

Cite this: *Chem. Sci.*, 2018, 9, 2348

A combined experimental and computational study on the reaction of fluoroarenes with Mg–Mg, Mg–Zn, Mg–Al and Al–Zn bonds†

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Through a combined experimental and computational (DFT) approach, the reaction mechanism of the addition of fluoroarenes to Mg–Mg bonds has been determined as a concerted S_NAr -like pathway in which one Mg centre acts as a nucleophile and the other an electrophile. The experimentally determined Gibbs activation energy for the addition of C_6F_6 to a Mg–Mg bond of a molecular complex, $\Delta G_{298\text{ K}}^\ddagger(\text{experiment}) = 21.3 \text{ kcal mol}^{-1}$ is modelled by DFT with the $\omega B97X$ functional, $\Delta G_{298\text{ K}}^\ddagger(\text{DFT}) = 25.7 \text{ kcal mol}^{-1}$. The transition state for C–F activation involves a polarisation of the Mg–Mg bond and significant negative charge localisation on the fluoroarene moiety. This transition state is augmented by stabilising closed-shell $Mg \cdots F_{ortho}$ interactions that, in combination with the known trends in C–F and C–M bond strengths in fluoroarenes, provide an explanation for the experimentally determined preference for C–F bond activation to occur at sites flanked by *ortho*-fluorine atoms. The effect of modification of both the ligand coordination sphere and the nature and polarity of the M–M bond (M = Mg, Zn, Al) on C–F activation has been investigated. A series of highly novel β -diketiminate stabilised complexes containing Zn–Mg, Zn–Zn–Zn, Zn–Al and Mg–Al bonds has been prepared, including the first crystallographic characterisation of a Mg–Al bond. Reactions of these new M–M containing complexes with perfluoroarenes were conducted and modelled by DFT. C–F bond activation is dictated by the steric accessibility, and not the polarity, of the M–M bond. The more open coordination complexes lead to enhanced $Mg \cdots F_{ortho}$ interactions which in turn lower the energy of the transition states for C–F bond activation.

Received 25th November 2017
Accepted 19th January 2018

DOI: 10.1039/c7sc05059c

rsc.li/chemical-science

Introduction

The activation of strong carbon–fluorine bonds remains a key academic and industrial challenge that is motivated by the prevalence of fluorine-containing molecules in the pharmaceutical, agricultural and materials industries. Recent advances have focused on the functionalisation of fluoroarenes, with aim of making synthetically useful building blocks.^{1,2} In particular, C–F activation and subsequent borylation has been reported to occur catalytically using a range of late transition metal catalysts.^{3–13}

The activation of aromatic sp^2 C–F bonds with transition metal complexes is known to proceed by several mechanisms, most common of which are oxidative addition (OA) and nucleophilic aromatic substitution (S_NAr).^{14–16} Oxidative addition is

typically observed with 14- or 16-electron complexes of the form ML_2 (M = Ni, Pd, Pt) or ML_3X (M = Rh, Ir), where higher oxidation states are easily accessible.

The concept of ligand-assisted C–F bond activation was introduced to rationalise experimentally observed fluorophosphines, formed during the reaction of perfluoroarenes with group 9 and 10 transition metal phosphine complexes.^{17,18} Originally reported by Milstein in the early 1990s, the reaction of C_6F_6 with $[(Et_3P)_3IrMe]$ forms $[(Et_3P)_2(FEt_2P)IrC_6F_5]$ along with ethene and methane. Density functional calculations were used to substantiate a pathway that occurs by 1,2-addition of the C–F to the Ir–P bond: nucleophilic attack of the electron-rich metal on the fluorocarbon occurs with simultaneous activation, and trapping, of the fluoride by the phosphine. The concept has been expanded to boryl-assisted C–F activation using a $[(Et_3P)_3RhBpin]$ complex and the mechanism used to explain the experimentally observed activation of pentafluoropyridine at the 2-position (Fig. 1 – ligand assisted OA).³

Lewis acid-assisted C–F bond activation, has been explored in a detailed experimental and theoretical study by Nakamura and co-workers. This mechanism is conceptually related to the ligand-assisted pathway but differs in that the Lewis acidic and nucleophilic metal centers are not directly bound to one

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† Electronic supplementary information (ESI) available: Experimental procedures, details of the DFT studies, single crystal X-ray data and multinuclear NMR spectra (DOI: 10.1039/c7sc05059c). X-ray crystallographic data for 2a, 2a-hexane, 2b, 3, 3-THF, 3a, 4, 6 and 7 (CIF). CCDC 1575549–1575558, 1577209. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7sc05059c



