF_3)X$ (X = Br, I) derivatives have also been obtained by the electrolysis of CF_3X using a zinc anode.[55,56]

In view of the paucity of trifluoromethyl zinc compounds, it is relevant to synthesize classes of trifluoromethyl zinc compounds that expand on $Zn(CF_3)_2$ and CF_3ZnX derivatives. In this regard, a useful approach for obtaining trifluoromethyl-metal compounds involves the reaction between a metal fluoride complex and Me_3SiCF_3 (the Ruppert-Prakash reagent).[57,58,59] As such, the above synthesis of the zinc fluoride compound $\{[Bptm]Zn(\mu\text{-}F)\}_2$ provides a means to obtain the trifluoromethyl derivative $[Bptm]ZnCF_3$ *via* reaction with Me_3SiCF_3 (Scheme 3), which has been characterized both spectroscopically and by using X-ray diffraction (Figure 4).



Scheme 3.

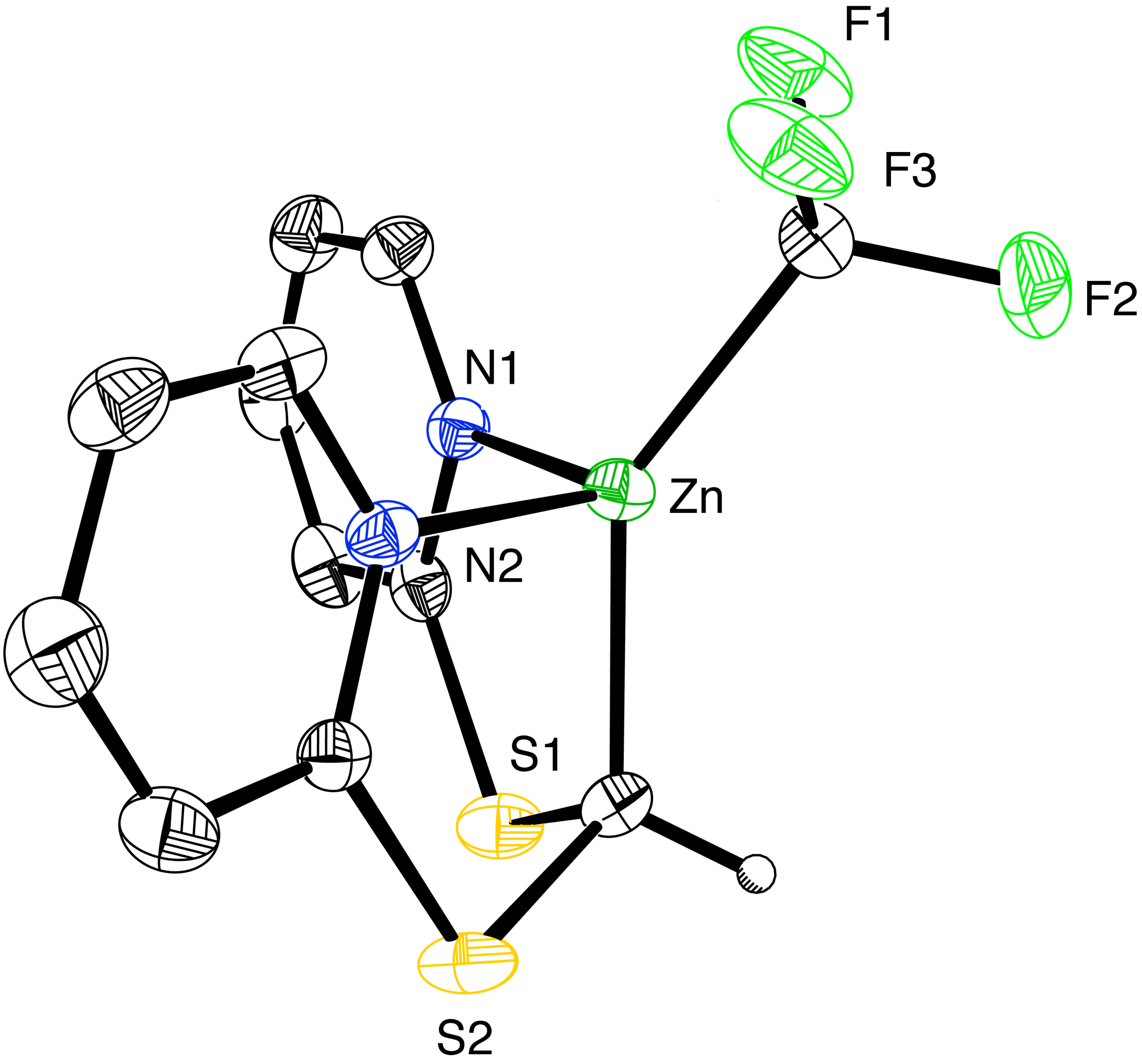


Figure 4. Molecular structure of [Bptm]$ZnCF_3$ (only one of the conformations of the CF_3 group is shown for clarity).

The structural characterization of [Bptm]$ZnCF_3$ is particularly noteworthy because there is very little metrical data pertaining to trifluoromethyl zinc compounds. Indeed, the CSD lists only one trifluoromethyl zinc compound, namely $py_2Zn(CF_3)_2$.[19,60] Examination of this structure, nevertheless, indicates that the Zn–CF_3 bond of

[Bptm]ZnCF$_3$ [2.016(3) Å] is short by comparison to those in py$_2$Zn(CF$_3$)$_2$ [2.056(3) Å and 2.069(4) Å].[19]

Another important aspect of the structure of [Bptm]ZnCF$_3$ is that comparison with that of the methyl derivative, [Bptm]ZnMe,[22] provides a means to assess how the Zn–CF$_3$ bond length compares with the Zn–CH$_3$ bond length in two structurally related molecules. The structural data for [Bptm]ZnCF$_3$ and [Bptm]ZnMe are presented in Table 6, from which it is evident that the Zn–CF$_3$ bond length [2.016(3) Å] is 0.032 Å longer than the corresponding Zn–CH$_3$ bond length [1.984(3) Å]. Significantly, a similar difference in Zn–CF$_3$ and Zn–CH$_3$ bond lengths (0.033 Å) is also observed for the DFT geometry optimized structures of [Bptm]ZnCF$_3$ and [Bptm]ZnMe (**Figure 5**).

Table 6. Comparison of metrical data for [Bptm]ZnCF$_3$ and [Bptm]ZnMe.

	[Bptm]ZnCF$_3$	**[Bptm]ZnMe^a**
d(Zn—C2) / Å	2.016(3)	1.984(3)
d(Zn—N1) / Å	2.054(2)	2.120(3)
d(Zn—N2) / Å	2.086(2)	2.119(3)
d(Zn—C1) / Å	2.028(3)	2.057(4)
C1—Zn—C2 / °	142.93(11)	146.09(16)
N1—Zn—N2 / °	107.27(8)	99.51(10)
C1—Zn—N1 / °	91.81(10)	89.50(15)
C1—Zn—N2 / °	90.88(9)	87.69(14)
C2—Zn—N1 / °	112.78(9)	110.27(14)
C2—Zn—N2 / °	106.52(9)	114.45(14)

(a) Data taken from reference 22.

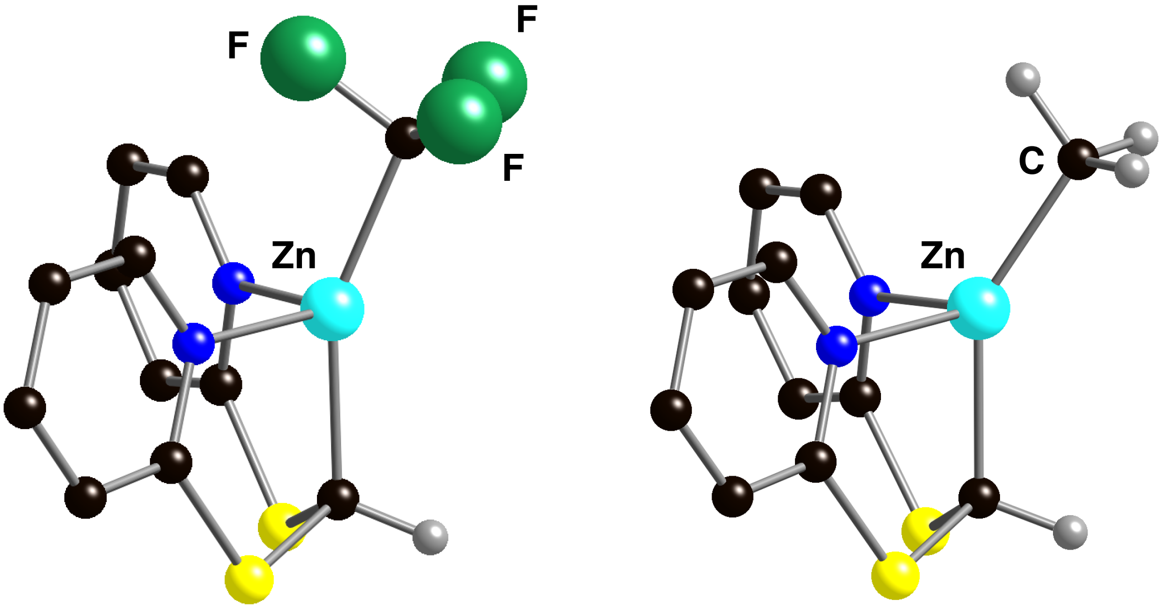


Figure 5. DFT geometry optimized structures of [Bptm]ZnCF$_3$ (left) and [Bptm]ZnMe (right).

While this difference is not large, the observation is significant because M–C bond lengths in fluoroalkyl compounds M–CF$_3$ are often expected to be ***shorter*** than metal-alkyl counterparts.[18] As an illustration, an early example was provided by the comparison of the Mn–CF$_3$ and Mn–CH$_3$ bond lengths in Mn(CO)$_5$CF$_3$[61] and Mn(CO)$_5$Me,[62] as determined by gas phase electron diffraction, which indicates that the Mn–CF$_3$ bond is 0.13 Å shorter than the Mn–CH$_3$ bond (Table 6). The fact that the Zn–CF$_3$ bond is longer than the Zn–CH$_3$ bond in [Bptm]ZnX is, nevertheless, supported by related studies on pyridine adducts, (py^R)$_2$ZnX$_2$. Thus, although the compounds possess different pyridine substituents, the Zn–CF$_3$ bond lengths in (py)$_2$Zn(CF$_3$)$_2$[19] are longer than the Zn–CH$_3$ bond lengths in (4-Bu^{t}py)$_2$ZnMe$_2$[63] and (4-Me$_2$Npy)$_2$ZnMe$_2$.[64] For example, the average Zn–CF$_3$ bond length in (py)$_2$Zn(CF$_3$)$_2$ is 0.064 Å longer than the average Zn–CH$_3$ bond length in (4-Bu^{t}py)$_2$ZnMe$_2$.

