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Synthesis, structure and reactivity of a terminal magnesium fluoride compound, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$: hydrogen bonding, halogen bonding and C–F bond formation†

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The bulky tris(3-*tert*-butyl-5-pyrazolyl)hydroborato ligand, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]$, has been employed to obtain the first structurally characterized example of a molecular magnesium compound that features a terminal fluoride ligand, namely $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$, via the reaction of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgMe}$ with Me_3SnF . The chloride, bromide and iodide complexes, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgX}$ ($X = \text{Cl}, \text{Br}, \text{I}$), can also be obtained by an analogous method using Me_3SnX . The molecular structures of the complete series of halide derivatives, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgX}$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) have been determined by X-ray diffraction. In each case, the Mg–X bond lengths are shorter than the sum of the covalent radii, thereby indicating that there is a significant ionic component to the bonding, in agreement with density functional theory calculations. The fluoride ligand of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$ undergoes halide exchange with Me_3SiX ($X = \text{Cl}, \text{Br}, \text{I}$) to afford $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgX}$ and Me_3SiF . The other halide derivatives $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgX}$ undergo similar exchange reactions, but the thermodynamic driving forces are much smaller than those involving fluoride transfer, a manifestation of the often discussed silyphilicity of fluorine. In accord with the highly polarized Mg–F bond, the fluoride ligand of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$ is capable of serving as a hydrogen bond and halogen bond acceptor, such that it forms adducts with indole and $\text{C}_6\text{F}_5\text{I}$. $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$ also reacts with Ph_3CCl to afford Ph_3CF , thereby demonstrating that $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$ may be used to form C–F bonds.

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Introduction

As a consequence of its small size, high electronegativity and low polarisability, the chemistry of fluorine is often distinctly different from that of the other halogens.^{1–4} For example, metal fluoride compounds often exhibit novel structures⁵ and reactivity,^{1b,2,6,7,8,9} but are generally more difficult to obtain than the other halide derivatives. As an illustration, while Grignard reagents (RMgX) are readily synthesized upon treatment of magnesium with RCl , RBr , or RI , the corresponding fluoro Grignard reagents are notoriously difficult to obtain^{2–4} and have been investigated to a negligible extent by comparison to the other halogen derivatives. The paucity of magnesium fluoride compounds is not, however, restricted to Grignard reagents, as illustrated by the fact that fluoride derivatives comprise only 2.4% of all structurally characterized magnesium halide compounds listed in the Cambridge Structural Database (CSD).¹⁰ Even more striking, in none of these compounds does fluorine serve the role of a terminal

ligand. Magnesium fluoride compounds are, nevertheless, of considerable importance in view of the role that they have played in biological systems. For example, the use of *in situ* generated $[\text{MgF}_3]^-$ to provide transition state analogues of the $[\text{PO}_3]^-$ moiety has generated information concerned with the mechanism of phosphoryl transfer as catalyzed by enzymes.^{11–13} Here, we report the synthesis and structural characterization of a terminal magnesium fluoride complex, together with its ability to participate in (i) hydrogen bonding and halogen bonding interactions (both of which are important with respect to crystal engineering),¹⁴ and also (ii) C–F bond formation, which is of note because of the significance of introducing fluorine into organic molecules.^{14a,15}

Results and discussion

We have previously employed tris(pyrazolyl)hydroborato ligands, $[\text{Tp}^{\text{R}, \text{R}'}]$,¹⁶ that feature bulky *tert*-butyl substituents, namely $[\text{Tp}^{\text{Bu}^t}]$, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]$ and $[\text{Tp}^{\text{Bu}^t_2}]$, to provide a sterically demanding pocket about a metal center that enables the isolation of a variety of novel compounds. For example, $[\text{Tp}^{\text{Bu}^t, \text{R}'}]$ ligands provided the first structurally characterized examples of (i) a monomeric zinc hydride compound, $[\text{Tp}^{\text{Bu}^t}]\text{ZnH}$,¹⁷ (ii) a monomeric terminal zinc hydroxide compound, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$,¹⁸ and (iii) a monomeric

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monovalent gallium compound, $[\text{Tp}^{\text{Bu}^t}]\text{Ga}$.¹⁹ This class of ligand was also used to synthesize monomeric magnesium chloride, bromide and iodide compounds,^{20,21} thereby suggesting the possibility that it could also afford a terminal magnesium fluoride compound.

Significantly, we have discovered that the fluoride compound $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgF}$ can indeed be obtained readily upon treatment of $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgMe}$ ²² in benzene with the tin reagent, Me_3SnF ,²³ as illustrated in Scheme 1. The chloride, bromide and iodide complexes, $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgX}$ can also be obtained by the analogous method using Me_3SnX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; Scheme 1).

The molecular structure of $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgF}$ has been determined by X-ray diffraction (Fig. 1), thereby demonstrating that the compound is mononuclear and possesses a terminal fluoride ligand. As noted above, there are no similar compounds listed in the CSD, with other magnesium fluoride derivatives exhibiting various types of bridging interactions, which include μ_2 -,^{24–26} μ_3 -,²⁷ and μ_4 -modes.^{28,29} Terminal Mg–F moieties have, nevertheless, been structurally characterized in protein structures.^{11a,d,e,h,i}

As would be expected, the Mg–F bond of $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgF}$ [1.7977(11) Å] is considerably shorter than those with bridging fluoride ligands.³⁰ For example, the Mg–F bond lengths of dinuclear $\{[\text{BDI}^{\text{Ar}}]\text{Mg}(\mu\text{-F})(\text{THF})\}_2$ with μ_2 -bridges are 1.951(2) Å,^{24,31} while those of trinuclear $[\text{Mg}_3(\mu_3\text{-F})(\mu_2\text{-TFA})_6(\text{OME})_2(\text{py})]^{3-}$ with a μ_3 -bridge range from 2.012(5) Å to 2.047(4) Å.²⁷ Correspondingly, magnesium fluoride compounds that feature μ_4 -bridges exhibit even longer Mg–F bonds that range from 2.12 Å to 2.21 Å.^{28,32,33} In addition to the Mg–F bond of $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgF}$ being shorter than other Mg–F bonds, it is also amongst the shortest Mg–X ($\text{X} \neq \text{H}$) bonds listed in the CSD, as illustrated by the magnesium oxide and alkoxide complexes, $[\{(\text{THF})[\text{BDI}^{\text{Ar}}]\text{Mg}\}_2(\mu\text{-O})]$ [1.8080(5) Å],³⁴ $[\text{MesC}\{(\text{C}_4\text{N})\text{Mes}\}_2]\text{Mg}(\text{O}^i\text{Bu})(\text{THF})$ [1.804(2) Å],³⁵ and $[(\text{ArO})\text{Mg}(\mu\text{-OAr})_2]\text{Mg}$ ($\text{Ar} = \text{C}_6\text{H}_3\text{Pr}^t_2$) [1.785(2) Å and 1.790(2) Å].³⁶