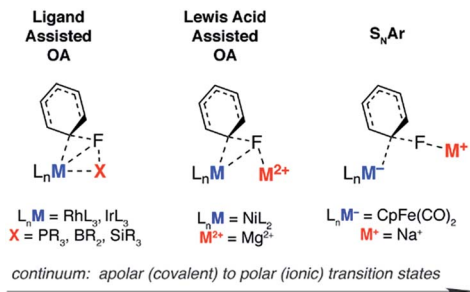


Fig. 1 Selected transition states for C–F bond activation of fluoroarenes.

another (Fig. 1 – Lewis acid assisted OA). Kumada–Tamao–Corriu cross-coupling reactions between aryl fluorides and Grignard reagents can be catalysed by $[\text{Ni}(\text{acac})_2]$.¹⁹ The use of a dinucleating hydroxyphosphine ligand leads to an active catalyst, which operates through a cooperative push–pull mechanism. The nickel and magnesium centers act as electron donors and acceptors respectively, facilitating C–F bond activation.

Nucleophilic mechanisms have been invoked for coordinatively saturated anionic 18-electron complexes, and are facilitated by the highly polar C–F bond. For example, C–F activation of fluoroarenes and fluoroalkenes using the Fp^- (cyclopentadienyliron dicarbonyl) anion is proposed to occur by nucleophilic aromatic substitution (Fig. 1 – $\text{S}_{\text{N}}\text{Ar}$) and nucleophilic vinylic substitution respectively.^{20,21} While the relative rates of reactions are consistent with the known nucleophilicity scale²⁰ of anionic transition metal carbonyl complexes,^{22,23} the true degree of charge separation in the proposed transition state for C–F bond activation remains a point of debate.²⁴ Related nucleophilic anionic intermediates, formed *via* deprotonation of $[\text{Cp}^*\text{M}(\text{PMe}_3)_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) are also postulated to be the active species in C–F bond activation reactions.^{25,26}

We recently reported the C–F bond activation of a series of perfluorinated and partially fluorinated arenes, using the low valent $\text{Mg}(\text{i})$ species **1** (Fig. 2).^{27,28}

The reaction results in the formation of a new Mg–C bond and a new Mg–F bond and may be considered as a homogeneous equivalent to Grignard formation. The new organometallic complexes have potential to be used as fluorinated building blocks in synthesis.²⁹ Initial mechanistic investigations provided support for a concerted two-electron reaction



Fig. 2 C–F bond activation of fluoroarenes using Mg–Mg reagents.

pathway, with no radical intermediates detected through trapping experiments. A plausible transition state for this reaction involves the 1,2-addition of the C–F bond across the apolar Mg–Mg bond.

Herein, we report a joint experimental and computational analysis of the carbon–fluorine bond activation of fluorinated arenes using low-valent complexes which contain M–M bonds ($\text{M} = \text{Mg}, \text{Zn}, \text{Al}$). We provide strong evidence for the proposed concerted pathway and a transition state reminiscent of those represented in Fig. 1 that involves dual nucleophilic and electrophilic sites that polarise and activate the C–F bond. We introduce additional experiments and prepare new M–M complexes in order to interrogate the key transition state for C–F activation. Specifically, the effects of steric accessibility and M–M bond polarity on reaction rates are reported.

Results

Concerted addition of C_6F_6 to **1**

The reaction mechanisms reported herein were studied by DFT using the Gaussian 09 suite (revision D.01)³⁰ and optimisations employed the ωB97X functional.³¹ Mg and Zn centers were described with Stuttgart SDDAll RECPs and associated basis sets whereas 6-31G** basis sets was used for all other atoms.^{32–36} Free energies are corrected for both benzene solvent using the Polarizable Continuum Model (PCM) approach and dispersion effects using $\omega\text{B97X-D}$.^{37,38}

The potential energy surface for the reaction of C_6F_6 with **1** is presented in Fig. 3a. C–F bond activation is initiated upon weak coordination of C_6F_6 to the ligand sphere of **1** to create the encounter complex, **Int-A**. Substrate association to **1** occurs by a network of non-covalent interactions (*e.g.* C–H \cdots F, C–H \cdots π , $\pi\cdots\pi$) which although individually weak contribute to a modest binding enthalpy of $\Delta H^\circ = -9.2 \text{ kcal mol}^{-1}$ (Fig. S27†).