Although there are no structurally characterized trifluoromethyl cadmium compounds, there are two structurally characterized trifluoromethyl mercury compounds for which the methyl counterparts are known, namely $Hg(CF_3)_2$ and CF_3HgN_3. With respect to the former, the Hg–C bond in $Hg(CF_3)_2$ is 0.026 Å longer than that in $HgMe_2$,[65,66,67] which is in accord with the above zinc compounds. Despite this agreement, however, the Hg–C bond in CF_3HgN_3 is 0.010 Å shorter than that in $MeHgN_3$.[68,69]

To place these observations in more context, the M–CF_3 and M–CH_3 bond lengths in structurally related metal complexes are presented in Table 7.[70-80] In addition, average M–CF_3 and M–CH_3 bond lengths for elements that possess structurally characterized trifluoromethyl compounds are summarized in Table 8. Examination of these data indicate that the notion that M–CF_3 bonds are shorter than corresponding M–CH_3 bonds is not universally observed. For example, with respect to metals of the first transition series, it has been noted that Ti–CF_3 bonds are longer than Ti–CH_3 bonds in titanocene compounds,[57c,d] while the Ni–CF_3 and Ni–CH_3 bond lengths in (dippe)Ni$(CF_3)_2$ and (dippe)NiMe_2 are virtually identical.[59b] The direct structural comparison of [Bptm]ZnCF_3 and [Bptm]ZnMe thus provides further evidence that the difference in M–CF_3 and M–CH_3 bond lengths is very dependent on the nature of the metal center. In this regard, it is also pertinent to note that, with respect to nonmetals, it has been observed that X–CF_3 (X = F, Cl, Br) bond lengths[81] are shorter than the corresponding values in X–CH_3 bond lengths and that the difference increases with the electronegativity of X, with a difference of 0.066 Å for the fluoride derivative.[81a] Consistent with this trend, the C–H bond in CF_3–H is slightly longer (0.003 Å) than that in CH_3–H.[81a] Likewise, a similar trend in the difference in CF_3–E and CH_3–E bond lengths has been observed for (i) $E(CF_3)_2/E(CH_3)_2$ (E = O, S, Se) and (ii) $E(CF_3)_3/E(CH_3)_3$ (E = N, P, As), with the more electronegative atoms having shorter E–CF_3 bonds (E = N, O), and the less electronegative congeners having longer E–CF_3 bonds (E = S, Se, P, As).[81]

Table 7. Comparison of M–CF_3 and M–CH_3 bond lengths in structurally related compounds.

L_nMCF_3	**L_nMCH_3**	***d*(M–CF_3)/Å**	***d*(M–CH_3)/Å**	**Δ /Å^a**	**CF_3 Ref**	**CH_3 Ref**
$Cp_2Ti(CF_3)N_3$	Cp_2TiMe_2	2.239(1)	2.176(av)	0.063	57d	70
$Cp_2Ti(CF_3)Cl$	Cp_2TiMe_2	2.301(6)	2.176(av)	0.125	57d	70
$Cp_2Ti(CF_3)F$	Cp_2TiMe_2	2.221(3)	2.176(av)	0.045	57c	70
$Cp^*Cr(CO)_3CF_3$	$(Cp^{Bu^t_3})Cr(CO)_3Me$	2.129(2)	2.2663(15)	-0.137	71	72
$Cp^*W(CO)_3CF_3$	$Cp^{Pr^i_4}W(CO)_3Me$	2.189(19)	2.288(5)	-0.099	71	73
$Mn(CO)_5CF_3$	$Mn(CO)_5Me$	2.056±0.005^b 2.067(3)	2.185±0.011^b	-0.13	61, 74	62
$(dippe)Ni(CF_3)_2$	$(dippe)NiMe_2$	1.971(3)	1.975(3)	-0.004	59b	59b
$(BOXAM)NiCF_3$^{c}	$(BOXAM)NiMe$^{c}	2.040(4)	2.077(4)	-0.037	59c	59c
$(SP)Pt(CF_3)_2$^{d}	$(SP)PtMe_2$^{d}	2.032(5) 2.082(5)	2.166(5) 2.052(6)	-0.052	75	75
$[Ph_2(CF_3)P]_2Pt(CF_3)Cl$	$(Ph_2MeP)_2PtMeCl$	2.09	2.081(6)	0.01	76	76
$[PPh_4][Au(CF_3)_2]$	$[NBu^n_4][AuMe_2]$	2.033(2)	2.075(av)	-0.042	77	78
$Hg(CF_3)N_3$	$HgMeN_3$	1.96(2)	2.058(15)	-0.10	68	69
$Hg(CF_3)_2$	$HgMe_2$	2.109(16)	2.083^b	0.026	65	66
$[Bptm]ZnCF_3$	$[Bptm]ZnMe$	2.016(3)	1.984(3)	0.032	this work	22
$(py)_2Zn(CF_3)_2$	$(4\text{-}Bu^tpy)_2ZnMe_2$	2.063(av)	1.999(av)	0.064	19	63
$(py)_2Zn(CF_3)_2$	$(4\text{-}Me_2Npy)_2ZnMe_2$	2.063(av)	2.0221(18)	0.046	19	64
$Sn(CF_3)_4$	$SnMe_4$	2.201±0.003^b	2.144±0.003^b	0.057	79	80

(a) Δ = *d*(M–CF_3) – *d*(M–CH_3); average values given where appropriate. (b) GED values. (c) BOXAM = bis(4-isopropyl-4,5-dihydrooxazol-2-yl)phenyl)amine). (d) SP = (2-vinylphenyl)diphenylphosphine.

Table 8. Comparison of average M–CF_3 and M–CH_3 bond lengths for structurally characterized compounds listed in the CSD.

Metal	***d*(M–CH_3)/Å**	***d*(M–CF_3)/Å**	**Δ/Å**[a]
Ti	2.129	2.235	0.106
Cr	2.081	2.090	0.009
Mn	2.126	2.067	-0.059
Co	2.001	1.938	-0.063
Ni	1.957	1.933	-0.024
Cu	1.941	1.955	0.014
Zn	1.967	2.047[b]	0.080
Ge	1.949	1.998	0.049
Mo	2.215	2.226	0.011
Rh	2.088	2.082	-0.006
Pd	2.050	2.052	0.002
Ag	2.097	2.092	-0.005
W	2.197	2.189	-0.008
Ir	2.131	2.121	-0.01
Pt	2.067	2.058	-0.009
Au	2.064	2.069	0.005
Hg	2.059	2.124	0.065

(a) $\Delta = d(\mathrm{M{-}CF_3}) - d(\mathrm{M{-}CH_3})$

(b) includes the value for [Bptm]ZnCF_3

In addition to the structure determination, the CF_3 moiety of [Bptm]ZnCF_3 is characterized spectroscopically by ^{19}F and ^{13}C NMR spectroscopic signals at –39.7 and 146.1 ppm respectively, with a $^{1}J_{C-F}$ coupling constant of 355 Hz. These spectroscopic data are in accord with the corresponding values reported for the trifluoromethyl moiety in other zinc compounds (Table 9).[82] It is also pertinent to note that the ^{19}F NMR signal for the [Bptm]Zn^{13}CF$_3$ isotopologue (–39.81 ppm) exhibits a secondary isotope shift, *i.e.* $^1\Delta^{19}$F($^{13/12}$C),[83] of -0.14 ppm relative to the [Bptm]Zn^{12}CF$_3$ isotopologue. For reference, a comparable value of $^1\Delta^{19}$F($^{13/12}$C) is observed for CF$_3$H (-0.13 ppm),[84] (CF$_3$)$_2$CO (-0.13 ppm),[85] and other organofluorine compounds.[83b,c]

Table 9. ^{13}C and ^{19}F NMR spectroscopic data for trifluoromethyl zinc compounds.

	δ ^{13}C/ppm	**δ ^{19}F/ppm**	**$^1J_{C-F}$/Hz**	**Ref**
[Bptm]ZnCF$_3$	146.1	-39.7	355	This work
py$_2$Zn(CF$_3$)$_2$	146.7	36.0[a]	–	19
MeZn(CF$_3$)$_2$	–	-44.5	–	50
Zn(CF$_3$)$_2$	–	-43.7	–	50
EtZn(CF$_3$)$_2$	–	-44.0	–	50
(dmpu)$_2$Zn(CF$_3$)$_2$	146.2	-43.5	359	40
(bpy)$_2$Zn(CF$_3$)$_2$	147.7	-42.8	359	41
(MeCN)$_2$Zn(CF$_3$)Br	145.5	-42.6	355	51
(DMF)$_2$Zn(CF$_3$)Br	–	-47.9	358	51

(a) See reference 82.

[Bptm]ZnCF$_3$ has also been investigated by using IR spectroscopy. In this regard, trifluoromethyl compounds, CF$_3$–X, typically exhibit two bands in the region ca. 950 cm^{-1} – 1250 cm^{-1} associated with the symmetric and asymmetric C–F stretches of the CF$_3$ moiety, as illustrated in Table 10. The assignment of the symmetric and asymmetric bands, however, depends critically on the system. Thus, while the higher frequency band is often considered to be the symmetric stretch for trifluoromethyl-metal compounds,[86] the order may sometimes be reversed. For example, the symmetric stretch for (CO)$_4$CoCF$_3$ is of lower energy than the asymmetric stretch.[87] As another illustration, whereas the symmetric stretch of CF$_3$SiH$_3$ is of higher energy than the asymmetric stretch, the opposite order is observed for CF$_3$PH$_2$, CF$_3$SH and CF$_3$Cl.[88]

Furthermore, it is pertinent to note that the original assignment of the symmetric and asymmetric stretches of $Hg(CF_3)_2$ has been reversed; for the new assignment, the symmetric stretch is of higher energy than the asymmetric stretch.[89] The relative change in energies of the symmetric and asymmetric stretches of CF_3X compounds as a function of the system is undoubtedly associated with the fact that the C–F motion is coupled to the C–X motion.

With respect to [Bptm]$ZnCF_3$, the bands associated with the C–F stretches are observed at 1140 cm^{-1} and 958 cm^{-1}. In accord with other trifluoromethyl-metal compounds,[90] these absorptions are at lower energies than typical nonmetal derivatives such as CF_3X (X = Cl, Br, I) and Me_3SiCF_3 (Table 10). More interestingly, however, while the symmetric C–F stretch of [Bptm]$ZnCF_3$ is comparable to that of halide derivatives, CF_3X (X = Cl, Br, I), the asymmetric stretch is of considerably lower energy (Table 10). Precedent for the observed C–F stretches of [Bptm]$ZnCF_3$ is, nevertheless, provided by the zinc and cadmium derivatives, $py_2Zn(CF_3)_2$[91] and $Cd(CF_3)_2$,[92] as summarized in Table 10.[93-114] Although the observation of low energy C–F stretching frequencies in transition metal trifluoromethyl compounds was once considered to be a consequence of π-backbonding,[118] it is now recognized that such changes are associated with the σ-bonding framework.[115,116,117]

By direct comparison of the symmetric and asymmetric stretches, the data in Table 10 also illustrate the more pronounced effect of X on the asymmetric stretch than the symmetric stretch of CF_3X compounds.[118] Recognizing that the symmetric and asymmetric stretches may have a different order (*vide supra*) is important because it could otherwise appear that substitution of X results in little effect. For example, while the C–F stretching frequencies of CF_3Cl (1210 cm^{-1} and 1102 cm^{-1})[93] and CF_3SiH_3 (1223 cm^{-1} and 1110 cm^{-1})[88,110] are similar, they have opposite assignments, with the high energy band corresponding to the asymmetric stretch for CF_3Cl, but the symmetric stretch for CF_3SiH_3.