Spectroscopically, $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgF}$ is characterized by a ¹⁹F NMR signal at –169.3 ppm, which is within the range exhibited by the related beryllium and zinc complexes, namely $[\text{Tp}]\text{BeF}$ (–149 ppm),³⁷ $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{ZnF}$ (–207 ppm),^{21a} and $[\text{Tp}^{\text{p-Tol},\text{Me}}]\text{ZnF}$ (–219 ppm),^{21a} but is very different from the values observed for the dinuclear compounds, $\{[\text{BDI}^{\text{Ar}}]\text{Mg}(\mu\text{-F})(\text{THF})\}_2$ (–25 ppm) and $\{[\text{BDI}^{\text{Ar}}]\text{Mg}(\mu\text{-F})\}_2$ (–26 ppm).²⁴ While this large difference could be taken as an indication that ¹⁹F NMR spectroscopy could be used as a probe of fluoride coordination mode,³⁸ we note that the chemical shift for $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgF}$ (–169.3 ppm) is also comparable to the solid state value for $\text{Mg}_6\text{F}_2(\text{OME})_{10}(\text{MeOH})_{14}$ (–174.5 ppm), which contains $\mu_4\text{-F}$ atoms.^{28a} As such, it is evident that ¹⁹F NMR

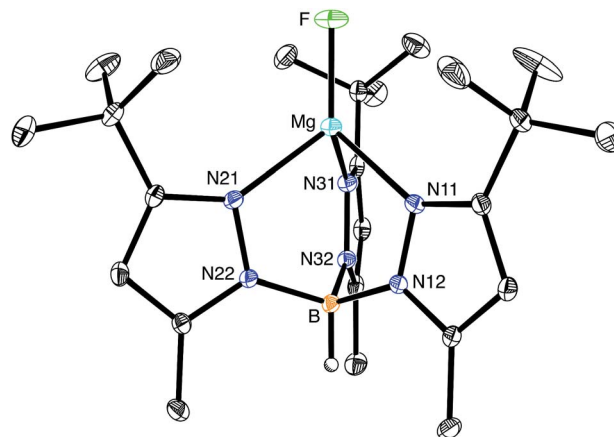


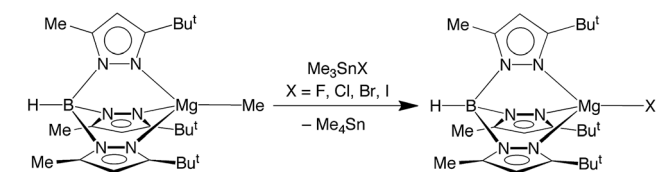
Fig. 1 Molecular structure of $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgF}$.

chemical shift data do not provide a definitive probe for the fluoride coordination mode in these systems. Nevertheless, ¹⁹F NMR data in a comparable region to that of $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgF}$ have been reported in protein systems;^{11c–h} for example, PGM– MgF_3 –G6P–TSA in 100% H_2O buffer exhibits ¹⁹F NMR chemical shifts of –147.0, –151.8, and –159.0 ppm.^{11d}

The molecular structures of $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have also been determined by X-ray diffraction.³⁹ In each case, the molecules possess approximately C_{3v} symmetry, with a magnesium coordination geometry that is distorted considerably from tetrahedral. Specifically, the τ_4 four-coordinate geometry indices⁴⁰ range from 0.79 to 0.82 (Table 1) and deviate considerably from the value of 1.00 for that of an idealized tetrahedron.

The availability of a complete series of structurally characterized halide compounds provides an opportunity to evaluate the bonding as a function of the halogen. The variation of the Mg–X bond lengths is illustrated in Table 1 and Fig. 2, which include, for comparison, the values predicted on the basis of the single bond covalent radii of the elements.

In this regard, it is pertinent to note that two sets of covalent radii have been recently proposed by Alvarez⁴¹ and Pyykkö,^{42,43} and that in each case the experimental Mg–X bond lengths are consistently smaller than those predicted by the sum of the covalent radii. With the exception of the fluoride derivative, the Pyykkö estimates are closer to the experimental bond lengths than are the Alvarez values. Specifically, the experimental Mg–X bond lengths are 0.13–0.19 Å shorter than the Alvarez values, and 0.05–0.23 Å shorter than the Pyykkö values. The magnesium–



Scheme 1 Synthesis of $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgX}$.

Table 1 Metrical data for $[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgX}$

	$d(\text{M-X})/\text{\AA}$	τ_4	$\text{B}\cdots\text{M-X}^\circ$
$[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgF}$	1.7977(11)	0.79	177.8
$[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgCl}$	2.2701(15)	0.81	179.2
	2.2677(15)	0.81	179.1
$[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgBr}$	2.425(2)	0.81	178.9
	2.425(2)	0.82	179.0
$[\text{Tp}^{\text{Bu}^t,\text{Me}}]\text{MgI}$	2.6696(9)	0.80	177.8



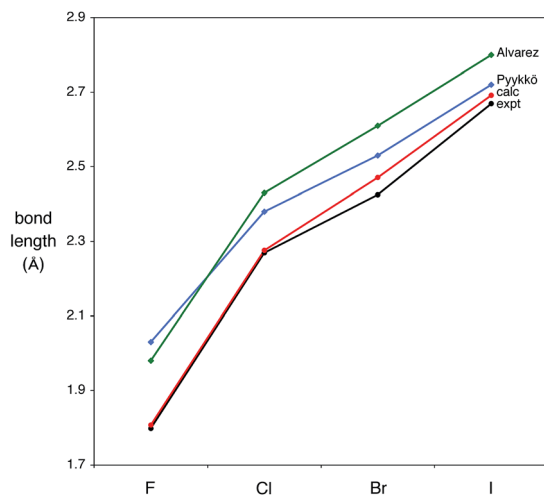


Fig. 2 Comparison of experimental and calculated Mg–X (X = F, Cl, Br, I) bond lengths, together with the sum of Pyykkö and Alvarez covalent radii.

methyl bond length of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgMe}$ [2.119(3) Å]²² is also shorter than the predicted values, although the difference (0.05 Å, Alvarez; 0.02 Å, Pyykkö) is much smaller than those for the halide derivatives. In addition to being smaller than the sum of the covalent radii, the experimental bond lengths are also shorter than the sum of the respective ionic radii.⁴⁴

In principle, M–X bond lengths that are shorter than the sum of single-bond covalent radii can be a consequence of either (i) an ionic contribution to the bonding or (ii) π -bonding.⁴⁵ To investigate this issue, we have examined the series of compounds, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgX}$ (X = F, Cl, Br, I), computationally. Firstly, density functional theory (DFT) geometry optimization calculations reproduce the experimental structures very well, as indicated by the close correspondence between the experimental and calculated Mg–X bond lengths (Fig. 2). Secondly, the calculations indicate that the bonds have a significant ionic component, as illustrated by the atomic charges on the halogen, be they derived from Mulliken, electrostatic potential, or Natural population analysis. Thirdly, the bonds have no M–X π -interactions,⁴⁶ such that it is the ionic component which provides a mechanism to shorten the Mg–X bond from that predicted by the sum of the covalent radii.⁴⁷ Thus, both the experimental observations and the theoretical calculations are consistent with the Mg–X bonds having a significant ionic component; furthermore, the

Table 2 Atomic charges (atomic units) on Mg and X in $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgX}$ (X = F, Cl, Br, I)