The increased ordering of the system is, however entropically unfavourable and thus fluoroarene binding is slightly endergonic ($\Delta G^\circ = 1.1 \text{ kcal mol}^{-1}$). The ligands in **Int-A** are oriented perpendicular to one another and rotation around the Mg–Mg bond is required to access the more reactive conformer **Int-A'**. **Int-A'** contains a reactive pocket and a sterically accessible Mg–Mg bond. C–F bond activation occurs *via* the concerted transition state **TS-1** ($\Delta G_{298 \text{ K}}^\ddagger = 25.7 \text{ kcal mol}^{-1}$). Decay from **TS-1** leads to the C–F activation product **Int-B** in which a newly formed Mg–C bond and bridging Mg–F–Mg bond contribute to a 6-membered ring structure. Overall C–F bond activation is extremely exergonic ($\Delta G_{\text{rxn}}^\circ = -112.2 \text{ kcal mol}^{-1}$).

An Eyring analysis on the reaction of **1** with C_6F_6 under pseudo first-order conditions, conducted over the temperature range 258–288 K, yielded activation parameters $\Delta H^\ddagger = 10.8 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -35 \text{ cal K}^{-1} \text{ mol}^{-1}$ (Fig. 3b and c). The experimental negative activation entropy is consistent with a highly ordered transition state, while the activation enthalpy is suggestive of a transition state with only minimal bond making and breaking having occurred. The Gibbs activation energy $\Delta G_{298 \text{ K}}^\ddagger = 21.3 \text{ kcal mol}^{-1}$ matches reasonably well with that determined from DFT, $\Delta G_{298 \text{ K}}^\ddagger = 25.7 \text{ kcal mol}^{-1}$.³⁹



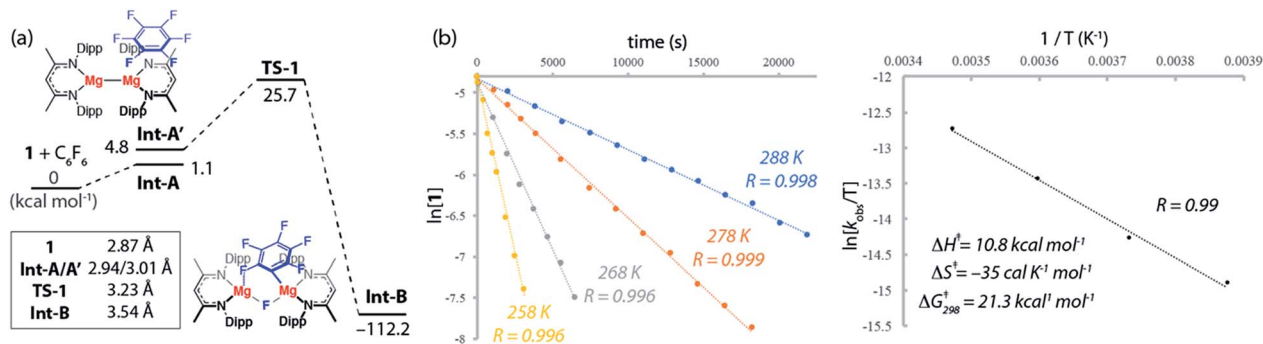


Fig. 3 (a) The calculated reaction pathway for C–F activation with **1**, inset shows Mg...Mg separation. (b) Kinetics of the reaction of **1** with 10 equiv. of C_6F_6 at various temperatures and Eyring analysis with determined activation parameters for C–F activation.

The transition state for C–F bond activation

The calculated **TS-1** is suggestive of an asynchronous concerted process: considerable Mg–C bond formation has occurred before any significant C–F bond breaking (Fig. 4). Formally, the transition state involves the concerted oxidative addition of the C–F bond to the Mg–Mg bond. Related pathways have been calculated for the addition of C–F bonds of fluoroarenes to single-site Al(I) and Si(II) centres.^{40–42} The bond lengths and angles around the *ipso*-carbon (Fig. S28a†), along with the charge distribution about the aromatic ring, however are consistent with an S_NAr -like mechanism for C–F activation with one Mg center acting as a nucleophile, attacking the aromatic ring, while the other acts as an electrophile, binding to and polarising the breaking C–F bond.