Table 10. Symmetric and asymmetric C–F vibrations for selected trifluoromethyl compounds.[a]

Compound	ν_s/cm^{-1}	ν_{as}/cm^{-1}	Ref
CF_3Cl	1102	1210	93
	1107	1217	94
	1106	1217	95
CF_3Br	1087	1207	93
	1081	1209	96
CF_3I	1076	1185	93
CF_3SH	1137	1199/1166	88
CF_3SeH	1125	1170	96
CF_3PH_2	1154	1187	88
CF_3AsH_2	1144	1160	96
CF_3SiH_3	1223	1110	88,110
Me_3SiCF_3	1227	1085	97
Me_3GeCF_3	(1194)	(1098)	98
CF_3GeF_3	1180	1166	96
CF_3GeCl_3	1165	1157	96
CF_3GeBr_3	1147	1153	96
$[HNMe_3][Ge(CF_3)_3]$	1056	1172	99
Me_3SnCF_3	(1152)	(1066)	101
Me_3PbCF_3	(1170)	(1040)	86
F_2BCF_3	(1190)	(1080)	102
$[Bptm]ZnCF_3$	1140	958	this work
$py_2Zn(CF_3)_2$	(1144, 1130)	(960, 945)	100
$Cd(CF_3)_2$	(1157, 1135)	(980, 960)	103
$Hg(CF_3)_2$	1148, 1133	1045	89
$Cp_2Ti(CF_3)F$	(1081)	-	104
$Cp_2Ti(CF_3)N_3$	(1065)	-	104
$Cp_2Ti(CF_3)Cl$	(1077)	-	104
$Cp_2Ti(CF_3)Br$	(1074)	-	104
$Cp_2Ti(CF_3)I$	(1061)	-	104
$Cp_2Ti(CF_3)OSO_2CF_3$	(1082)	-	104
$CpCr(NO)_2CF_3$	(1071)	(994)	105
$CpMo(CO)_3CF_3$	(1073)	(1006)	106
$Mn(CO)_5CF_3$	1063	1045	107

Compound	ν_s/cm^{-1}	ν_{as}/cm^{-1}	Ref
$CpFe(CF_3)(CO)_2$	(1068, 1042)	(1015)	106
$Ru(CO)_2(PPh_3)_2(CF_3)Cl$	(1073)	(1006)	108
$Co(CO)_4CF_3$	1057	1096	87
$Co(PPh_3)(CO)_3CF_3$	(1050)	(1029)	109
$CpCo(CO)(CF_3)I$	(1067)	(1053)	110
$CpRh(CO)(CF_3)I$	(1073)	(1040)	112
$Ir(PPh_3)_2(CO)_2CF_3$	(1088)	(1005)	113
$CpNi(CO)CF_3$	(1069)	(1024)	114
$Pd(PPh_3)_2(CF_3)I$	(1068)	(1024)	86
$PtI(PPh_3)_2CF_3$	(1085)	(1022)	86

(a) For situations in which ν_s and ν_{as} assignments have not been reported, the data are listed in parentheses with the higher value being arbitrarily placed in the column associated with ν_s.

CONCLUSIONS

In summary, [Bptm]ZnH and [Bptm]ZnN$(SiMe_3)_2$ react with Me_3SnF to afford the dinuclear zinc fluoride complex, {[Bptm]Zn(μ-F)}$_2$. The dimeric nature of {[Bptm]Zn(μ-F)}$_2$ contrasts with the monomeric structures of the other zinc halides [Bptm]ZnX (X = Cl, Br, I), a difference that is supported by DFT calculations. Significantly, {[Bptm]Zn(μ-F)}$_2$ undergoes metathesis with Me_3SiCF_3 to form the first organozinc trifluoromethyl complex, namely [Bptm]ZnCF_3. An interesting feature of [Bptm]ZnCF_3 is that the Zn–CF_3 bond is longer than the corresponding Zn–CH_3 bond in the methyl counterpart, [Bptm]ZnMe, a difference that is of relevance because the opposite trend is often observed, with M–CF_3 bonds being shorter than corresponding M–CH_3 bonds. [Bptm]ZnCF_3 has also been characterized spectroscopically and a noteworthy aspect is that the asymmetric C–F stretch, while comparable to those of similar zinc and cadmium species, is of low energy relative to transition metal counterparts.

EXPERIMENTAL SECTION

General considerations

All manipulations were performed by using a combination of glovebox, high vacuum, and Schlenk techniques under an argon atmosphere unless otherwise specified.[119] Solvents were purified and degassed by using standard procedures. ^{1}H NMR spectra were measured on Bruker AVIII 300, and Bruker 500 DMX spectrometers. ^{1}H chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C_6D_5H).[120] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 128.06 for C_6D_6).[120] ^{19}F NMR chemical shifts are reported in ppm relative to $CFCl_3$ ($\delta = 0.0$) and were obtained by using the $\Xi/100\%$ value of 94.094011.[121] 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. [Bptm]ZnH and [Bptm]ZnN($SiMe_3$)$_2$ were prepared by the literature methods.[22]

X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. The structures were solved by 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).[122] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2198748-2198749).

Computational Details

Calculations were carried out by using DFT as implemented in the Jaguar 8.9 (release 15) suite of *ab initio* quantum chemistry programs.[123] Geometry optimizations were performed with the B3LYP density functional using the LACVP** basis sets that were also used for obtaining thermodynamic data. Cartesian coordinates are provided in the Supporting Information.

Synthesis of $\{[\mathrm{Bptm}]\mathrm{Zn}(\mu\text{-F})\}_2$

(*i*) A solution of $[\mathrm{Bptm}]\mathrm{ZnN(SiMe_3)_2}$ (51 mg, 0.111 mmol) in benzene (*ca.* 1 mL) was treated with $\mathrm{Me_3SnF}$ (21 mg, 0.115 mmol), resulting in the deposition of colorless crystals suitable for X-ray diffraction over a period of 4 days. The crystals were isolated by decantation, washed with pentane (2 × 1 mL), and dried *in vacuo* to give $\{[\mathrm{Bptm}]\mathrm{Zn}(\mu\text{-F})\}_2$. Yield: 30 mg (85 %). ^{1}H NMR ($\mathrm{C_6D_6}$): 3.69 [s, 2H, $\{(\mathrm{C_5H_4NS})_2\underline{\mathrm{H}}\mathrm{CZnF}\}_2$], 6.02 [m, 4H, $\{(\mathrm{C_5\underline{H}_4NS})_2\mathrm{HCZnF}\}_2$], 6.44 [m, 4H, $\{(\mathrm{C_5\underline{H}_4NS})_2\mathrm{HCZnF}\}_2$], 6.69 [m, 4H, $\{(\mathrm{C_5\underline{H}_4NS})_2\mathrm{HCZnF}\}_2$], 8.95 [m, 4H, $\{(\mathrm{C_5\underline{H}_4NS})_2\mathrm{HCZnF}\}_2$]. ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): 13.2 [$\{(\mathrm{C_5H_4NS})_2\mathrm{H}\underline{\mathrm{C}}\mathrm{ZnF}\}_2$] (identified by HSQC), 118.6 [4C, $\{(\underline{\mathrm{C}}_5\mathrm{H_4NS})_2\mathrm{HCZnF}\}_2$], 121.6 [4C, $\{(\underline{\mathrm{C}}_5\mathrm{H_4NS})_2\mathrm{HCZnF}\}_2$], 137.5 [4C, $\{(\underline{\mathrm{C}}_5\mathrm{H_4NS})_2\mathrm{HCZnF}\}_2$], 148.9 [4C, $\{(\underline{\mathrm{C}}_5\mathrm{H_4NS})_2\mathrm{HCZnF}\}_2$], 164.6 [4C, $\{(\underline{\mathrm{C}}_5\mathrm{H_4NS})_2\mathrm{HCZnF}\}_2$]. ^{19}F NMR ($\mathrm{C_6D_6}$): -196.8. IR data (ATR, cm^{-1}): 2914 (w), 1590 (m), 1556 (m), 1451 (m), 1416 (m), 1280 (m), 1188 (m), 1130 (m), 1043 (m), 765 (s), 721 (m), 683 (m), 553 (vs), 484 (m).

(*ii*) A solution of $[\mathrm{Bptm}]\mathrm{ZnH}$ (3 mg, 0.010 mmol) in $\mathrm{C_6D_6}$ (*ca.* 0.5 mL) was treated with $\mathrm{Me_3SnF}$ (2 mg, 0.011 mmol) in an NMR tube equipped with a J. Young valve. The solution was monitored by ^{1}H NMR spectroscopy over the course of 1 day, thereby demonstrating quantitative formation of $\{[\mathrm{Bptm}]\mathrm{Zn}(\mu\text{-F})\}_2$.

Synthesis of $[\mathrm{Bptm}]\mathrm{ZnCF_3}$

A suspension of $\{[\mathrm{Bptm}]\mathrm{Zn}(\mu\text{-F})\}_2$ (9 mg, 0.028 mmol) in $\mathrm{C_6D_6}$ (*ca.* 0.5 mL) was treated with $\mathrm{Me_3SiCF_3}$ (30 mg, 0.211 mmol) in an NMR tube equipped with a J. Young valve. The solution was heated at 90˚C for 24 hours and monitored by ^{1}H and ^{19}F NMR spectroscopy, thereby demonstrating quantitative conversion to $[\mathrm{Bptm}]\mathrm{ZnCF_3}$ and $\mathrm{Me_3SiF}$. The solution was lyophilized to afford $[\mathrm{Bptm}]\mathrm{ZnCF_3}$ as a white solid. Colorless crystals suitable for X-ray diffraction were obtained *via* slow evaporation from a solution in benzene. ^{1}H NMR (C_6D_6): 3.23 [s, 1H, $(C_5H_4NS)_2\underline{H}CZnCF_3$], 6.07 [m, 2H, $(C_5\underline{H}_4NS)_2HCZnCF_3$], 6.40 [m, 2H, $(C_5\underline{H}_4NS)_2HCZnCF_3$], 6.53 [m, 2H, $(C_5\underline{H}_4NS)_2HCZnCF_3$], 8.24 [m, 2H, $(C_5\underline{H}_4NS)_2HCZnCF_3$]. ^{13}C{^{1}H} NMR ($C_6D_6$): 18.1 [s, 1C, $(C_5H_4NS)_2H\underline{C}ZnCF_3$], 119.4 [s, 2C, $(\underline{C}_5H_4NS)_2HCZnCF_3$], 121.9 [s, 2C, $(\underline{C}_5H_4NS)_2HCZnCF_3$], 137.9 [s, 2C, $(\underline{C}_5H_4NS)_2HCZnCF_3$], 146.1 [q, $^1J_{C\text{-}F}$ = 355 Hz, 1C, $(C_5H_4NS)_2HCZn\underline{C}F_3$], 147.0 [s, 2C, $(\underline{C}_5H_4NS)_2HCZnCF_3$], 165.9 [s, 2C, $(\underline{C}_5H_4NS)_2HCZnCF_3$]. ^{19}F NMR ($C_6D_6$): -39.7 [$^1J_{C\text{-}F}$ = 355 Hz]. IR data (ATR, cm^{-1}): 2842 (w), 1594 (s), 1554 (m), 1463 (m), 1417 (vs), 1285 (m), 1199 (w), 1140 (vs), 1098 (w), 1047 (w), 1012 (w), 958 (vs), 903 (s), 881 (w), 766 (vs), 757 (s), 722 (m), 674 (m), 646 (w), 483 (w).

Comparison of the reactivity of {[Bptm]Zn(μ-F)}$_2$ and [Tptm]ZnF towards indole

A suspension of {[Bptm]Zn(μ-F)}$_2$ (2 mg, 0.003 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with indole (1 mg, 0.009 mmol) in an NMR tube equipped with a J. Young valve. The sample was monitored by ^{1}H NMR spectroscopy over the course of 1 day, thereby demonstrating negligible perturbation of the chemical shifts of either species. The solution was subsequently treated with [Tptm]ZnF (2 mg, 0.005 mmol) and monitored by ^{1}H NMR spectroscopy, thereby demonstrating an immediate change in the chemical shifts of both [Tptm]ZnF and indole.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at 10.1021/acs.organomet.xxxxx.

NMR spectra (PDF).

Cartesian coordinates for geometry optimized structures (XYZ).

Accession Codes

CCDC 2127030-2127039 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interests.

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REFERENCES

(1) O'Hagan, D. "Understanding organofluorine chemistry. An introduction to the C-F bond" *Chem. Soc. Rev.* **2008**, *37*, 308-319.

(2) Ogawa, Y.; Tokunaga, E.; Kobayashi, O.; Hirai, K.; Shibata, N. "Current contributions of organofluorine compounds to the agrochemical industry" *iScience* **2020**, *23*, 101467.

(3) Hagmann, W. K. "The many roles for fluorine in medicinal chemistry" *J. Med. Chem.* **2008**, *51*, 4359-4369.