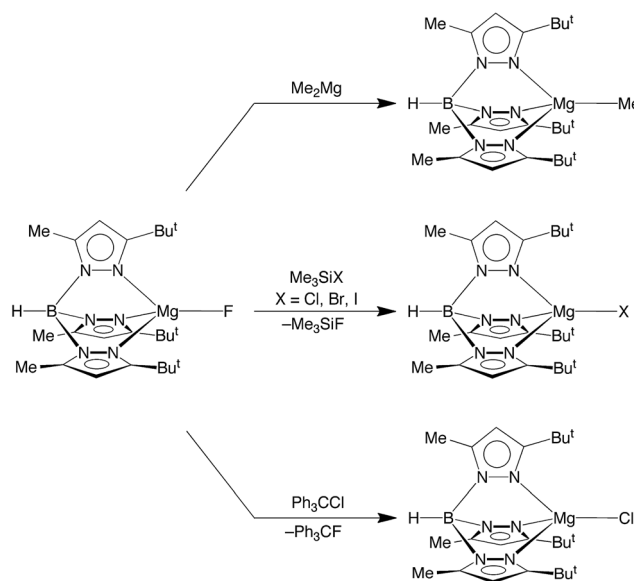
	NPA		Mulliken		ESP	
	q_{Mg}/e	q_{X}/e	q_{Mg}/e	q_{X}/e	q_{Mg}/e	q_{X}/e
F	1.733	−0.828	0.658	−0.496	0.334	−0.516
Cl	1.660	−0.809	0.526	−0.408	0.358	−0.431
Br	1.624	−0.767	0.516	−0.385	0.400	−0.426
I	1.597	−0.736	0.534	−0.400	0.448	−0.393

calculations indicate that this is greatest for the fluoride derivative (Table 2).

In terms of reactivity, the fluoride compound $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$ reacts with Me_2Mg to regenerate the methyl derivative, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgMe}$ (Scheme 2). Furthermore, the well known silyphilicity of fluorine^{48,49} provides a means to convert the fluoride complex $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$ to the other halide derivatives *via* reaction with Me_3SiX (X = Cl, Br, I),⁵⁰ as illustrated in Scheme 2.

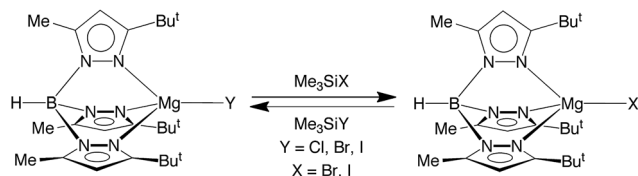
More interesting than its reactivity towards Me_3SiX , $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$ also reacts with Ph_3CCl to afford $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgCl}$ and Ph_3CF (Scheme 2). The ability of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$ to fluorinate Ph_3CCl is of note because of the current significance of introducing fluorine into organic molecules,^{14,15} which is of interest due to their role in pharmaceuticals and agrochemicals. The incorporation of fluorine into such molecules is, however, nontrivial, due to the facts that (i) fluoride has a large hydration energy and (ii) bonds to fluorine are strong.¹ Therefore, considerable attention has been directed towards using metal-mediated transformations for introducing fluorine. The majority of studies, however, have focused on the use of transition metals.¹⁵ For example, $[\text{RuF}(\text{dppp})_2]^+$ has also been used to convert Ph_3CCl to Ph_3CF .⁵¹ Thus, the corresponding reaction of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$ provides a novel example of C–F bond formation mediated by a covalent main group metal compound.

In addition to $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$ undergoing halogen exchange with Me_3SiX (X = Cl, Br, I), the chloride and bromide complexes, $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgCl}$ and $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgBr}$, also undergo halogen exchange with the heavier Me_3SiX derivatives (Scheme 3). The magnitude of the equilibrium constants are such that they may be determined by NMR spectroscopy (Table 3), thereby indicating that the thermodynamics for the exchange between congeneric pairs of halogens, *i.e.* $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgY}$ (Y = F, Cl, Br) and Me_3SiX (X = Cl, Br, I), becomes less exoergic upon descending the periodic table. The derived equilibrium



Scheme 2 Reactivity of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{MgF}$.





Scheme 3 Halide exchange reactions.

constants for the reactions of $[\text{Tp}^{\text{Bu}^t, \text{Me}^e}]\text{MgY}$ ($Y = \text{F}, \text{Cl}, \text{Br}, \text{I}$) with Me_3SiI are also listed in Table 3, which indicates that the reaction which involves formation of the Si-F bond is more exoergic than that which involves formation of the Si-I bond. As such, the data provide quantitative evidence that the phenomenological siliphilicity of the halogens increases in the sequence $\text{I} \approx \text{Br} < \text{Cl} \ll \text{F}$. While this trend is in accord with the Si-F bond being stronger than the Si-I bond,⁵² it is important to emphasize that the thermodynamics are actually dictated by the relative values of Mg-X and Si-X bond energies.

Another interesting aspect of the reactivity of $[\text{Tp}^{\text{Bu}^t, \text{Me}^e}]\text{MgF}$ pertains to its ability to participate in intermolecular interactions. In this regard, while fluorine is well recognized as an important structure-directing element by virtue of its ability to bridge two or more metal centers (*vide supra*),⁵³ it may also serve a structural role by participating in hydrogen bonding⁵⁴ and halogen bonding⁵⁵⁻⁵⁷ interactions. The latter is a directional attractive noncovalent interaction between a covalently bound halogen atom (X), *e.g.* R-X or X-X, and a Lewis base, and results from the electron density distribution about X being anisotropic, such that it creates a belt of high electron density perpendicular to the covalent bond, but a region of low electron density (a so-called σ -hole) in the direction of the bond.⁵⁵ Albeit much less heavily investigated than hydrogen bonding, halogen bonding has been shown to be an important tool in crystal engineering,⁵⁵ with geometrical preferences that are similar to hydrogen bonding interactions, *i.e.* linear $\text{A} \cdots \text{X} \cdots \text{D}$ motifs, where A is the acceptor for the halogen bond and D is the donor. However, despite many structural investigations pertaining to intermolecular interactions involving metal fluoride ligands,^{54b,g} there are few reports that detail the thermodynamics associated with either hydrogen bonding,^{50b,58-60} or halogen bonding

Table 3 Thermodynamics for $[\text{Tp}^{\text{Bu}^t, \text{Me}^e}]\text{MgY}/\text{Me}_3\text{SiX}$ halogen exchange reactions