An electron density difference map illustrates the depletion of electron density between the breaking C–F and Mg–Mg bonds along with the simultaneous accumulation of electron density between Mg and C at the forming Mg–C bond (Fig. 4a). Electron density accumulation also occurs at both *ortho*- and *para*-carbons of the fluoroarene. The electron density redistribution in **TS-1** is mirrored by the NBO analysis showing the difference in the NPA charges between **TS-1** and **Int-A'** (Fig. 4b). The loss of electron density at the Mg centers ($\Delta = +0.52$ e) is redistributed

to the fluoroarene ring ($\Delta = -0.53$ e) and approximately half of the redistributed electron density is localised at *ipso*-carbon ($\Delta = -0.27$ e).

The effect of functional group substitution on the reaction rates of concerted S_NAr pathways is well understood: stabilisation of the negative charge on aromatic ring through inductive and mesomeric effects leads to an increase in reaction rate. Rate constants were measured for the reaction of **1** with a series of fluoroarenes of the form C_6F_5R . The group *para*- to the breaking C–F bond was varied and rate constants were measured under pseudo first-order conditions (Table S1†). Broadly the relative rate increases with stabilisation of negative charge on the *ipso*-carbon, leading to the general reactivity trend: $R = CF_3 > F > C_6F_5 > CH_3$.

Importance of secondary Mg...F_{ortho} interactions in the TS for C–F activation

In addition to the expected Mg...F_{*ipso*} interaction derived from the breaking C–F bond, there is a significant Mg...F_{*ortho*} interaction in **TS-1** that is retained in **Int-B**. The presence of a strong Mg...F_{*ortho*} interaction is evidenced by a short Mg...F_{*ortho*} distance (2.34 Å). The QTAIM molecular graph of **TS-1** (Fig. 4c) identifies the presence of a bond critical point (BCP) between



Fig. 4 (a) Energy density difference map (EDDM) for **TS-1**, (b) the change (Δ) in NPA charges from **Int-A'** to **TS-1** and (c) QTAIM data on **TS-1**: $\rho(r)$ values in bold, $\nabla^2\rho$ values in parentheses. Full QTAIM for **TS-1** in Fig. S28b.†



Mg and F_{ortho} . The attributes of the BCP (small $\rho_{(r)}$, small positive $\nabla^2\rho$) are indicative of a weak, closed shell interaction. The DFT prediction of this secondary $Mg\cdots F$ interaction is particularly noteworthy, as experimentally the addition of C–F bonds of fluoroarenes to the Mg–Mg bond of **1** always proceeds to give regioisomers in which at least one *ortho*-fluorine atom is adjacent to the C–F bond that breaks.

The effect of the position of fluorine substitution and the importance of the secondary $Mg\cdots F_{ortho}$ interaction on the C–F bond cleavage transition state was interrogated by calculating the pathway for the addition of C_6F_5H to **1**. Fig. 5 compares the change in Gibbs activation energy for the regioisomeric transition states (relative to **TS-1**). DFT calculations predict that substitution at positions X^2 and X^3 should lead to lowest energy transition states. Experimentally, regioisomeric products of C–F activation of both these positions of C_6F_5H are observed.²⁷

Substitution (of fluorine for hydrogen) at X^1 is highly disfavored and removes the *ortho*-fluorine substituent that anchors the substrate in the C–F bond activation TS ($\Delta\Delta G = +5.1$ kcal mol⁻¹). For comparison, X^5 is not involved in appreciable $Mg\cdots F_{ortho}$ bonding in the transition state and substitution here only raises the TS by +1.8 kcal mol⁻¹. Substitution at X^4 also raises the energy of the C–F activation TS ($\Delta\Delta G = +2.8$ kcal mol⁻¹). This position is expected to exert a secondary influence on the $Mg\cdots F_{ortho}$ binding energy. The fluorine atom in position X^4 is a weak π -donor and will increase the electron density on X^1 . Replacing X^4 with a hydrogen atom will remove this effect diminishing the electrostatic interaction between Mg and F_{ortho} .

The importance of the *ortho*-fluorine substituents was further exemplified by calculating the transition state for C–F bond activation of 1,3- $C_6F_4H_2$ in which both positions *ortho*- to the breaking C–F bond are occupied by hydrogen atoms (Fig. S30†). The absence of any $Mg\cdots F_{ortho}$ anchor results in a reorganisation of the TS to a conformer in which the breaking C–F bond is parallel with the Mg–Mg bond ($\Delta\Delta G = +9.5$ kcal mol⁻¹ relative to **TS-1**). The geometry of this reorganised TS is consistent with that reported for the addition of CO_2 to **1** reported by Maron and co-workers.⁴³

Effect of sterics on the TS for C–F activation

A number of analogues of **1** are known. These include a series of β -diketiminate complexes which differ in the steric profile of the flanking aromatic groups on the ligand. Consideration of the data above leads to the obvious question, what are the effects of sterics in C–F bond activation by addition to a Mg–Mg bond?