(4) Roesky, H. W.; Haiduc, I. "Fluorine as a structure-directing element in organometallic fluorides: discrete molecules, supramolecular self-assembly and host-guest complexation" *J. Chem. Soc. Dalton Trans.* **1999**, 2249-2264.

(5) (a) Doherty, N. M.; Hoffman, N. W. "Transition-metal fluoro compounds containing carbonyl, phosphine, arsine, and stibine ligands" *Chem. Rev.* **1991**, *91*, 553-573.

(b) Murphy, E. F.; Murugavel, R.; Roesky, H. W. "Organometallic fluorides: Compounds containing carbon-metal-fluorine fragments of d-block metals" *Chem. Rev.* **1997**, *97*, 3425-3468.

(c) Roesky, H. W. "Playing the keyboard of fluorine chemistry" *Inorg. Chem.* **1999**, *38*, 5934-5943.

(d) Jagirdar, B. R.; Murphy, E. F.; Roesky, H. W. "Organometallic fluorides of the main group metals containing the C-M-F fragment" *Prog. Inorg. Chem.* **1999**, *48*, 351-455.

(e) Nikiforov, G. B.; Roesky, H. W.; Koley, D. "A survey of titanium fluoride complexes, their preparation, reactivity, and applications" *Coord. Chem. Rev.* **2014**, *258*, 16-57.

(f) Grushin, V. V. "The organometallic fluorine chemistry of palladium and rhodium: studies toward aromatic fluorination" *Acc. Chem. Res.* **2010**, *43*, 160-171.

(g) Mezzetti, A.; Becker, C. "Swimming against the stream? A discussion of the bonding in d^6 and d^8 fluoro complexes and its consequences for catalytic applications" *Helv. Chim. Acta* **2002**, *85*, 2686-2703.

(h) Winfield, J. M. "Transition metal fluorides" *J. Fluor. Chem.* **1986**, *33*, 159-178.

(6) Fagnou, K.; Lautens, M. "Halide effects in transition metal catalysis" *Angew. Chem. Int. Edit.* **2002**, *41*, 26-47.

(7) Hascall, T.; Rabinovich, D.; Murphy, V. J.; Beachy, M. D.; Friesner, R. A.; Parkin, G. "Mechanistic and theoretical analysis of the oxidative addition of H_2 to six-coordinate molybdenum and tungsten complexes $M(PMe_3)_4X_2$ (M = Mo, W; X = F, Cl, Br, I): An inverse equilibrium isotope effect and an unprecedented halide dependence" *J. Am. Chem. Soc.* **1999**, *121*, 11402-11417.

(8) (a) Perutz, R. N.; Braun, T. "Transition-metal mediated C-F bond activation" in *Comprehensive Organometallic Chemistry III*, Volume 1, Chapter 1.26; Crabtree, R. H. and Mingos, D. M. P. (Eds), Elsevier, Oxford, 2007.

(b) Amii, H.; Uneyama, K. "C-F bond activation in organic synthesis" *Chem. Rev.* **2009**, *109*, 2119-2183.

(c) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. "Recent advances in C-F bond activation" *Chem. Ber.* **1997**, *130*, 145-154.

(d) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. "Activation of carbon fluorine bonds by metal-complexes" *Chem. Rev.* **1994**, *94*, 373-431.

(9) (a) Pagenkopf, B. L.; Carreira, E. M. "Transition metal fluoride complexes in asymmetric catalysis" *Chem. Eur. J.* **1999**, *5*, 3437-3442.

(b) Duthaler, R. O.; Hafner, A. "Fluorotitanium compounds—Novel catalysts for the addition of nucleophiles to aldehydes" *Angew. Chem. Int. Edit. Engl.* **1997**, *36*, 43-45.

(c) Kollár, L.; Kégl, T.; Bakos, J. "Platinum-catalyzed enantioselective hydroformylation of styrene - Platinum diphosphine tin(II) fluoride catalytic-system - a novel asymmetric hydroformylation catalyst" *J. Organomet. Chem.* **1993**, *453*, 155-158.

(d) Hamada, T.; Manabe, K.; Kobayashi, S. "Catalytic asymmetric Mannich-type reactions activated by ZnF_2 chiral diamine in aqueous media" *Chem. Eur. J.* **2006**, *12*, 1205-1215.

(e) Lv, J.; Li, X.; Zhong, L.; Luo, S.; Cheng, J.-P. "Asymmetric binary-acid catalysis with chiral phosphoric acid and MgF_2: Catalytic enantioselective Friedel-Crafts reactions of β,γ-unsaturated α-ketoesters" *Org. Lett.* **2011**, *12*, 1096-1099.

(10) (a) Pagenkopf, B. L.; Carreira, E. M. "Transition metal fluoride complexes in asymmetric catalysis" *Chem. Eur. J.* **1999**, *5*, 3437-3442.

(b) Kemnitz, E. "Nanoscale metal fluorides: a new class of heterogeneous catalysts" *Catal. Sci. Technol.* **2015**, *5*, 786-806.

(11) Hua, X.; Eggeman, A. S.; Castillo-Martinez, E.; Robert, R.; Geddes, H. S.; Lu, Z. H.; Pickard, C. J.; Meng, W.; Wiaderek, K. M.; Pereira, N.; Amatucci, G. G.; Midgley, P. A.; Chapman, K. W.; Steiner, U.; Goodwin, A. L.; Grey, C. P. "Revisiting metal fluorides as lithium-ion battery cathodes" *Nat. Mater.* **2021**, *20*, 841-850.

(12) Brekhovskikh, M. N.; Moiseeva, L. V.; Batygov, S. K.; Zhidkova, I. A.; Fedorov, V. A. "Glasses on the basis of heavy metal fluorides" *Inorg. Mater.* **2015**, *51*, 1348-1361.

(13) Cambridge Structural Database (CSD version 5.42). Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. "The Cambridge Structural Database" *Acta Cryst.* **2016**, *B72*, 171-179.

(14) For examples of zinc compounds with terminal fluoride ligands, see:

(a) Sattler, W.; Ruccolo, S.; Parkin, G. "Synthesis, structure, and reactivity of a terminal organozinc fluoride compound: Hydrogen bonding, halogen bonding, and donor-acceptor interactions" *J. Am. Chem. Soc.* **2013**, *135*, 18714-18717.

(b) Klaui, W.; Schilde, U.; Schmidt, M. "Fluoro[η^3-hydrotris(3-R-5-methylpyrazol-1-yl)borato]zinc(II): The first TpZnF complexes, convenient precursors to zinc hydride complexes" *Inorg. Chem.* **1997**, *36*, 1598-1601.

(c) Weis, K.; Vahrenkamp, E. "Simple zinc complexes of pyridyl-substituted tris(pyrazolyl)borate ligands" *Inorg. Chem.* **1997**, *36*, 5592-5596.

(d) Tesmer, M.; Shu, M. H.; Vahrenkamp, H. "Sulfur-rich zinc chemistry: New tris(thioimidazolyl)hydroborate ligands and their zinc complex chemistry related to the structure and function of alcohol dehydrogenase" *Inorg. Chem.* **2001**, *40*, 4022-4029.

(e) Hahn, F. E.; Jocher, C.; Lugger, T.; Pape, T. "Coordination chemistry of aliphatic, tripodal ligands with zinc salts" *Z. Anorg. Allg. Chem.* **2003**, *629*, 2341-2347.

(f) Ambrosi, G.; Formica, M.; Fusi, V.; Giorgi, L.; Macedi, E.; Micheloni, M.; Paoli, P.; Pontellini, R.; Rossi, P. "A macrocyclic ligand as receptor and Zn^{II}-complex receptor for anions in water: Binding properties and crystal structures" *Chem. Eur. J.* **2011**, *17*, 1670-1682.

(g) Rauch, M.; Rong, Y.; Sattler, W.; Parkin, G. "Synthesis of a terminal zinc hydride compound, $[Tp^{Bu^t,Me}]ZnH$, from a hydroxide derivative, $[Tp^{Bu^t,Me}]ZnOH$: Interconversions with the fluoride complex, $[Tp^{Bu^t,Me}]ZnF$" *Polyhedron* **2016**, *103*, 135-140.

(h) Li, X.; Wu, J.; He, C.; Zhang, R.; Duan, C. "Multicomponent self-assembly of a pentanuclear Ir-Zn heterometal-organic polyhedron for carbon dioxide fixation and sulfite sequestration" *Chem. Commun.* **2016**, *52*, 5104-5107.

(i) Stauber, J. M.; Alliger, G. E.; Nocera, D. G.; Cummins, C. C. "Second-coordination-sphere assisted selective colorimetric turn-on fluoride sensing by a mono-metallic Co(II) hexacarboxamide cryptand complex" *Inorg. Chem.* **2017**, *56*, 7615-7619.

(15) For examples of zinc compounds with bridging fluoride ligands, see:
(a) Hao, H. J.; Cui, C. M.; Roesky, H. W.; Bai, G. C.; Schmidt, H. G.; Noltemeyer, M. "Syntheses and structures of the first examples of zinc compounds with bridging fluorine and hydrogen atoms" *Chem. Commun.* **2001**, 1118-1119.
(b) Tomat, E.; Cuesta, L.; Lynch, V. M.; Sessler, J. L. "Binuclear fluoro-bridged zinc and cadmium complexes of a Schiff base expanded porphyrin: Fluoride abstraction from the tetrafluoroborate anion" *Inorg. Chem.* **2007**, *46*, 6224-6226.
(c) Gobeze, W. A.; Milway, V. A.; Moubaraki, B.; Murray, K. S.; Brooker, S. "Solvent control: dinuclear versus tetranuclear complexes of a bis-tetradentate pyrimidine-based ligand" *Dalton Trans.* **2012**, *41*, 9708-9721.
(d) Juraj, N. P.; Muratovic, S.; Peric, B.; Vujicic, N. S.; Vianello, R.; Zilic, D.; Jaglicic, Z.; Kirin, S. I. "Structural variety of isopropyl-bis(2-picolyl)amine complexes with zinc(II) and copper(II)" *Cryst. Growth Des.* **2020**, *20*, 2440-2453.

(16) (a) Jackson, R. F. W. "Preparation and use of organozinc halides" in *Organozinc Reagents: a Practical Approach*, Knochel, P.; Jones, P. (Eds.), Oxford University Press, Oxford, 1999, Chapter 3, pp. 37-56.
(b) Leitner, A. "Organozinc halides in catalysis" *Spec. Chem. Mag.* **2010**, *30*, 12-14.
(c) Knochel, P.; Singer, R. D. "Preparation and reactions of polyfunctional organozinc reagents in organic synthesis" *Chem. Rev.* **1993**, *93*, 2117-2188.

(17) The only other organozinc fluoride compound listed in the CSD is a cluster that features fluoride bridging zinc and titanium centers, namely $[(Cp^*TiF)_2(\mu\text{-}F)_4(\mu_3\text{-}F)(ZnMe)]$. See: Yu, P.; Müller, P.; Roesky, H. W.; Noltemeyer, M.; Demsar, A.; Usón, I. "Organotitanium fluorides as matrices for trapping molecular ZnF_2 and MeZnF" *Angew. Chem. Int. Edit.* **1999**, *38*, 3319-3321.

(18) (a) García-Monforte, M. A.; Martinez-Salvador, S.; Menjón, B. "The trifluoromethyl group in transition metal chemistry" *Eur. J. Inorg. Chem.* **2012**, 4945-4966.

(b) Morrison, J. A. "Trifluoromethyl-containing transition metal complexes" *Adv. Organomet. Chem.* **1993**, *35*, 211-239.

(c) Morrison, J. A. "Trifluoromethyl derivatives of the transition metal elements" *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 293-316.

(d) Hughes, R. P. "Organo-transition metal compounds containing perfluorinated ligands" *Adv. Organomet. Chem.* **1990**, *31*, 183-267.