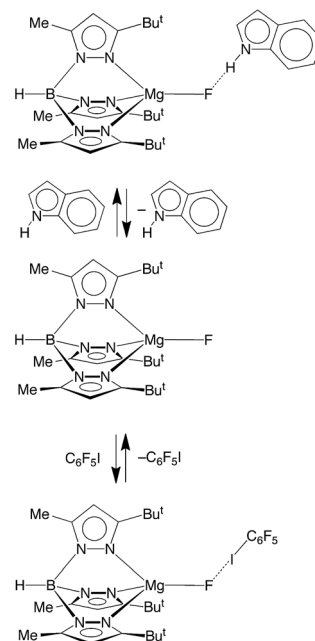
Reactants ^a	Products ^a	<i>K</i>
$[\text{Mg}]\text{F} + \text{Me}_3\text{SiCl}$	$[\text{Mg}]\text{Cl} + \text{Me}_3\text{SiF}$	$>1000^b$
$[\text{Mg}]\text{Cl} + \text{Me}_3\text{SiBr}$	$[\text{Mg}]\text{Br} + \text{Me}_3\text{SiCl}$	13.4 ± 1.2^b
$[\text{Mg}]\text{Br} + \text{Me}_3\text{SiI}$	$[\text{Mg}]\text{I} + \text{Me}_3\text{SiBr}$	0.93 ± 0.15^b
$[\text{Mg}]\text{F} + \text{Me}_3\text{SiI}$	$[\text{Mg}]\text{I} + \text{Me}_3\text{SiF}$	$>12\,500^c$
$[\text{Mg}]\text{Cl} + \text{Me}_3\text{SiI}$	$[\text{Mg}]\text{I} + \text{Me}_3\text{SiCl}$	12.5^c
$[\text{Mg}]\text{Br} + \text{Me}_3\text{SiI}$	$[\text{Mg}]\text{I} + \text{Me}_3\text{SiBr}$	0.93^b
$[\text{Mg}]\text{I} + \text{Me}_3\text{SiI}$	$[\text{Mg}]\text{I} + \text{Me}_3\text{SiI}$	1^d

^a $[\text{Mg}] = [\text{Tp}^{\text{Bu}^t, \text{Me}^e}]\text{Mg}$. ^b Experimental value. ^c Derived from experimentally measured *K* values. ^d Defined value.

interactions.^{50b,58,61,62} Therefore, we have examined the ability of the fluoride ligand of $[\text{Tp}^{\text{Bu}^t, \text{Me}^e}]\text{MgF}$ to serve as a hydrogen bond and halogen bond acceptor.

Hydrogen bonding interactions involving magnesium fluoride species are of relevance to the use of *in situ* generated $[\text{MgF}_3]^-$ to provide transition state analogues of phosphoryl transfer.^{11,12,63} In this regard, indole is a useful probe for quantitative studies because, although it is a good hydrogen bond donor, it is neither a good hydrogen bond acceptor nor a good nitrogen donor ligand,^{58,64} both of which would otherwise complicate the analysis. In this regard, Job plots⁶⁵ based on ¹H and ¹⁹F NMR spectroscopic data demonstrate that the interaction between $[\text{Tp}^{\text{Bu}^t, \text{Me}^e}]\text{MgF}$ and indole involves formation of a 1 : 1 adduct in benzene (Scheme 4 and Fig. 3).⁶⁶ Analysis of the variation of the ¹⁹F NMR chemical shift as a function of indole concentration provides a binding constant of $K = 39 \pm 6 \text{ M}^{-1}$ at 300 K for formation of the 1 : 1 adduct, $[\text{Tp}^{\text{Bu}^t, \text{Me}^e}]\text{MgF} \cdot \text{indole}$.⁶⁷ For comparison, there are few reports pertaining to the thermodynamics of hydrogen bonding of indole to a terminal fluoride ligand, namely $[\kappa^4\text{-Tp}^{\text{Bu}^t, \text{Me}^e}]\text{ZnF}$ (85 M^{-1}),^{50b} $(\text{Et}_3\text{P})_2\text{Ni}(\text{C}_5\text{NF}_4)\text{F}$ (57.9 M^{-1}),^{58,68} and $\text{Cp}^*\text{M}_2\text{F}_2$ ($\text{M} = \text{Ti}, 5.4 \text{ M}^{-1}$; $\text{M} = \text{Zr}, 1.4 \text{ M}^{-1}$; $\text{M} = \text{Hf}, 1.4 \text{ M}^{-1}$),⁶⁹ from which it is evident that $[\text{Tp}^{\text{Bu}^t, \text{Me}^e}]\text{MgF}$ must be considered a significant hydrogen bond acceptor.

The ability of $[\text{Tp}^{\text{Bu}^t, \text{Me}^e}]\text{MgF}$ to participate in halogen bonding interactions has been investigated by a related study using $\text{C}_6\text{F}_5\text{I}$. Thus, ¹⁹F NMR spectroscopy demonstrates that the fluoride ligand of $[\text{Tp}^{\text{Bu}^t, \text{Me}^e}]\text{MgF}$ serves as a halogen bond acceptor (Scheme 4) with the ¹⁹F NMR chemical signal shifting downfield upon addition of $\text{C}_6\text{F}_5\text{I}$.⁷⁰ The derived binding constant ($1.6 \pm 0.3 \text{ M}^{-1}$) is approximately an order of magnitude smaller than the hydrogen bonding interaction involving indole, but is

Scheme 4 Hydrogen and halogen bonding interactions of $[\text{Tp}^{\text{Bu}^t, \text{Me}^e}]\text{MgF}$.

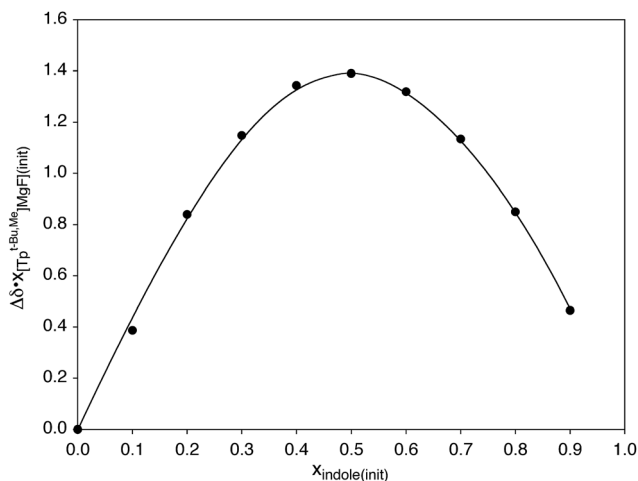


Fig. 3 Job plot for coordination of indole to $[\text{Tp}^{\text{Bu}^i,\text{Me}^t}]\text{MgF}$ as measured by ^1H NMR spectroscopy.

comparable to the few reports of halogen bonding interactions involving fluoride ligands, namely $[\kappa^4\text{-Tp}]\text{ZnF}$ (9.0 M^{-1}) and $\text{trans}(\text{R}_3\text{P})_2\text{M}(\text{Ar})\text{F}$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}; 2.4 \text{ to } 5.2 \text{ M}^{-1}$).^{58,61a}

Conclusions

In summary, the first structurally characterized example of a molecular magnesium compound that features a terminal fluoride ligand, namely $[\text{Tp}^{\text{Bu}^i,\text{Me}^t}]\text{MgF}$, has been obtained by the reaction of $[\text{Tp}^{\text{Bu}^i,\text{Me}^t}]\text{MgMe}$ with Me_3SnF . The chloride, bromide and iodide complexes, $[\text{Tp}^{\text{Bu}^i,\text{Me}^t}]\text{MgX}$, can also be obtained by analogous methods using Me_3SnX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). Structural characterization by X-ray diffraction demonstrates that, in each case, the $\text{Mg}-\text{X}$ bond lengths are shorter than the sum of the covalent radii, thereby indicating that there is a significant ionic component to the bonding, which is in accord with density functional theory calculations.