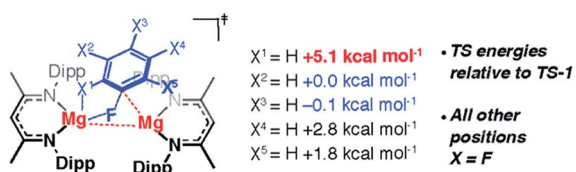


Fig. 5 Effect of H-atom regiochemistry in the TS for C–F activation of C_6F_5H .

The potential energy surface for C–F bond activation of C_6F_6 by **2** ($^{Mes}BDIMg-MgBDI^{Mes}$) was calculated and compared to that of **1** ($^{Dipp}BDIMg-MgBDI^{Dipp}$). The reduced steric bulk of the mesityl substituents results in greater access to the Mg–Mg bond. Consequently, the substrate coordinates to Mg in **2** through a short $Mg\cdots F$ interaction (2.76 Å) to give **Int-C**. Overall, the formation of **Int-C** is facile ($\Delta G = 0.3$ kcal mol⁻¹). Rotation about the Mg–Mg bond in **Int-C** gives the more reactive conformer **Int-C'** which contains a stronger $Mg\cdots F$ interaction (2.66 Å) in the form of a κ^1 -bound fluoroarene adduct.^{44,45} The transition state for C–F cleavage **TS-2** is located 23.0 kcal mol⁻¹ above the reactants and leads to **Int-D** (Fig. 6a). Significantly **TS-2** contains two $Mg\cdots F_{ortho}$ interactions as evidenced by the short $M\cdots F_{ortho}$ distances (Fig. S31a†) and quantified by QTAIM analysis (Fig. 6b). These electrostatic interactions undoubtedly contribute to transition state stabilisation and explain the lower energy of **TS-2** relative to **TS-1** (Fig. 6a).

Experimental data were collected to verify the hypothesis that **2** is more reactive to fluoroarenes than **1** (Fig. 6c). The reaction between **2** (0.02 M) and 10 equiv. of C_6F_6 in C_6D_6 was facile, with immediate observation of ¹⁹F NMR resonances at $\delta = -118.5$, -157.1 and -158.3 ppm corresponding to the Mg– C_6F_5 moiety. A further resonance at $\delta = -183.3$ ppm is assigned to a Mg–F by-product.⁴⁶ A competition reaction between **1**, **2**, and C_6F_6 , led exclusively to products derived from C–F bond activation with **2**. Further experiments replacing C_6F_6 with 2-(2,3,4,5,6-pentafluorophenyl)-pyridine (2-Py- C_6F_5) again led to exclusive reaction of **2** with no evidence for the participation of **1** despite its known reaction with the same substrate. As with the analogous reaction using **1**, **2** reacts with 2-Py- C_6F_5 at the 2-position. Both the C–F activation product **2a** and the fluoride-containing by-product [$\{^{Mes}BDIMg\}_3(\mu-F)_3$] (**2b**) have been characterised by single crystal X-ray diffraction, the latter complex forming a fluoride bridged trimer in the solid state.⁴⁷

Effect of M–M bond polarisation on the TS for C–F activation

The polarisation of the Mg–Mg bond in **TS-1** and **TS-2** raises a further question: do reactions of polar M–M bonds proceed faster than apolar M–M bonds? To address this question a series of new heterobimetallic complexes with polar M–M' bonds (M = Mg, M' = Zn, Al; M = Zn, M' = Al) were prepared. Complexes **3**, **4**, **6**, **7** are novel M–M containing species, and their synthesis was inspired by recently described methods, namely metathesis,^{48–52} and insertion of an Al(I) reagent^{53–59} into metal–carbon bonds.^{60,61} Despite the exploitation of known methods, this represents a highly novel series of main group complexes containing metal–metal bonds, including the first example of a crystallographically characterised Mg–Al bond and rare examples of Mg–Zn, Zn–Al and Zn–Zn–Zn bonds for which there is limited precedent.