(e) Tomashenko, O. A.; Grushin, V. V. "Aromatic trifluoromethylation with metal complexes" *Chem. Rev.* **2011**, *111*, 4475-4521.

(f) Brothers, P. J.; Roper, W. R. "Transition-metal dihalocarbene complexes" *Chem. Rev.* **1988**, *88*, 1293-1326.

(g) Stone, F. G. A. "Fluorocarbon derivatives of transition metals" *Endeavour* **1966**, 25, 33-38.

(h) Treichel, P. M.; Stone, F. G. A. "Fluorocarbon derivatives of metals" *Adv. Organomet. Chem.* **1964**, *1*, 143-220.

(19) Behm, J.; Lotz, S. D.; Herrmann, W. A. "Crystal and molecular structure of bis(pyridine)bis(trifluoromethyl)zinc" *Z. Anorg. Allg. Chem.* **1993**, *619*, 849-852.

(20) (a) Reedijk, J. "Formation of fluoride-containing coordination compounds by decomposition of transition-metal tetrafluoroborates" *Comments Inorg. Chem.* **1982**, *1*, 379-389.

(b) Gorrell, I. B.; Parkin, G. "*Tris*(3-t-butylpyrazolyl)hydroborato manganese, iron, cobalt and nickel halide derivatives: Facile abstraction of fluoride from $[BF_4]^-$" *Inorg. Chem.* **1990**, *29*, 2452-2456.

(c) Olguin, J.; Bernes, S.; Gasque, L. "Fluoride ion as ligand and hydrogen bond acceptor: Crystal structures of two dinuclear Cu^{II} complexes built on a diazecine template" *Crystals* **2012**, *2*, 1357-1365.

(d) Reference 15b.

(21) For the use of Me_3SnF as a fluorinating agent, see references 5b-e and

(a) Herzog, A.; Liu, F.-Q.; Roesky, H. W.; Demsar, A.; Keller, K.; Noltemeyer, M.; Pauer, F. "Trimethyltin fluoride: A new fluorinating reagent for the preparation of organometallic fluorides" *Organometallics* **1994**, *13*, 1251-1256.

(b) Schmidbaur, H.; Weidlein, J.; Klein, H.-F.; Eiglmeier, K. "Preparation and spectroscopy of dialkyl gallium fluorides" *Chem. Ber.* **1968**, *101*, 2268-2277.

(c) Kagan, B. D.; Lichtscheidl, A. G.; Erickson, K. A.; Monreal, M. J.; Scott, B. L.; Nelson, A. T.; Kiplinger, J. L. "Synthesis of actinide fluoride complexes using trimethyltin fluoride as a mild and selective fluorinating reagent" *Eur. J. Inorg. Chem.* **2018**, 1247-1253.

(d) Rauch, M.; Ruccolo, S.; Mester, J. P.; Rong, Y.; Parkin, G. "Synthesis, structure and reactivity of a terminal magnesium fluoride compound, $[Tp^{Bu^t}]MgF$: Hydrogen bonding, halogen bonding and C-F bond formation" *Chem. Sci.* **2016**, *7*, 142-149.

(22) Shlian, D. G.; Amemiya, E.; Parkin, G. "Synthesis of bis(2-pyridylthio)methyl zinc hydride and catalytic hydrosilylation and hydroboration of CO_2" *Chem. Commun.* **2022**, *58*, 4188-4191.

(23) For comparison, the ^{19}F NMR spectroscopic signal for [Tptm]ZnF is observed at δ –217.9 ppm. See reference 14a.

(24) (a) Ruccolo, S.; Sattler, W.; Rong, Y.; Parkin, G. "Modulation of Zn–C bond lengths induced by ligand architecture in zinc carbatrane compounds" *J. Am. Chem. Soc.* **2016**, *138*, 14542-14545.

(b) Ruccolo, S.; Rauch, M.; Parkin, G. "Synthesis and structural characterization of tris(isopropylbenzimidazol-2-ylthio)methyl zinc complexes, $[Titm^{Pr^iBenz}]ZnX$:

Modulation of transannular Zn-C interactions” *Organometallics* **2018**, *37*, 1708-1718.

(25) (a) Hao, H. J.; Roesky, H. W.; Ding, Y.; Cui, C.; Schormann, M.; Schmidt, H.-G.; Noltemeyer, M.; Žemva, B. “Access to the structures of fluoromagnesium compounds: synthesis and structural characterization of the β-diketiminato magnesium fluoride $[\{CH(CMeNAr)_2\}Mg(\mu\text{-}F)(THF)]_2$•toluene" *J. Fluor. Chem.* **2002**, *115*, 143-147.

(b) Bakewell, C.; White, A. J. P.; Crimmin, M. R. “Addition of carbon-fluorine bonds to a Mg(I)-Mg(I) bond: An equivalent of Grignard formation in solution” *J. Am. Chem. Soc.* **2016**, *138*, 12763-12766.

(c) Bailey, P.; Parsons, S.; Messenger, D.; Liddle, S. “Experimental crystal structure determination” *CSD Communication*, 2005 (CCDC 276761).

(d) Bailey, P. Liddle, S. T.; Parsons, S.; Messenger, D. “Experimental crystal structure determination” *CSD Communication*, 2005 (CCDC 276765).

(e) Bonyhady, S. J.; Jones, C.; Nembenna, S.; Stasch, A.; Edwards, A. J.; McIntyre, G. J. “β-diketiminate-stabilized magnesium(I) dimers and magnesium(II) hydride complexes: Synthesis, characterization, adduct formation, and reactivity studies” *Chem. Eur. J.* **2010**, *16*, 938-955.

(26) Krossing, I.; Nöth, H.; Tacke, C.; Schmidt, M.; Schwenk, H. “Synthesis and structures of bis(tetramethylpiperidino)aluminum halides – X-ray crystal structures of tmp_2AlX (X=Cl, Br, I) and $[tmp_2Al(\mu\text{-}F)]_2$” *Chem. Ber. Recl.* **1997**, *130*, 1047-1052.

(27) (a) Uhl, W.; Graupner, R.; Hahn, I.; Spies, T.; Frank, W. “The reactions of $R_2Ga\text{-}GaR_2$ and $R_2In\text{-}InR_2$ [R = $CH(SiMe_3)_2$] with protic reagents: Substituent exchange versus cleavage of the element-element bond” *Eur. J. Inorg. Chem.* **1998**, 355-360.

(b) Uhl, W.; Bock, H. R.; Claesener, M.; Layh, M.; Tiesmeyer, I.; Würthwein, E. U. “*cis*/*trans* isomerism of hydroalumination and hydrogallation products—

reflections on stability and rearrangement mechanism" *Chem. Eur. J.* **2008**, *14*, 11557-11564.

(28) χF = 4.0, χCl = 3.2, χBr = 3.0, χI = 2.7. See: L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 3rd edn, 1960.

(29) (a) Parkin, G. "Zinc: Organometallic chemistry" in *Encyclopedia of Inorganic Chemistry*, Vol 8., 4451-4467.

(b) Grévy, J. M. "Zinc: Organometallic chemistry" in *Encyclopedia of Inorganic and Bioinorganic Chemistry*, Wiley, Hoboken, NJ, 2011.

(c) Jiménez-Halla, J. O. C.; Bickelhaupt, F. M.; Solà, M. "Organomagnesium clusters: Structure, stability, and bonding in archetypal models" *J. Organomet. Chem.* **2011**, *696*, 4104-4111.

(d) Tinga, M. A. G. M; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Horn, E.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L. "Synthesis of cyclic bifunctional organomagnesium compounds. X-ray crystal structures of tetrameric organomagnesium clusters" *J. Am. Chem. Soc.* **1993**, *115*, 2808-2817.

(e) O'Neill, M. E.; Wade, K. in *Comprehensive Organometallic Chemistry*, Vol. 1, 1-42. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Eds., Pergamon Press (Oxford), 1982.

(30) For examples of hydrogen bonding interactions involving halogens as hydrogen bond acceptors, see:

(a) Brammer, L.; Bruton, E. A.; Sherwood, P. "Understanding the behavior of halogens as hydrogen bond acceptors" *Cryst. Growth Des.* **2001**, *1*, 277-290.

(b) Brammer, L.; Bruton, E. A.; Sherwood, P. "Fluoride ligands exhibit marked departures from the hydrogen bond acceptor behavior of their heavier halogen congeners" *New J. Chem.* **1999**, *23*, 965-968.

(c) Kovács, A.; Varga, Z. "Halogen acceptors in hydrogen bonding" *Coord. Chem. Rev.* **2006**, *250*, 710-727.

(d) Sony, S. M. M.; Ponnuswamy, M. N. "Geometrical analysis to understand the ability of halogen atoms to act as hydrogen-bond acceptors: A structural database study" *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1766-1772.

(e) Steiner, T. "Hydrogen-bond distances to halide ions in organic and organometallic crystal structures: Up-to-date database study" *Acta Crystallogr.* **1998**, *B54*, 456-463.

(f) Mascal, M. "A statistical analysis of halide•••H-A (A = OR, NR_2, N^+R_3) hydrogen bonding interactions in the solid state" *J. Chem. Soc. Perkin Trans. 2* **1997**, 1999-2001.

(g) Richmond, T. G. "Hydrogen bonding in transition metal fluorides" *Coord. Chem. Rev.* **1990**, *105*, 221-250.

(31) For example, while the chemical shift of the most downfield pyridyl signal of $\{[\text{Bptm}]\text{Zn}(\mu\text{-F})\}_2$ shifted by only 0.01 ppm in the presence of indole, the corresponding signal of [Tptm]ZnF shifted by 0.12 ppm.

(32) For some examples of bridging fluoride ligands that participate in hydrogen bonding interactions, see reference 15b.

(33) Inoue, M.; Sumii, Y.; Shibata, N. "Contribution of organofluorine compounds to pharmaceuticals" *ACS Omega* **2020**, *5*, 10633-10640.

(34) Ogawa, Y.; Tokunaga, E.; Kobayashi, O.; Hirai, K.; Shibata, N. "Current contributions of organofluorine compounds to the agrochemical industry" *iScience* **2020**, *23*, 101467.

(35) Ma, J. A.; Cahard, D. "Strategies for nucleophilic, electrophilic, and radical trifluoromethylations" *J. Fluorine Chem.* **2007**, *128*, 975-996.

(36) Alonso, C.; de Marigorta, E. M.; Rubiales, G.; Palacios, F. "Carbon trifluoromethylation reactions of hydrocarbon derivatives and heteroarenes" *Chem. Rev.* **2015**, *115*, 1847-1935.

(37) (a) McClinton, M. A.; McClinton, D. A. “Trifluoromethylations and related reactions in organic chemistry” *Tetrahedron* **1992**, *48*, 6555-6666.

(b) Burton, D. J.; Yang, Z.-Y. “Fluorinated organometallics: Perfluoroalkyl and functionalized perfluoroalkyl organometallic reagents in organic synthesis" *Tetrahedron* **1992**, *48*, 189-275.

(38) In addition to trifluoromethyl, other fluoroalkyl groups have also found useful applications, as illustrated by being components of ligands such as tertiaryphosphine and tris(pyrazolyl)borate ligands. See, for example:

(a) Law, C.-k. E.; Horvath, I. T. “Synthesis and applications of fluorous phosphines” *Org. Chem. Front.* **2016**, *3*, 1048-1062.

(b) Gladysz, J. A.; Jurisch, M. “Structural, physical, and chemical properties of fluorous compounds” *Top. Curr. Chem.* **2012**, *308*, 1-24.

(c) Brisdon, A. K.; Herbert, C. J. “Fluoroalkyl-containing phosphines” *Coord. Chem. Rev.* **2013**, *257*, 880-901.