The fluoride ligand of $[\text{Tp}^{\text{Bu}^i,\text{Me}^t}]\text{MgF}$ undergoes halide exchange with Me_3SiX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) to afford $[\text{Tp}^{\text{Bu}^i,\text{Me}^t}]\text{MgX}$. The other halide derivatives $[\text{Tp}^{\text{Bu}^i,\text{Me}^t}]\text{MgX}$ undergo similar exchange reactions, but the thermodynamic driving forces are much smaller than those involving fluoride transfer, a manifestation of the often discussed silaphilicity of fluorine. $[\text{Tp}^{\text{Bu}^i,\text{Me}^t}]\text{MgF}$ also undergoes metathesis with Ph_3CCl to afford Ph_3CF , thereby demonstrating that $[\text{Tp}^{\text{Bu}^i,\text{Me}^t}]\text{MgF}$ has applications in the formation of C–F bonds.

In accord with the highly polarized nature of the $\text{Mg}-\text{F}$ bond, the fluoride ligand of $[\text{Tp}^{\text{Bu}^i,\text{Me}^t}]\text{MgF}$ is capable of serving as a hydrogen bond and halogen bond acceptor to indole and $\text{C}_6\text{F}_5\text{I}$, respectively. The ability of $[\text{Tp}^{\text{Bu}^i,\text{Me}^t}]\text{MgF}$ to participate in hydrogen bonding interactions mimics the involvement of magnesium fluoride species in biological systems.

Acknowledgements

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Notes and references

- (a) D. O'Hagan, *Chem. Soc. Rev.*, 2008, **37**, 308–319; (b) K. Fagnou and M. Lautens, *Angew. Chem., Int. Ed.*, 2002, **41**, 26–47.
- J. L. Kiplinger, T. G. Richmond and C. E. Osterberg, *Chem. Rev.*, 1994, **94**, 373–431.
- B. R. Jagirdar, E. F. Murphy and H. W. Roesky, *Prog. Inorg. Chem.*, 1999, **48**, 351–455.
- (a) E. C. Ashby, S. H. Yu and R. G. Beach, *J. Am. Chem. Soc.*, 1970, **92**, 433–435; (b) S. H. Yu and E. C. Ashby, *J. Org. Chem.*, 1971, **36**, 2123–2128; (c) E. C. Ashby and J. A. Nackashi, *J. Organomet. Chem.*, 1970, **24**, C17–C19; (d) E. C. Ashby and J. Nackashi, *J. Organomet. Chem.*, 1974, **72**, 11–20; (e) E. C. Ashby and S. Yu, *J. Organomet. Chem.*, 1971, **29**, 339–348; (f) G. B. Sergeev, V. V. Smirnov and F. Z. Badaev, *J. Organomet. Chem.*, 1982, **224**, C29–C30.
- H. W. Roesky and I. Haiduc, *J. Chem. Soc., Dalton Trans.*, 1999, 2249–2264.
- (a) N. M. Doherty and N. W. Hoffman, *Chem. Rev.*, 1991, **91**, 553–573; (b) E. F. Murphy, R. Murugavel and H. W. Roesky, *Chem. Rev.*, 1997, **97**, 3425–3468; (c) H. W. Roesky, *Inorg. Chem.*, 1999, **38**, 5934–5943; (d) V. V. Grushin, *Acc. Chem. Res.*, 2010, **43**, 160–171; (e) A. Mezzetti and C. Becker, *Helv. Chim. Acta*, 2002, **85**, 2686–2703.
- T. Hascall, D. Rabinovich, V. J. Murphy, M. D. Beachy, R. A. Friesner and G. Parkin, *J. Am. Chem. Soc.*, 1999, **121**, 11402–11417.
- (a) R. N. Perutz and T. Braun, in *Comprehensive Organometallic Chemistry III*, ed. R. H. Crabtree and D. M. P. Mingos, Elsevier, Oxford, 2007, vol. 1, ch. 1.26; (b) H. Amii and K. Uneyama, *Chem. Rev.*, 2009, **109**, 2119–2183; (c) J. Burdeniuc, B. Jedlicka and R. H. Crabtree, *Chem. Ber.*, 1997, **130**, 145–154.
- (a) B. L. Pagenkopf and E. M. Carreira, *Chem.–Eur. J.*, 1999, **5**, 3437–3442; (b) R. O. Duthaler and A. Hafner, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 43–45; (c) L. Kollár, T. Kégl and J. Bakos, *J. Organomet. Chem.*, 1993, **453**, 155–158; (d) T. Hamada, K. Manabe and S. Kobayashi, *Chem.–Eur. J.*, 2006, **12**, 1205–1215; (e) J. Lv, X. Li, L. Zhong, S. Luo and J.-P. Cheng, *Org. Lett.*, 2011, **12**, 1096–1099.
- F. H. Allen and O. Kennard, *Cambridge Structural Database (version 5.36). 3D Search and Research Using the Cambridge Structural Database, Chemical Design Automation News*, 1993, **8**(1), pp. 1 & 31–37.
- (a) D. L. Graham, P. N. Lowe, G. W. Grime, M. Marsh, K. Rittinger, S. J. Smerdon, S. J. Gamblin and J. F. Eccleston, *Chem. Biol.*, 2002, **9**, 375–381; (b) M. Golcnik, *Acta Chim. Slov.*, 2010, **57**, 272–287; (c) N. J. Baxter, L. F. Olguin, M. Golcnik, G. Feng, A. M. Hounslow, W. Bermel, G. M. Blackburn, F. Hollfelder, J. P. Waltho and N. H. Williams, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 14732–14737; (d) N. J. Baxter, M. W. Bowler, T. Alizadeh, M. J. Cliff, A. M. Hounslow, B. Wu, D. B. Berkowitz, N. H. Williams, G. M. Blackburn and J. P. Waltho, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**,