Complex **3**, containing a new Mg–Zn bond, was synthesised by the stoichiometric reaction of the corresponding zinc iodide with **2** (Scheme 1). The reaction occurs with concomitant formation of one equiv. of the β -diketiminate supported magnesium(II) iodide and **3** could be isolated cleanly by exploitation of the difference in solubility between the two products (54%



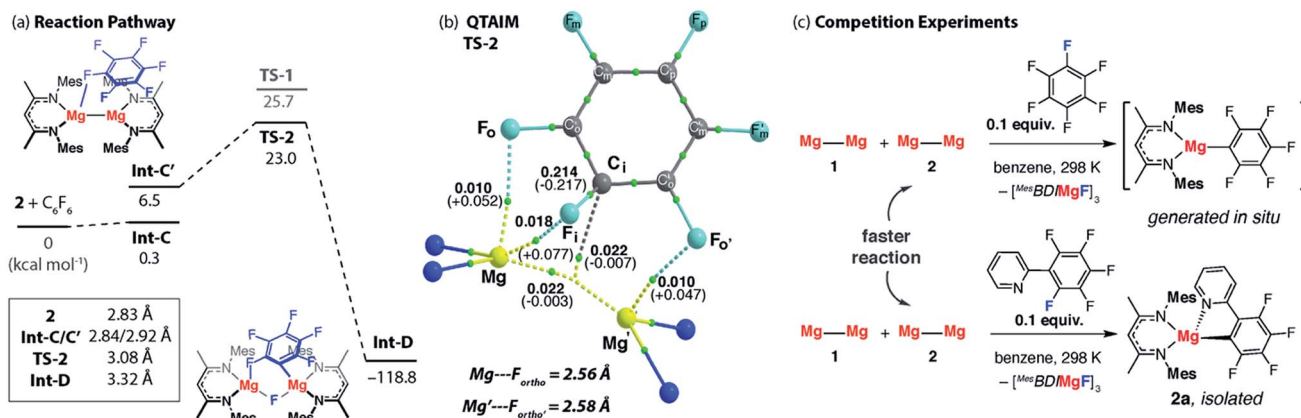


Fig. 6 (a) The calculated reaction pathway for C–F activation with 2, inset shows Mg \cdots Mg separation. (b) QTAIM plot of TS-2: $\rho(r)$ values in bold, $\nabla^2\rho$ values in parentheses. Full QTAIM for TS-2 in Fig. S31b.† (c) Competition experiments between 1 or 2 and fluoroarenes.

isolated yield). Compound 3 was found to be unstable in solution, degrading slowly over time (days) to form the mixed bis- β -diketiminate complex [Mg^(Dipp)BDI]^(Mes)BDI along with a black precipitate (presumed to be Zn⁰). Compound 3 can, however, be stored over a prolonged period of time at 238 K, as a solid or in hydrocarbon solution. This complex may be trapped by insertion of a carbodiimide (RN=C=NR, R = Cy, i-Pr) into the Mg–Zn bond and details of these experiments are provided in the ESI.† An analogue of 3 bearing solely mesityl substituted ligands was also prepared but could not be isolated cleanly.

X-ray quality crystals of 3 were grown from *n*-hexane at 238 K. The Mg–Zn bond length in 3 is 2.5993(8) Å, which is comparable with the only two previously reported examples of complexes containing a magnesium–zinc bond (Fig. 7, Table 1).⁴⁸ This value lies between the bond lengths of analogous Mg–Mg (2.8078–2.8700(9) Å) and Zn–Zn (2.3586(7)–2.3813(8) Å) β -diketiminate complexes.^{27,51,62–64} Comparison of the series of structures reveals that the complexes adopt a number of conformers in the solid state which differ by the dihedral angle between the

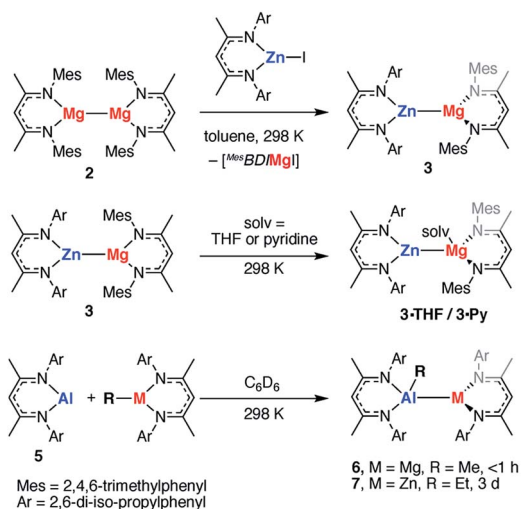
two β -diketiminate planes. A low energy difference between these conformers is anticipated, as would be consistent with the small calculated energy difference between **Int-A** and **Int-A'** (Fig. 3).