(d) Palcic, J. D.; Kapoor, P. N.; Roddick, D. M.; Peters, R. G. ”Perfluoroalkylphosphine coordination chemistry of platinum: synthesis of $(C_2F_5)_2PPh$ and $(C_2F_5)PPh_2$ complexes of platinum(II)” *Dalton Trans.* **2004**, 1644-1647.

(e) Phelps, J.; Butikofer, J. L.; Thapaliya, B.; Gale, E.; Vowell, C. L.; Debnath, S.; Arulsamy, N.; Roddick, D. M. “Structural and reactivity properties of perfluoroalkylphosphine complexes of platinum(0)” *Polyhedron* **2016**, *116*, 197-203.

(f) Dias, H. V. R.; Wang, Z.; Jin, W. “Synthesis and chemistry of hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borato silver(I) complexes” *Inorg. Chem.* **1997**, *36*, 6205-6215.

(g) van Dijkman, T. F.; Siegler, M. A.; Bouwman, E. “Copper(I) complexes of naphthyl-substituted fluorinated trispyrazolylborate ligands with ethene and carbon monoxide" *Eur. J. Inorg. Chem.* **2016**, 2586-2594.

(h) Ridlen, S. G.; Kulkarni, N. V.; Dias, H. V. R. "Partially fluorinated scorpionate $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]^-$ as a supporting ligand for silver(I)-benzene, -carbonyl, and -PPh_3 complexes" *Polyhedron* **2017**, *125*, 68-73.

(i) Fekl, U.; van Eldik, R.; Lovell, S.; Goldberg, K. I. "Effects of trifluoromethyl substituents in a tris(pyrazolyl)borate ligand: A structural and spectroscopic study of analogous platinum(IV) trimethyl complexes" *Organometallics* **2000**, *19*, 3535-3542.

(39) Pan, S.; Wang, X.; Ni, C.; Hu, J. "Nucleophilic trifluoromethylation of azinium salts with $Zn(CF_3)_2{\cdot}bpy$" *Tetrahedron* **2021**, *100*, 132477.

(40) Aikawa, K.; Nakamura, Y.; Yokota, Y.; Toya, W.; Mikami, K. "Stable but reactive perfluoroalkylzinc reagents: Application in ligand-free copper-catalyzed perfluoroalkylation of aryl iodides" *Chem. Eur. J.* **2015**, *21*, 96-100.

(41) Xiao, H; Liu, Z.; Shen, H.; Zhang, B.; Zhu, L.; Li, C. "Copper-catalyzed late-stage benzylic $C(sp^3)$-H trifluoromethylation" *Chem* **2019**, *5*, 940-949.

(42) Shen, H.; Xiao, H.; Zhu, L.; Li, C. "Copper-catalyzed radical bis(trifluoromethylation) of alkynes and 1,3-enynes" *Synlett* **2020**, *31*, 41-44.

(43) (a) Xiao, H.; Shen, H.; Zhu, L.; Li, C. "Copper-catalyzed radical aminotrifluoromethylation of alkenes" *J. Am. Chem. Soc.* **2019**, *141*, 11440-11445.

(b) Zhang, Z.; Zhu, L.; Li, C. "Copper-catalyzed carbotrifluoromethylation of unactivated alkenes driven by trifluoromethylation of alkyl radicals" *Chin. J. Chem .* **2019**, *37*, 452-456.

(44) Liu, Z.; Xiao, H.; Zhang, B.; Shen, H.; Zhu, L.; Li, C. "Copper-catalyzed remote $C(sp^3)$-H trifluoromethylation of carboxamides and sulfonamides" *Angew. Chem. Int. Ed.* **2019**, *58*, 2510-2513.

(45) Liu, Z.; Shen, H.; Xiao, H.; Wang, Z.; Zhu, L.; Li, C. "Copper-catalyzed ring-opening radical trifluoromethylation of cycloalkanone oximes" *Org. Lett.* **2019**, *21*, 5201-5205.

(46) Zhang, H.; Xiao, H.; Jiang, F.; Fang, Y.; Zhu, L.; Li, C. "Copper-catalyzed ring-opening 1,3-aminotrifluoromethylation of arylcyclopropanes" *Org. Lett.* **2021**, *23*, 2268-2272.

(47) Trifluoromethyl zinc compounds can also be used to introduce CF_2 groups. See, for example: Tyrra, W.; Naumann, D.; Pasenok, S. V.; Yagupolskii, Y. L. "Carbenoid reactions of trifluoromethylelement compounds. Part 4. Reactions of trifluoromethylzinc bromide with enamines and methylene bases" *J. Fluorine Chem.* **1995**, *70*, 181-185.

(48) Liu, E. K. S.; Asprey, L. B. "Chemistry of trifluoromethyl compounds. 1. NMR evidence for bis(trifluoromethyl)zinc and methyl(trifluoromethyl)zinc" *J. Organomet. Chem.* **1979**, *169*, 249-254.

(49) Liu, E. K. S. "Chemistry of trifluoromethyl compounds. 2. Synthesis and characterization of bis(pyridine)bis(trifluoromethyl)zinc" *Inorg. Chem.* **1980**, *19*, 266-268.

(50) Lange, H.; Naumann, D. "Perfluoroorgano-zinc compounds: synthesis and properties of $(R_f)_2Zn$ complexes ($R_f = CF_3, C_2F_5, C_3F_7, C_6F_5$)" *J. Fluorine Chem.* **1984**, *26*, 435-444.

(51) Naumann D.; Tyrra, W.; Kock, B.; Rudolph, W.; Wilkes, B. "Preparation and properties of $ZnBr(CF_3){\bullet}2L$ - a convenient route for the preparation of CF_3I" *J. Fluorine Chem.* **1994**, *67*, 91-93.

(52) Kremlev, M. M.; Tyrra, W.; Mushta, A. I.; Naumann, D.; Yagupolskii, Y. L. "The solid complex $Zn(CF_3)Br{\bullet}2DMF$ as an alternative reagent for the preparation of both, trifluoromethyl and pentafluoroethyl copper, $CuCF_3$ and CuC_2F_5" *J. Fluorine Chem.* **2010**, *131*, 212-216.

(53) Grobe, J.; Hegge, J. "Electrochemical and chemical syntheses of trifluoromethylating reagents and trifluoromethyl substituted compounds" *Z. Anorg. Allg. Chem.* **2008**, *634*, 1975-1990.

(54) $Zn(CF_3)X$ species have also been generated *via* reaction of zinc powder with CF_2X_2 (X = Br, Cl). See: Burton, D. J.; Wiemers, D. M. "A remarkably simple preparation of (trifluoromethyl)cadmium and -zinc reagents directly from difluorodihalomethanes" *J. Am. Chem. Soc.* **1985**, *107*, 5014-5015.

(55) Habeeb, J. J.; Osman, A.; Tuck, D. G. "Electrochemical synthesis of neutral and anionic organozinc halides" *J. Organomet. Chem.* **1980**, *185*, 117-127.

(56) Grobe, J.; Hegge, J. "Electrochemical and chemical syntheses of trifluoromethylating reagents and trifluoromethyl substituted compounds" *Z. Anorg. Allg. Chem.* **2008**, *634*, 1975-1990.

(57) (a) Vicente, J.; Gil-Rubio, J.; Bautista, D. "Synthesis and reactivity of fluoro complexes. Part 1. Cyclooctadiene rhodium(I) complexes" *Inorg. Chem.* **2001**, *40*, 2636-2637.

(b) Vicente, J.; Gil-Rubio, J.; Guerrero-Leal, J.; Bautista, D. "Synthesis of the first family of rhodium(I) perfluoroalkyl complexes from rhodium(I) fluoro complexes" *Organometallics* **2004**, *23*, 4871-4881.

(c) Taw, F. L.; Scott, B. L.; Kiplinger, J. L. "Early transition-metal perfluoroalkyl complexes" *J. Am. Chem. Soc.* **2003**, *125*, 14712-14713.

(d) Taw, F. L.; Clark, A. E.; Mueller, A. H.; Janicke, M. T.; Cantat, T.; Scott, B. L.; Hay, P. J.; Hughes, R. P.; Kiplinger, J. L. "Titanium(IV) trifluoromethyl complexes: new perspectives on bonding from organometallic fluorocarbon chemistry" *Organometallics* **2012**, *31*, 1484-1499.

(e) Grushin, V. V.; Marshall, W. J. "Facile Ar-CF_3 bond formation at Pd. Strikingly different outcomes of reductive elimination from $[(Ph_3P)_2Pd(CF_3)Ph]$ and $[(Xantphos)Pd(CF_3)Ph]$" *J. Am. Chem. Soc.* **2006**, *128*, 12644-12645.

(f) Goodman, J.; Grushin, V. V.; Larichev, R. B.; Macgregor, S. A.; Marshall, W. J.; Roe, D. C. “Fluxionality of $[(Ph_3P)_3M(X)]$ (M = Rh, Ir). The red and orange forms of $[(Ph_3P)_3Ir(Cl)]$. Which phosphine dissociates faster from Wilkinson's catalyst?” *J. Am. Chem. Soc.* **2010**, *132*, 12013-12026.

(g) Nebra, N.; Grushin, V. V. “Distinct mechanism of oxidative trifluoromethylation with a well-defined Cu(II) fluoride promoter: Hidden catalysis” *J. Am. Chem. Soc.* **2014**, *136*, 16998-17001.

(h) Bramananthan, N.; Carmona, M.; Lowe, J. P.; Mahon, M. F.; Poulten, R. C.; Whittlesey, M. K. “Rh-FHF and Rh-F complexes containing small *N*-alkyl substituted six-membered ring N-heterocyclic carbenes” *Organometallics* **2014**, *33*, 1986-1995.

(i) Nielsen, M. C.; Bonney, K. J.; Schoenebeck, F. “Computational ligand design for the reductive elimination of $ArCF_3$ from a small bite angle Pd^{II} complex: remarkable effect of a perfluoroalkyl phosphine” *Angew. Chem. Int. Ed.* **2014**, *53*, 5903-5906.

(j) Berger, J.; Braun, T.; Ahrens, T.; Klaring, P.; Laubenstein, R.; Braun-Cula, B. “The versatile behavior of platinum alkyne complexes towards XeF_2: formation of fluorovinyl and fluorido complexes” *Chem. Eur. J.* **2017**, *23*, 8886-8900.

(k) Pu, M.; Sanhueza, I. A.; Senol, E.; Schoenebeck, F. “Divergent reactivity of stannane and silane in the trifluoromethylation of Pd^{II}: Cyclic transition state versus difluorocarbene release” *Angew. Chem. Int. Ed.* **2018**, *57*, 15081-15085.

(l) Winter, M.; Limberg, N.; Ellwanger, M. A.; Pérez-Bitrián, A.; Sonnenberg, K.; Steinhauer, S.; Riedel, S. “Trifluoromethylation of $[AuF_3(SIMes)]$: preparation and characterization of $[Au(CF_3)_xF_{3-x}(SIMes)]$ ($x = 1$-3) Complexes” *Chem. Eur. J.* **2020**, *26*, 16089-16097.

(m) Rachor, S. G.; Müller, R.; Wittwer, P.; Kaupp, M.; Braun, T. “Synthesis, reactivity, and bonding of gold(I) fluorido-phosphine complexes” *Inorg. Chem.*

2022, *61*, 357-367.

(n) Martínez de Salinas, S.; Mudarra, A. L.; Benet-Buchholz, J.; Parella, T.; Maseras, F.; Pérez-Temprano, M. H. "New vistas in transmetalation with discrete '$AgCF_3$' species: implications in Pd-mediated trifluoromethylation reactions" *Chem. Eur. J.* **2018**, *24*, 11895-11898.

(58) The first reports of the reactions between a metal fluoride and Me_3SiCF_3, however, afforded difluorocarbene fluoride compounds of the type $[M](CF_2)F$, rather than trifluoromethyl complexes.[a,b] Other examples of this transformation have also been reported.[c]

(a) Huang, D.; Caulton, K. G. "New entries to and new reactions of fluorocarbon ligands" *J. Am. Chem. Soc.* **1997**, *119*, 3185-3186.