- 4555–4560; (e) Y. Jin, D. Bhattasali, E. Pellegrini, S. M. Forget, N. J. Baxter, M. J. Cliff, M. W. Bowler, D. L. Jakeman, G. M. Blackburn and J. P. Waltho, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 12384–12389; (f) N. J. Baxter, G. M. Blackburn, J. P. Marston, A. M. Hounslow, M. J. Cliff, W. Bermel, N. H. Williams, F. Hollfelder, D. E. Wemmer and J. P. Waltho, *J. Am. Chem. Soc.*, 2008, **130**, 3952–3958; (g) Y. Jin, M. J. Cliff, N. J. Baxter, H. R. W. Dannatt, A. M. Hounslow, M. W. Bowler, G. M. Blackburn and J. P. Waltho, *Angew. Chem., Int. Ed.*, 2012, **51**, 12242–12245; (h) M. J. Cliff, M. W. Bowler, A. Varga, J. P. Marston, J. Szabó, A. M. Hounslow, N. J. Baxter, G. M. Blackburn, M. Vas and J. P. Waltho, *J. Am. Chem. Soc.*, 2010, **132**, 6507–6516; (i) J. Y. Lee and W. Yang, *Cell*, 2006, **127**, 1349–1360.
- 12 It has also been reported that magnesium fluoride can activate heterotrimeric G proteins and that the structures of some protein·nucleotide complexes that have previously been proposed to contain aluminum fluoride may, in fact, be magnesium derivatives. See: D. L. Graham, J. F. Eccleston, C. W. Chung and P. N. Lowe, *Biochemistry*, 1999, **38**, 14981–14987.
- 13 *In situ* generated $[\text{MgF}_4]^{2-}$ has also been employed. See, for example: (a) M. Laursen, M. Bublitz, K. Moncoq, C. Olesen, J. V. Møller, H. S. Young, P. Nissen and J. P. Morth, *J. Biol. Chem.*, 2009, **284**, 13513–13518; (b) K. Moncoq, C. A. Trieber and H. S. Young, *J. Biol. Chem.*, 2007, **282**, 9748–9757; (c) C. Toyoshima, H. Nomura and T. Tsuda, *Nature*, 2004, **432**, 361–368; (d) S. Danko, K. Yamasaki, T. Daiho and H. Suzuki, *J. Biol. Chem.*, 2004, **279**, 14991–14998; (e) C. Toyoshima, H. Nomura and Y. Sugita, *FEBS Lett.*, 2003, **555**, 106–110.
- 14 (a) F. Meyer and P. Dubois, *CrystEngComm*, 2013, **15**, 3058–3071; (b) E. D. Glowacki, M. Irimia-Vladu, S. Bauer and N. S. Sariciftci, *J. Mater. Chem. B*, 2013, **1**, 3742–3753.
- 15 (a) T. Liang, C. N. Neumann and T. Ritter, *Angew. Chem., Int. Ed.*, 2013, **52**, 8214–8264; (b) M. G. Campbell and T. Ritter, *Chem. Rec.*, 2014, **14**, 482–491; (c) M. G. Campbell and T. Ritter, *Chem. Rev.*, 2015, **115**, 612–633.
- 16 (a) S. Trofimenko, *Scorpionates – The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999; (b) C. Pettinari, *Scorpionates II: Chelating Borate Ligands*, Imperial College Press, London, 2008; (c) G. Parkin, *Chem. Rev.*, 2004, **104**, 699–767; (d) G. Parkin, *Chem. Commun.*, 2000, 1971–1985; (e) G. Parkin, *Metal Ions in Biological Systems*, ed. A. Sigel and H. Sigel, M. Dekker, New York, 2001, vol. 38, ch. 14, pp. 411–460; (f) G. Parkin, *Adv. Inorg. Chem.*, 1995, **42**, 291–393; (g) C. Santini, M. Pelli, G. G. Lobbia and G. Papini, *Mini-Rev. Org. Chem.*, 2010, **7**, 84–124; (h) N. Kitajima and W. B. Tolman, *Prog. Inorg. Chem.*, 1995, **43**, 419–531.
- 17 (a) R. Han, I. B. Gorrell, A. G. Looney and G. Parkin, *J. Chem. Soc., Chem. Commun.*, 1991, 717–719; (b) A. Looney, R. Han, I. B. Gorrell, M. Cornebise, K. Yoon, G. Parkin and A. L. Rheingold, *Organometallics*, 1995, **14**, 274–288.
- 18 (a) A. Looney, R. Han, K. McNeill and G. Parkin, *J. Am. Chem. Soc.*, 1993, **115**, 4690–4697; (b) R. Alsasser, S. Trofimenko, A. Looney, G. Parkin and H. Vahrenkamp, *Inorg. Chem.*, 1991, **30**, 4098–4100.
- 19 M. C. Kuchta, J. B. Bonanno and G. Parkin, *J. Am. Chem. Soc.*, 1996, **118**, 10914–10915.
- 20 (a) R. Han and G. Parkin, *J. Am. Chem. Soc.*, 1992, **114**, 748–757; (b) R. Han, M. Bachrach and G. Parkin, *Polyhedron*, 1990, **9**, 1775–1778; (c) R. Han, A. Looney and G. Parkin, *J. Am. Chem. Soc.*, 1989, **111**, 7276–7278; (d) R. Han and G. Parkin, *Organometallics*, 1991, **10**, 1010–1020.
- 21 For $[\text{Tp}^{\text{R,R}}]\text{MF}$ compounds for metals other than magnesium, see: (a) W. Kläui, U. Schilde and M. Schmidt, *Inorg. Chem.*, 1997, **36**, 1598–1601; (b) M. Rombach, H. Brombacher and H. Vahrenkamp, *Eur. J. Inorg. Chem.*, 2002, 153–159; (c) F. A. Jové, C. Pariya, M. Scoblete, G. P. A. Yap and K. H. Theopold, *Chem.–Eur. J.*, 2011, **17**, 1310–1318; (d) I. B. Gorrell and G. Parkin, *Inorg. Chem.*, 1990, **29**, 2452–2456; (e) D. Naglav, D. Bläser, C. Wölper and S. Schulz, *Inorg. Chem.*, 2014, **53**, 1241–1249.
- 22 O. Michel, H. M. Dietrich, R. Litlabø, K. W. Törnroos, C. Maichle-Mössmer and R. Anwänder, *Organometallics*, 2012, **31**, 3119–3127.
- 23 For the use of Me_3SnF as a fluorinating agent, see: A. Herzog, F.-Q. Liu, H. W. Roesky, A. Demsar, K. Keller, M. Noltemeyer and F. Pauer, *Organometallics*, 1994, **13**, 1251–1256.
- 24 H. Hao, H. W. Roesky, Y. Ding, C. Cui, M. Schormann, H.-G. Schmidt, M. Noltemeyer and B. Žemva, *J. Fluorine Chem.*, 2002, **115**, 143–147.
- 25 J. A. Rood, S. E. Hinman, B. C. Noll and K. W. Henderson, *Eur. J. Inorg. Chem.*, 2008, 3935–3942.
- 26 A. Distler, D. L. Lohse and S. C. Sevov, *J. Chem. Soc., Dalton Trans.*, 1999, 1805–1812.
- 27 J. Noack, C. Fritz, C. Flugel, F. Hemmann, H.-J. Glasel, O. Kahle, C. Dreyer, M. Bauer and E. Kemnitz, *Dalton Trans.*, 2013, **42**, 5706–5710.
- 28 (a) S. Wuttke, A. Lehmann, G. Scholz, M. Feist, A. Dimitrov, S. I. Troyanov and E. Kemnitz, *Dalton Trans.*, 2009, 4729–4734; (b) A. Dimitrov, S. Wuttke, S. Troyanov and E. Kemnitz, *Angew. Chem., Int. Ed.*, 2008, **47**, 190–192.
- 29 For examples of compounds in which fluoride bridges magnesium and another metal, see: (a) F.-Q. Liu, A. Kuhn, R. Herbst-Irmer, D. Stalke and H. W. Roesky, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 555–556; (b) B. Neumüller and F. Gahlmann, *Z. Anorg. Allg. Chem.*, 1993, **619**, 718–726.
- 30 The Mg–F bond length is also comparable to values that have been observed in protein systems (ref. 11a, d, e, h and i). For example, PGM– MgF_3 –G6P–TSA exhibits Mg–F bond lengths of 1.8–1.9 Å (ref. 11d).
- 31 $[\text{BDI}^{\text{Ar}}] = \text{HC}\{\text{C}(\text{Me})\text{NAr}\}_2$, Ar = 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$. This ligand is also referred to as $[\text{P}^{\text{ip}}\text{Nacnac}]$.
- 32 For further comparison, the Mg–F bond lengths in MgF_2 are 1.984(1) Å at 300 K and 1.979 Å at 52 K. See: G. Vidal-Valat, J.-P. Vidal, C. M. E. Zeyen and K. Kurki-Suonio, *Acta Crystallogr.*, 1979, **35**, 1584–1590.
- 33 Mg–F bond lengths of 1.759(28) Å and 1.902(27) Å have been reported for a bridging fluoride ligand in a compound that was obtained as a minor side product of a reaction, with no other characterization. However, a different crystalline