Addition of the coordinating solvents, THF and pyridine, to 3 led to the formation of the coordination complexes 3·THF and 3·Py, respectively. Integration of the ¹H NMR spectra indicates that in both cases only one equiv. of solvent is bound (Scheme 1). This was confirmed by the X-ray structure of 3·THF, which shows one molecule of tetrahydrofuran coordinated to magnesium, whilst the zinc remains in a three-coordinate geometry (Fig. 7).

The Mg–Zn bond length of 3·THF (2.6816(8) Å) is significantly longer than that of 3, a phenomenon also observed in the di-solvated solid-state structures of 1 (where solv. = THF, pyridine, DMAP).⁶⁵ 3·THF is a loose approximation of **Int-C'** (Fig. 6a) and suggests that substrate coordination to a single metal center is a feasible proposition in the pathway for C–F bond activation.

Following isolation of 3, further small amounts of bright yellow crystals were observed to form in the reaction filtrate. Single crystal X-ray diffraction revealed formation of the novel tri-zinc species, 4. Compound 4 is only the second reported example of a linear tri-zinc complex.⁴⁸ 4 is *C*₁ symmetric and the Zn–Zn–Zn bond is linear (180°). The Zn–Zn bond length of 2.3908(3) Å is slightly longer than in the previously reported example bearing mono-dentate amide ligands. Compound 4 is iso-structural with a previously reported Zn–Hg–Zn complex.^{52,66}

Related Mg–Al and Zn–Al complexes were also prepared. The stoichiometric reaction of 5 with magnesium and zinc alkyl complexes in C₆D₆ resulted in the formation of new asymmetric products, 6 and 7, respectively (Scheme 1). Deep red crystals of 6 and yellow crystals of 7 were grown from concentrated *n*-hexane solutions at 238 K (Fig. 7). Single crystal X-ray diffraction studies confirmed the presence of a newly formed aluminium–metal bond, which measured 2.7687(5) Å for Al–Mg and 2.488(1) Å for Al–Zn.⁶⁰ The aluminium centers in 6 and 7 have a distorted tetrahedral geometry, with τ_4 values of 0.87 and 0.93, respectively. Both compounds 6 and 7 were found to be remarkably



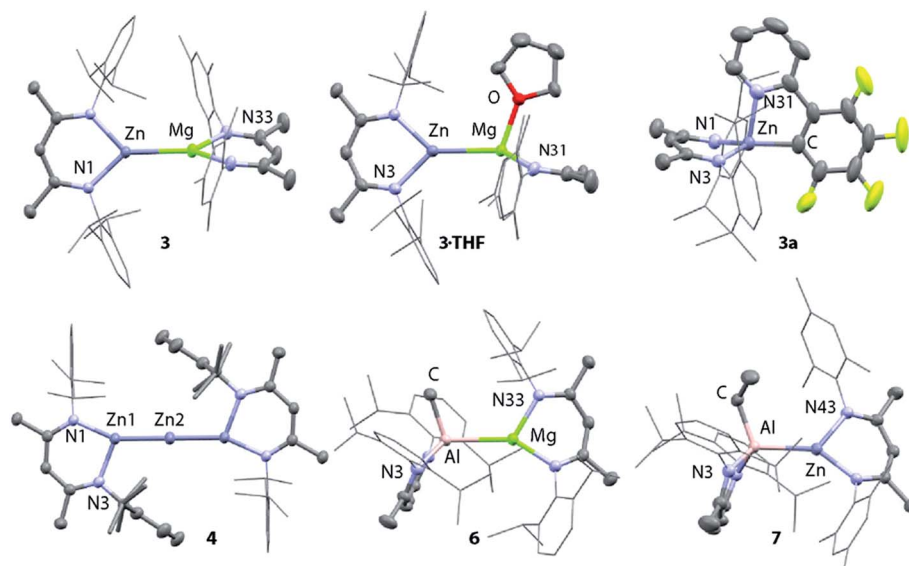


Fig. 7 The crystal structures of **3**, **3·THF**, **3a**, **4**, **6** and **7**.