(b) Huang, D.; Koren, P. R.; Folting, K.; Davidson, E. R.; Caulton, K. G. "Facile and reversible cleavage of C-F bonds. Contrasting thermodynamic selectivity for $Ru–CF_2H$ vs $F–Os{=}CFH$" *J. Am. Chem. Soc.* **2000**, *122*, 8916-8931.

(c) Goodman, J.; Grushin, V. V.; Larichev, R. B.; Macgregor, S. A.; Marshall, W. J.; Roe, D. C. "Fluxionality of $[(Ph_3P)_3Rh(X)]$: The Extreme Case of $X = CF_3$" *J. Am. Chem. Soc.* **2009**, *131*, 4236-4238.

(59) For other reactions employing Me_3SiCF_3 that afford trifluoromethyl complexes, see:

(a) Vicente, J.; Gil-Rubio, J.; Guerrero-Leal, J.; Bautista, D. "Synthesis and reactivity of trifluoromethyl isocyanide rhodium(I) complexes" *Organometallics* **2005**, *24*, 5634-5643.

(b) Dubinina, G. G.; Brennessel, W. W.; Miller, J. L.; Vicic, D. A. "Exploring trifluoromethylation reactions at nickel: a structural and reactivity study" *Organometallics* **2008**, *27*, 3933-3938.

(c) Kieltsch, I.; Dubinina, G. G.; Hamacher, C.; Kaiser, A.; Torres-Nieto, J.; Hutchison, J. M.; Klein, A.; Budnikova, Y.; Vicic, D. A. "Magnitudes of electronwithdrawing effects of the trifluoromethyl ligand in organometallic complexes of copper and nickel" *Organometallics* **2010**, *29*, 1451-1456.

(d) Madhira, V. N.; Ren, P.; Vechorkin, O.; Hu, X. L.; Vicic, D. A. "Synthesis and electronic properties of a pentafluoroethyl-derivatized nickel pincer complex" *Dalton Trans.* **2012**, *41*, 7915-7919.

(e) Yamaguchi, Y.; Ichioka, H.; Klein, A.; Brennessel, W. W.; Vicic, D. A. "Linear bis(perfluoroalkyl) complexes of nickel bipyridine" *Organometallics* **2012**, *31*, 1477-1483.

(f) Zhang, C.-P.; Wang, H.; Klein, A.; Biewer, C.; Stimat, K.; Yamaguchi, Y.; Xu, L.; Gomez-Benitez, V.; Vicic, D. A. "A five-coordinate nickel(II) fluoroalkyl complex as a precursor to a spectroscopically detectable Ni(III) species" *J. Am. Chem. Soc.* **2013**, *135*, 8141-8144.

(g) Shreiber, S. T.; DiMucci, I. M.; Khrizanforov, M. N.; Titus, C. J.; Nordlund, D.; Dudkina, Y.; Cramer, R. E.; Budnikova, Y.; Lancaster, K. M.; Vicic, D. A. "$[(MeCN)Ni(CF_3)_3]^-$ and $[Ni(CF_3)_4]^{2-}$: Foundations toward the development of trifluoromethylations at unsupported nickel" *Inorg. Chem.* **2020**, *59*, 9143-9151.

(h) Hu, W.-Q.; Pan, S.; Xu, X.-H.; Vicic, D. A.; Qing, F.-L. "Nickel-mediated trifluoromethylation of phenol derivatives by aryl C-O bond activation" *Angew. Chem. Int. Ed.* **2020**, *59*, 16076-16082.

(i) Shreiber, S. T.; Vicic, D. A. "Solvated nickel complexes as stoichiometric and catalytic perfluoroalkylation agents" *Angew. Chem. Int. Ed.* **2021**, *60*, 18162-18167.

(j) Shreiber, S. T.; Amin, F.; Schäfer, S. A.; Cramer, R. E.; Klein, A.; Vicic, D. A. "Synthesis, structure, and electrochemical properties of $[LNi(R_f)(C_4F_8)]^-$ and $[LNi(R_f)_3]^-$ complexes" *Dalton Trans.* **2022**, *51*, 5515-5523.

(60) The structure of $(tmeda)Zn(CF_3)_2$ has also been cited in an article (reference 40); however, no structural data are listed in either the article or the CSD.

(61) Beagley, B.; Young, G. G. "Molecular structure of trifluoromethyl manganese pentacarbonyl. A study by gas-phase electron diffraction" *J. Mol. Struct.* **1977**, *40*, 295-297.

(62) Seip, H. M.; Seip, R. "On the structure of methylmanganese pentacarbonyl, $CH_3Mn(CO)_5$" *Acta. Chem. Scand.* **1970**, *24*, 3431-3433.

(63) Schulz, S.; Schäper, R.; Krech, D.; Schuchmann, D.; Bläser, D.; Boese, R. "Synthesis and crystal structures of *t*-butyl-pyridine adducts of ZnR_2 (R = Me, *i*-Pr, *t*-Bu, Cp*)" *Z. Anorg. Allg. Chem.* **2011**, *637*, 83-86.

(64) Thomas, F.; Schulz, S.; Nieger, M. "Synthesis of thermolabile zinc-pentel compounds under kinetically controlled reaction conditions" *Angew. Chem. Int. Ed.* **2005**, *44*, 5668-5670.

(65) Brauer, D. J.; Bürger, H.; Eujen, R. "Vibrational spectra and normal coordinate analysis of CF_3 compounds. XIX. Molecular structure and vibrational spectra of bis(trifluoromethyl)mercury, $(CF_3)_2Hg$" *J. Organomet. Chem.* **1977**, *135*, 281-299.

(66) Kashiwabara, K.; Konaka, S.; Iijima, T.; Kimura, M. "Electron diffraction study of dimethylmercury" *Bull. Chem. Soc. Jpn.* **1973**, *46*, 407-409.

(67) Liao, M.-S.; Huang, S.-P. D. "A theoretical study of gas-phase and solid-state $Hg(CF_3)_2$" *J. Organomet. Chem.* **2000**, *598*, 374-380.

(68) Brauer, D. J.; Bürger, H.; Pawelke, G.; Flegler, K. H.; Haas, A. "Schwingungsspektren und normalkoordinatenanalyse von CF_3-verbindungen: XXVI. Molekülstrukturen und schwingungsspektren von α-CF_3HgN_3 und CF_3HgNCO" *J. Organomet. Chem.* **1978**, *160*, 389-401.

(69) Klapötke, T. M.; Krumm, B.; Moll, R. "Synthetic and structural studies on methyl-, *tert*-butyl- and phenylmercury(II) azide" *Z. Anorg. Allg. Chem.* **2011**, *637*, 507-514.

(70) Thewalt, U.; Wöhrle, T. "The structure of Cp_2TiMe_2" *J. Organomet. Chem.* **1994**, *464*, C17-C19.

(71) Huang, H.; Hughes, R. P.; Rheingold, A. L. "Synthesis and structural characterization of new perfluoroacyl and perfluoroalkyl group 6 transition metal compounds" *Organometallics* **2010**, *29*, 1948-1955.

(72) Smytschkow, I.; Gidt, W.; Kunz, C.; Sun, Y.; Langer, J.; Oelkers, B.; Böttcher, T.; Sitzmann, H. "Chromium(III) and chromium(II) phenolate complexes with bulky alkylcyclopentadienyl ligands" *Eur. J. Inorg. Chem.* **2019**, 2742-2749.

(73) Bastian, M.; Morales, D.; Poli, R.; Richard, P.; Sitzmann, H. "Synthesis of new half sandwich tetrachloro derivatives of molybdenum(V) and tungsten(V). X-ray structures of $(C_5HPr^i_4)W(CO)_3(CH_3)$ and $(C_5Et_5)WCl_4$" *J. Organomet. Chem.* **2002**, *654*, 109-116.

(74) Morales-Cerrada, R.; Fliedel, C.; Daran, J. C.; Gayet, F.; Ladmiral, V.; Améduri, B.; Poli, R. "Fluoroalkyl radical generation by homolytic bond dissociation in pentacarbonylmanganese derivatives" *Chem. Eur. J.* **2019**, *25*, 296-308.

(75) Bennett, M. A.; Chee, H. K.; Jeffery, J. C.; Robertson, G. B. "Comparison of σ-alkyl and σ-perfluoroalkyl groups as ligands. 2. Crystal and molecular-structures of dimethyl[(2-vinylphenyl)diphenylphosphine]platinum(II) and bis(trifluoromethyl)[(2-vinylphenyl)diphenylphosphine]platinum(II)" *Inorg. Chem.* **1979**, *18*, 1071-1076.

(76) Bennett, M. A.; Chee, H. K.; Robertson, G. B. "Comparison of ortho-alkyl and ortho-perfluoroalkyl groups as ligands. 1. Crystal and molecular structures of the methylplatinum(II), (trifluoromethyl)platinum(II), and (pentafluoroethyl)platinum(II) complexes *trans*-$PtClR(PMePh_2)_2$ ($R = CH_3, CF_3, C_2F_5$)" *Inorg. Chem.* **1979**, *18*, 1061-1070.

(77) Martínez-Salvador, S.; Falvello, L. R.; Martín, A.; Menjón, B. "Gold(I) and gold(III) trifluoromethyl derivatives" *Chem. Eur. J.* **2013**, *19*, 14540-14552.

(78) Zhu, D. M.; Lindeman, S. V.; Kochi, J. K. "X-ray crystal structures and the facile oxidative (Au-C) cleavage of the dimethylaurate(I) and tetramethylaurate(III) homologues" *Organometallics* **1999**, *18*, 2241-2248.

(79) Eujen, R.; Bürger, H.; Oberhammer, H. "Vibrational spectra and normal coordinate analysis of CF_3 compounds. Part XXXV. Vibrational spectra, normal coordinate analysis and electron diffraction studies of $(CF_3)_4Sn$" *J. Mol. Struct.* **1981**, *71*, 109-116.

(80) Nagashima, M.; Fujii, H.; Kimura, M. "Electron-diffraction investigation of molecular structure of tetramethyltin" *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3708-3711.

(81) (a) Oberhammer, H. "On the structural effects of CF_3 groups" *J. Fluor. Chem.* **1983**, *23*, 147-162.

(b) Yokozeki, A.; Bauer, S. H. "The geometric and dynamic structures of fluorocarbons and related compounds" *Top. Curr. Chem.* **1975**, *53*, 71-119.

(82) It is pertinent to note that the positive ^{19}F NMR spectroscopic chemical shift reported for $py_2Zn(CF_3)_2$ (reference 19) is significantly different to that for other trifluoromethyl complexes which have negative values and is, therefore, anomalous.

(83) (a) de Dios, A. C.; Jameson, C. J. "The NMR chemical shift: insight into structure and environment" *Ann. Rep. NMR. Spectrosc.* **1994**, *29*, 1-69.

(b) Hansen, P. E. "Isotope effects on nuclear shielding" *Ann. Rep. NMR Spectrosc.* **1983**, *15*, 105-234.

(b) Hansen, P. E. "Isotope effects in nuclear shielding" *Prog. NMR Spectrosc.* **1988**, *20*, 207-255.

(d) Jankowski, S. "Application of NMR spectroscopy in isotope effects studies" *Ann. Rep. NMR Spectrosc.* **2009**, *68*, 149-191.

(e) Jameson, C. J. "Understanding NMR chemical shifts" *Annu. Rev. Phys. Chem.* **1996**, *47*, 135-169.

(84) (a) Jameson, C. J. "Correlation between the ^{19}F absolute nuclear magnetic shielding and its temperature dependence in the fluoromethanes" *Mol. Phys.* **1985**, *54*, 73-79.