- form of the same compound is characterized by significantly a different pair of Mg–F bond lengths of 1.851(8) Å and 1.828(8) Å. The site occupied by the proposed fluoride ligand in these structures was also disordered with an unidentified organic ligand and so it was noted that the bond lengths associated with this bridging fluoride ligand were to be treated with caution. In particular, the short value of 1.759(28) Å is questionable. See ref. 25.
- 34 R. Lalrempuia, A. Stasch and C. Jones, *Chem. Sci.*, 2013, **4**, 4383–4388.
- 35 M. H. Chisholm, K. Choojun, J. C. Gallucci and P. M. Wambua, *Chem. Sci.*, 2012, **3**, 3445–3457.
- 36 C. A. Zechmann, T. J. Boyle, M. A. Rodriguez and R. A. Kemp, *Polyhedron*, 2000, **19**, 2557–2564.
- 37 D. Naglav, D. Bläser, C. Wölper and S. Schulz, *Inorg. Chem.*, 2014, **53**, 1241–1249.
- 38 Indeed, terminal fluoride ligands are also observed at higher field than μ -F bridging fluoride ligands in Cu, Ag and Au complexes. See: C. M. Wyss, B. K. Tate, J. Bacsá, M. Wieliczko and J. P. Sadighi, *Polyhedron*, 2014, **33**, 87–95.
- 39 See ESI†
- 40 $\tau_4 = [360 - (\alpha + \beta)]/141$, where $\alpha + \beta$ is the sum of the two largest angles. See: L. Yang, D. R. Powell and R. P. Houser, *Dalton Trans.*, 2007, 955–964.
- 41 B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán and S. Alvarez, *Dalton Trans.*, 2008, 2832–2838.
- 42 (a) P. Pykkö and M. Atsumi, *Chem.–Eur. J.*, 2009, **15**, 186–197; (b) P. Pykkö, *J. Phys. Chem. A*, 2015, **119**, 2326–2337.
- 43 The principal difference between these two sets of covalent radii are that (i) the Alvarez values are determined by analysis of more than 228 000 experimental bond distances in the CSD that involve either carbon (0.762 Å), nitrogen (0.706 Å) or oxygen (0.661 Å), and using fixed values of these elements to determine the covalent radius of the partner, while (ii) the Pykkö radii do not use fixed values for any element, but are derived self-consistently by a least-squares fit of an array of bond lengths that include both experimental and theoretical values (albeit a much smaller array of 410 data points than that used by Alvarez). However, the Pykkö values exclude transition metal halide and chalcogenide compounds due to the possibility of the values being influenced by multiple bonding.
- 44 $d(\text{Mg–F}) = 1.90 \text{ \AA}$; $d(\text{Mg–Cl}) = 2.38 \text{ \AA}$; $d(\text{Mg–Br}) = 2.53 \text{ \AA}$; $d(\text{Mg–I}) = 2.77 \text{ \AA}$. See: R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.*, 1976, **32**, 751–767.
- 45 For discussions pertaining to the ionic shortening of covalent bonds, see: (a) R. Blom and A. Haaland, *J. Mol. Struct.*, 1985, **128**, 21–27; (b) R. H. Cayton, M. H. Chisholm, E. R. Davidson, V. F. Distasi, P. Du and J. C. Huffman, *Inorg. Chem.*, 1991, **30**, 1020–1024; (c) A. R. Barron, *Polyhedron*, 1995, **14**, 3197–3207; (d) R. C. Fischer and P. P. Power, *Chem. Rev.*, 2010, **110**, 3877–3923; (e) P. P. Power, *Chem. Rev.*, 1999, **99**, 3463–3503; (f) M. A. Petrie, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1991, **113**, 8704–8708; (g) A. C. Hillier, S. Y. Liu, A. Sella and M. R. J. Elsegood, *Inorg. Chem.*, 2000, **39**, 2635–2644; (h) W. A. Howard, T. M. Trnka and G. Parkin, *Inorg. Chem.*, 1995, **34**, 5900–5909; (i) W. A. Howard and G. Parkin, *J. Am. Chem. Soc.*, 1994, **116**, 606–615; (j) J. G. Melnick and G. Parkin, *Dalton Trans.*, 2006, 4207–4210; (k) J. G. Melnick, A. Docrat and G. Parkin, *Chem. Commun.*, 2004, 2870–2871; (l) Y. Rong, A. Al-Harbi, B. Kriegel and G. Parkin, *Inorg. Chem.*, 2013, **52**, 7172–7182.
- 46 The absence of π -interactions is in accord with calculations on [Tp]GaE (E = O, S, Se, Te) which indicate that each chalcogen possesses three lone pairs so that the bonding is best represented as [Tp]Ga⁺–E[–]. See: J. C. Green and J. L. Suter, *J. Chem. Soc., Dalton Trans.*, 1999, 4087–4092.
- 47 Despite the highly polar nature of the bonding, it is still appropriate to consider the molecules covalent. For a discussion, see: A. Haaland, T. U. Helgaker, K. Ruud and D. J. Shorokhov, *J. Chem. Educ.*, 2000, **77**, 1076–1080.
- 48 S. K. Agbossou, C. Roger, A. Igau and J. A. Gladysz, *Inorg. Chem.*, 1992, **31**, 419–424.
- 49 M. A. Brook, *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, 2000, pp. 27–38.
- 50 For other examples of M–F substitution employing Me₃SiX reagents, see: (a) ref. 21a and b; (b) W. Sattler, S. Rucolo and G. Parkin, *J. Am. Chem. Soc.*, 2013, **135**, 18714–18717.
- 51 (a) P. Barthazy, R. M. Stoop, M. Wörle, A. Togni and A. Mezzetti, *Organometallics*, 2000, **19**, 2844–2852; (b) P. Barthazy, L. Hintermann, R. M. Stoop, M. Wörle, A. Mezzetti and A. Togni, *Helv. Chim. Acta*, 1999, **82**, 2448–2453.
- 52 For example, the Si–X bond dissociation energies of Me₃SiX decrease from F to I (F, 159.9 kcal mol^{–1}; Cl, 109.5 kcal mol^{–1}; Br, 101.4 kcal mol^{–1}; I, 82.1 kcal mol^{–1}). See: Luo Y.-R., in *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, 2007, ch. 9.
- 53 H. W. Roesky and I. Haiduc, *J. Chem. Soc., Dalton Trans.*, 1999, 2249–2264.
- 54 For examples of hydrogen bonding interactions involving halogens as hydrogen bond acceptors, see: (a) L. Brammer, E. A. Bruton and P. Sherwood, *Cryst. Growth Des.*, 2001, **1**, 277–290; (b) L. Brammer, E. A. Bruton and P. Sherwood, *New J. Chem.*, 1999, **23**, 965–968; (c) A. Kovács and Z. Varga, *Coord. Chem. Rev.*, 2006, **250**, 710–727; (d) S. M. M. Sony and M. N. Ponnuswamy, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 1766–1772; (e) T. Steiner, *Acta Crystallogr.*, 1998, **B54**, 456–463; (f) M. Mascall, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1999–2001; (g) T. G. Richmond, *Coord. Chem. Rev.*, 1990, **105**, 221–250.
- 55 (a) P. Metrangolo, H. Neukirch, T. Pilati and G. Resnati, *Acc. Chem. Res.*, 2005, **38**, 386–395; (b) M. Fourmigue, *Curr. Opin. Solid State Mater. Sci.*, 2009, **13**, 36–45; (c) G. Cavallo, P. Metrangolo, T. Pilati, G. Resnati, M. Sansotera and G. Terraneo, *Chem. Soc. Rev.*, 2010, **39**, 3772–3783; (d) P. Metrangolo, F. Meyer, T. Pilati, G. Resnati and G. Terraneo, *Angew. Chem., Int. Ed.*, 2008, **47**, 6114–6127; (e) E. Persch, O. Dumele and F. Diederich, *Angew. Chem., Int. Ed.*, 2015, **54**, 3290–3327; (f) L. P. Wolters, P. Schyman, M. J. Pavan, W. L. Jorgensen, F. M. Bickelhaupt and