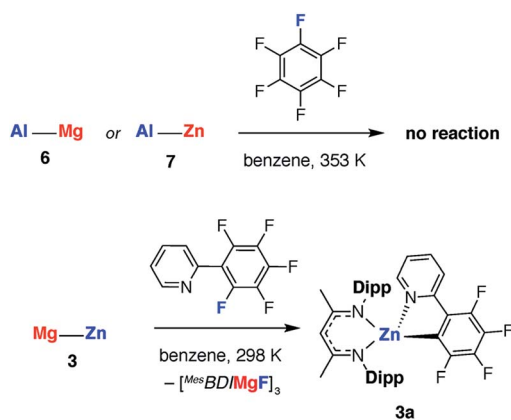
stable in solution, with no degradation observed when heated for 48 h at 353 K.⁶⁷

The effect of polarity on C–F activation with main group compounds containing M–M' bonds was investigated. Reaction of the heterobimetallic species **3**, **6** and **7**, with fluoroarenes were conducted in hydrocarbon solution. No evidence of C–F bond activation was observed upon reaction of Mg–Al (**6**) or Zn–Al (**7**) containing compounds with a range of fluorocarbons (*e.g.* C₆F₆, C₆F₅H and 2-Py-C₆F₅) between 298 and 353 K. While **3** does react slowly with C₆F₆ at room temperature this reaction is competitive with decomposition of the Mg–Zn reagent.^{68,69} A clean reaction was observed between **3** and 2-Py-C₆F₅ to form the Zn complex **3a** and the corresponding magnesium fluoride (Scheme 2, Fig. 7).

The reaction pathway for the addition of C₆F₆ to **3** was calculated and shown to be analogous to that described for **1**. C–F bond cleavage occurs *via* an asymmetric transition state **TS-3** (Fig. S32†) which leads to Zn–C and Mg–F bond formation and is 26.4 kcal mol^{−1} higher in energy than the separated reactants. Consideration of the difference in electronegativity between Mg ($\chi_p = 1.31$) and Zn ($\chi_p = 1.65$) explains the geometry of the transition state and the destination of the fluorine atom in the reaction. All attempts to locate a transition state that resulted in Mg–C and Zn–F bond formation led to **TS-3** and it is clear that

polarisation of the M–M' bond is a key factor in determining the outcome of the reaction (Fig. 8a).

In combination, these experiments suggest that Mg–Zn, Mg–Al and Zn–Al reagents prepared herein are all less reactive toward fluoroarenes than **1** or **2**. This finding was borne out by competition experiments using both C₆F₆ and 2-Py-C₆F₅. The rate of reaction of **3** with 2-Py-C₆F₅ is marginally slower than



Scheme 2 Reactions of polar M–M bonds with fluoroarenes.

Table 1 Selected bond lengths from the X-ray data of **3–7**^a

	3	3·THF	2a	3a	4	6	7
M–M	2.5993(8)	2.6816(8)	—	—	2.3908(3)	2.7687(8)	2.4877(10)
fsr	0.99	1.03	—	—	0.98	1.06	1.00
M–N	2.0243(18)	2.0782(19)	2.037(3)	1.979(2)	1.9761(18)	2.0862(10)	2.034(3)
	2.0540(19)	2.0999(19)	2.035(3)	1.973(2)	2.016(3)	1.9739(10)	1.933(3)
M–X	—	2.1116(18)	2.156(4)	1.980(3)	—	1.9856(13)	1.980(3)
		X = O	X = C	X = C		X = C	X = C

^a fsr is the formal shortness ratio defined as the bond length/sum of the single bond radii (Pauling).



herein we suggest that C–F bond activation by M–M reagents could be best described as being subject to:

(i) an *ortho*-fluorine influence that results in destabilisation of the starting materials and stabilisation of the reaction products due to weakened C–F bond strengths and increased M–C bond strengths.

(ii) an *ortho*-fluorine effect that results in a rate-acceleration through stabilisation of the transition state for C–F bond activation by secondary M⋯F interactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to the Royal Society for provision of a University Research Fellowship (MRC) and to the Leverhulme Trust (RPG-2015-248) and ERC (FluoroFix: 677367) for generous funding. Prof. Stuart Macgregor is thanked for insightful discussions and his seminal contributions to the mechanistic analysis of reactions that break C–F bonds.

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- 67 It was not possible to form new species containing Mg–Al bonds by reaction of aluminium(III) diiodide or aluminium(III) dimethyl complexes with **2**.
- 68 Addition of 10 equiv. of C₆F₆ to a 0.02 M solution of **3** in C₆D₆ resulted in the slow formation of a mixture of compounds and after 5 days the mixture contained 7% [Zn(DiPPBDI)C₆F₅], 7% [MesBDIMg(μ-F)]₃, and 13% [Mg(MesBDI)(DiPPBDI)] (Fig. S11 and S12†). Attempts to use higher reaction temperatures only led to the accelerated degradation of **3**.
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