(b) Jameson, C. J.; Osten, H. J. "Rovibrational averaging of molecular magnetic properties of CH_3F, CH_2F_2, and CHF_3" *Mol. Phys.* **1985**, *56*, 1083-1095.

(c) Jameson, C. J.; Osten, H. J. "Systematic trends in the variation of ^{19}F nuclear magnetic shielding with bond extension in halomethanes" *Mol. Phys.* **1985**, *55*, 383-395.

(85) Sutcliffe, L. H.; Taylor, B. "^{19}F NMR spectra and ^{13}C satellite spectra of some fluorochloroacetones" *Spectrochim. Acta* **1972**, *28A*, 619-626.

(86) Johnson, M. P. "The effect of the metal-carbon sigma bond on C-F stretching frequencies in trifluoromethyl compounds" *Inorg. Chim. Acta* **1969**, *3*, 232-234.

(87) v. d. Berg, G. C.; Oskam, A.; Vrieze, K. "Vibrational assignments for some $X_3MCo(CO)_4$ molecules. 2. M = C, Ge, and X = H, D, F" *J. Organomet. Chem.* **1974**, *69*, 169-177.

(88) Fernandez, L. E.; Varetti, E. L. "Scaled quantum mechanical force fields for the isoelectronic molecules CF_3X ($X = SiH_3$, PH_2, SH, Cl)" *Z. Anorg. Allg. Chem.* **2007**, *633*, 2678-2682.

(89) (a) Brauer, D. J.; Bürger, H.; Eujen, R. "Vibrational-spectra and normal coordinate analysis of CF_3 compounds. XIX. Molecular structure and vibrational spectra of bis(trifluoromethyl)mercury, $(CF_3)_2Hg$" *J. Organomet. Chem.* **1977**, *135*, 281-299.

(b) Downs, A. J. "Spectroscopic Studies of bistrifluoromethylmercury in solution" *J. Chem. Soc.* **1963**, 5273-5278.

(90) Cotton, F. A.; McCleverty, J. A. "Evidence for multiple bonding in metal-to-fluoroalkyl bonds" *J. Organomet. Chem.* **1965**, *4*, 490.

(91) Liu, E. K. S. "Chemistry of trifluoromethyl compounds. 2. Synthesis and characterization of bis(pyridine)bis(trifluoromethyl)zinc" *Inorg. Chem.* **1980**, *19*, 266-268.

(92) Eujen, R.; Hoge, B. "Donor-free bis(trifluoromethyl)cadmium, $(CF_3)_2Cd$: a readily available low-temperature difluorocarbene source" *J. Organomet. Chem.* **1995**, *503*, C51-C54.

(93) McGee, P. R.; Cleveland, F. F.; Meister, A. G.; Decker, C. E. "Substituted methanes. X. Infrared spectral data, assignments, potential constants, and calculated thermodynamic properties for CF_3Br and CF_3I" *J. Chem. Phys.* **1953**, *21*, 242-246.

(94) Davidson, G.; Davies, C. L. "Raman spectroscopy in liquid xenon solutions: Trifluorohalomethanes" *Spectrochim. Acta* **1989**, *45A*, 371-373.

(95) Clark, R. J. H.; Ellestad, O. H. "The vapour phase Raman spectra, Raman band contour analyses, Coriolis coupling constants, and e-species force constants for the molecules HCF_3, $ClCF_3$, $BrCF_3$, and ICF_3" *Mol. Phys.* **1975**, *30*, 1899-1911.

(96) Burger, H.; Eujen, R. "Vibrational spectra and normal coordinate analysis of CF_3 compounds. 9. Compounds CF_3GeX_3 (X = F, Cl, Br, I)" *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.* **1975**, *31*, 1645-1654.

(97) Eujen, R. "Vibrational spectra and normal co-ordinate analysis of CF_3 compounds. Trimethyl(trifluoromethyl)silane, $CF_3Si(CH_3)_3$ and $CF_3Si(CD_3)_3$" *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.* **1987**, *43*, 1165-1169.

(98) Clark, H. C.; Tsai, J. H. "Bonding in fluorinated organometallic compounds" *J. Organomet. Chem.* **1967**, *7*, 515-517.

(99) Eujen, R. "Vibrational spectra and normal coordinate analysis of CF_3 compounds. The perfluorotrimethylgermyl anion, $(CF_3)_3Ge^-$" *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.* **1986**, *42*, 1295-1299.

(100) Liu, E. K. S. "Chemistry of trifluoromethyl compounds. 2. Synthesis and characterization of bis(pyridine)bis(trifluoromethyl)zinc" *Inorg. Chem.* **1980**, *19*, 266-268.

(101) Kaesz, H. D.; Phillips, J. R.; Stone, F. G. A. "Preparation and study of some perfluoroalkyl compounds of tin and lead" *J. Am. Chem. Soc.* **1960**, *82*, 6228-6232.

(102) Parsons, T. D.; Self, J. M.; Schaad, L. H. "Trifluoromethyl-substituted boranes. Trifluoromethyldi-*n*-butylborane and trifluoromethylboron difluoride" *J. Am. Chem. Soc.* **1967**, *89*, 3446-3448.

(103) Eujen, R.; Hoge, B. "Donor-free bis(trifluoromethyl)cadmium, $(CF_3)_2Cd$: a readily available low-temperature difluorocarbene source" *J. Organomet. Chem.* **1995**, *503*, C51-C54.

(104) Taw, F. L.; Clark, A. E.; Mueller, A. H.; Janicke, M. T.; Cantat, T.; Scott, B. L.; Hay, P. J.; Hughes, R. P.; Kiplinger, J. L. "Titanium(IV) trifluoromethyl complexes: new perspectives on bonding from organometallic fluorocarbon chemistry" *Organometallics* **2012**, *31*, 1484-1499.

(105) Loizou, D. C.; Castillo, J.; Oki, A. R.; Hosmane, N. S.; Morrison, J. A. "Synthesis of cyclopentadienyldinitrosyl(trifluoromethyl)chromium(0), $CpCr(NO)_2CF_3$, and cyclopentadienyldinitrosyl(trifluoromethyl)molybdenum(0), $CpMo(NO)_2CF_3$. Crystal structure of $CpCr(NO)_2CF_3$" *Organometallics* **1992**, *11*, 4189-4193.

(106) King, R. B.; Bisnette, M. B. "Preparation and decarbonylation of acyl derivatives of cyclopentadienyl metal carbonyls" *J. Organomet. Chem.* **1964**, *2*, 15-37.

(107) Cotton, F. A.; Wing, R. M. "Vibrational spectra and bonding in metal carbonyls VI. Evidence for a π-interaction between manganese pentacarbonyl and perfluoromethyl group" *J. Organomet. Chem.* **1967**, *9*, 511-517.

(108) Clark, G. R.; Hoskins, S. V.; Roper, W. R. "Difluorocarbene complexes of ruthenium derived from trifluoromethyl compounds. $RuCl_2(CF_2)(CO)(PPh_3)_2$,

$RuCl_2(CFNMe_2)(CO)(PPh_3)_2$, $RuCl_2(CFOMe)(CO)(PPh_3)_2$ and the structure of $Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$" *J. Organomet. Chem.* **1982**, *234*, C9-C12.

(109) Hieber, W.; Beck, W.; Lindner, E. "Trifluoracetyl- und trifluormethyl-metallcarbonyle" *Z. Naturforsch. B.* **1961**, *16b*, 229-231.

(110) Beckers, H.; Bürger, H.; Eujen, R.; Rempfer, B.; Oberhammer, H. "Vibrational spectra and normal coordinate analysis of CF_3 compounds. Part XLVII. Vibrational spectra, normal coordinate analysis and electron diffraction investigation of CF_3SiH_3 and its deuterated varieties" *J. Mol. Struct.* **1986**, *140*, 281-301.

(111) King, R. B.; Stone, F. G. A.; Treichel, P. M. "Chemistry of metal carbonyls. XII. New complexes derived from cyclopentadienylcobalt dicarbonyl" *J. Am. Chem. Soc.* **1961**, *83*, 3593-3597.

(112) McCleverty, J. A.; Wilkinson, G. "Transition-metal fluorocarbon complexes. Part VI. Nuclear magnetic resonance studies of perfluoroalkyl compounds of cobalt and rhodium" *J. Chem. Soc.* **1964**, 4200-4203.

(113) Brothers, P. J.; Burrell, A. K.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R. "Trifluoromethyl, difluorocarbene and tetrafluoroethylene complexes of iridium and the crystal-structures of $IrI(CH_3)(CF_3)(CO)(PPh_3)_2$, $Ir(CF_3)(C_2F_4)(CO)(PPh_3)_2$ and $Ir(CF_3)(=CF_2)(CO)(PPh_3)_2$" *J. Organomet. Chem.* **1990**, *394*, 615-642.

(114) McBride, D. W.; Dudek, E.; Stone, F. G. A. "Chemistry of metal carbonyls. Part XXV. Fluorocarbonderivatives of nickel" *J. Chem. Soc.* **1964**, 1752-1759.

(115) Graham, W. A. G. "An approach to the separation of inductive and mesomeric effects in complexes of the types $LMn(CO)_5$ and $LMo(CO)_5$" *Inorg. Chem.* **1968**, *7*, 315-321.

(116) Hall, M. B.; Fenske, R. F. "Electronic structure and bonding in methyl(pentacarbonyl)manganese and perfluoromethyl(pentacarbonyl)manganese" *Inorg. Chem.* **1972**, *11*, 768-775.

(117) Algarra, A. G.; Grushin, V. V.; Macgregor, S. A. "Natural bond orbital analysis of the electronic structure of $L_nM(CH_3)$ and $L_nM(CF_3)$ complexes" *Organometallics* **2012**, *31*, 1467-1476.

(118) Cotton, F. A.; Wing, R. M. "Vibrational spectra and bonding in metal carbonyls VI. Evidence for a π-interaction between manganese pentacarbonyl and perfluoromethyl group" *J. Organomet. Chem.* **1967**, *9*, 511-517.

(119) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. "Cannula techniques for the manipulation of air-sensitive materials" 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. "Vacuum line techniques for handling air-sensitive organometallic compounds" 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.; Drezdzon, M. A.; *The Manipulation of Air-Sensitive Compounds*, 2nd Edition; Wiley-Interscience: New York, 1986.

(120) (a) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. "NMR chemical shifts of common laboratory solvents as trace impurities" *J. Org. Chem.* **1997**, *62*, 7512-7515.

(b) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. "NMR chemical shifts of trace impurities: Common laboratory solvents, organics, and gases in deuterated solvents relevant to the organometallic chemist" *Organometallics* **2010**, *29*, 2176-2179.

(121) (a) Harris, R. K.; Becker, E. D.; De Menezes, S. M. C.; Goodfellow, R.; Granger, P., "NMR nomenclature. Nuclear spin properties and conventions for chemical shifts - (IUPAC recommendations 2001)" *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. "Further conventions for NMR shielding and chemical shifts (IUPAC recommendations 2008)" *Pure Appl. Chem.* **2008**, *80*, 59-84.

(122) (a) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981.

(b) Sheldrick, G. M. "A short history of SHELX" *Acta Cryst.* **2008**, *A64*, 112-122.

(c) Sheldrick, G. M. "Crystal structure refinement with SHELXL" *Acta Cryst.* **2015**, *A71*, 3-8.

(123) (a) Jaguar, version 8.9, Schrodinger, Inc., New York, NY, 2015.

(b) Bochevarov, A. D.; Harder, E.; Hughes, T. F.; Greenwood, J. R.; Braden, D. A.; Philipp, D. M.; Rinaldo, D.; Halls, M. D.; Zhang, J.; Friesner, R. A. "Jaguar: A high-performance quantum chemistry software program with strengths in life and materials sciences" *Int. J. Quantum Chem.* **2013**, *113*, 2110–2142.