- S. Kozuch, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2014, **4**, 523–540; (g) R. W. Troff, T. Makela, F. Topic, A. Valkonen, K. Raatikainen and K. Rissanen, *Eur. J. Org. Chem.*, 2013, 1617–1637; (h) A. Mukherjee, S. Tothadi and G. R. Desiraju, *Acc. Chem. Res.*, 2014, **47**, 2514–2524; (i) *Halogen Bonding I: Impact on Materials Chemistry and Life Sciences. Topics in Current Chemistry*, ed. P. Metrangolo and G. Resnati, Springer, New York, 2014, vol. 358; (j) M. R. Scholfield, C. M. V. Zanden, M. Carter and P. S. Ho, *Protein Sci.*, 2013, **22**, 139–152.
- 56 (a) L. Brammer, G. M. Espallargas and S. Libri, *CrystEngComm*, 2008, **10**, 1712–1727; (b) L. Brammer, G. M. Espallargas and H. Adams, *CrystEngComm*, 2003, **5**, 343–345; (c) F. Zordan and L. Brammer, *Cryst. Growth Des.*, 2006, **6**, 1374–1379.
- 57 (a) T. M. Beale, M. G. Chudzinski, M. G. Sarwar and M. S. Taylor, *Chem. Soc. Rev.*, 2013, **42**, 1667–1680; (b) M. Erdelyi, *Chem. Soc. Rev.*, 2012, **41**, 3547–3557; (c) A. V. Jentzsch, *Pure Appl. Chem.*, 2015, **87**, 15–41; (d) C. C. Robertson, R. N. Perutz, L. Brammer and C. A. Hunter, *Chem. Sci.*, 2014, **5**, 4179–4183.
- 58 S. Libri, N. A. Jasim, R. N. Perutz and L. Brammer, *J. Am. Chem. Soc.*, 2008, **130**, 7842–7844.
- 59 C. E. Osterberg, M. A. King, A. M. Arif and T. G. Richmond, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 888–890.
- 60 D.-H. Lee, H. J. Kwon, B. P. Patel, L. M. Liable-Sands, A. L. Rheingold and R. H. Crabtree, *Organometallics*, 1999, **18**, 1615–1621.
- 61 (a) T. Beweries, L. Brammer, N. A. Jasim, J. E. McGrady, R. N. Perutz and A. C. Whitwood, *J. Am. Chem. Soc.*, 2011, **133**, 14338–14348; (b) N. Cheng, Y. Liu, C. Zhang and C. Liu, *J. Mol. Model.*, 2013, **19**, 3821–3829.
- 62 For an example of halogen bonding involving a metal hydride derivative, see: D. A. Smith, L. Brammer, C. A. Hunter and R. N. Perutz, *J. Am. Chem. Soc.*, 2014, **136**, 1288–1291.
- 63 It is worth noting that, in aqueous solution, the only magnesium fluoride species present in significant concentration is cationic, *i.e.* $[\text{MgF}]^+$, although anionic variants have been evaluated theoretically. See: (a) M. R. Montes, M. S. Ferreira-Gomes, M. Centeno and R. C. Rossi, *Biochim. Biophys. Acta*, 2015, **1848**, 1514–1523; (b) R. E. Connick and M. S. Tsao, *J. Am. Chem. Soc.*, 1954, **76**, 5311–5314; (c) N. Shibata, H. Sato, S. Sakaki and Y. Sugita, *J. Phys. Chem. B*, 2011, **115**, 10553–10559.
- 64 (a) J. Wessel, J. C. Lee Jr, E. Peris, G. P. A. Yap, J. B. Fortin, J. S. Ricci, G. Sini, A. Albinati, T. F. Koetzle, O. Eisenstein, A. L. Rheingold and R. H. Crabtree, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2507–2509; (b) P. Desmurs, K. Kavallieratos, W. Yao and R. H. Crabtree, *New J. Chem.*, 1999, **23**, 1111–1115.
- 65 (a) J. S. Renny, L. L. Tomasevich, E. H. Tallmadge and D. B. Collum, *Angew. Chem., Int. Ed. Engl.*, 2013, **52**, 11998–12013; (b) E. Bruneau, D. Lavabre, G. Levy and J. C. Micheau, *J. Chem. Educ.*, 1992, **69**, 833–837.
- 66 It should be noted that ^{19}F NMR chemical shifts are also influenced by the hydrogen bonding environment of $[\text{MgF}_3]^-$ in proteins. See, for example, ref. 11c–g and K. N. Leigh and C. E. Webster, *Dalton Trans.*, 2014, **43**, 3039–3043.
- 67 Binding constants were determined by using WinEQNMR2. See: M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311–312.
- 68 The activity based equilibrium constant reported was based on the assumption that the activity was equal to the molar concentration and so the M^{-1} units have been included here to facilitate direct comparison.
- 69 D. A. Smith, T. Beweries, C. Blasius, N. Jasim, R. Nazir, S. Nazir, C. C. Robertson, A. C. Whitwood, C. A. Hunter, L. Brammer and R. N. Perutz, *J. Am. Chem. Soc.*, 2015, **137**, 11820–11831.
- 70 There are relatively few studies pertaining to the use of ^{19}F NMR spectroscopy to measure halogen bonding interactions but, for some examples, see ref. 58 and (a) D. Hauchecorne, B. J. van der Veken, W. A. Herrebout and P. E. Hansen, *Chem. Phys.*, 2011, **381**, 5–10; (b) P. Metrangolo, W. Panzeri, F. Recupero and G. Resnati, *J. Fluorine Chem.*, 2002, **114**, 27–33.

