A series of neutral magnesium and calcium complexes bearing an extremely bulky diamido ligand have been synthesised and crystallographically characterised. A number of these complexes feature rare group 2 metal–aromatic interactions, such as the $\eta^6$-coordination of benzene and ‘agostic-like’ C–H coordination, the latter previously unseen in neutral Mg and Ca complexes.

The coordination of aromatic molecules to s-block elements plays an important role in many biological and chemical processes. In biology, arene-to-cation interactions with s-block metals are critical in maintaining the 3D structure of multiple enzymes, whilst similar interactions also play a pivotal role in the transport of K$^+$ and Ca$^{2+}$ through cell membranes. In synthetic chemistry, these s-block to arene interactions also govern a wide range of chemical transformations. This effect has recently been found to be highly significant in the emerging field of synergistic reactivity, where coordination of an arene to an s-block atom has been shown to ‘activate’ aromatic substrates prior to reaction. A number of recent, notable transformations have been shown and/or calculated to proceed via this route, including the organocalcium-mediated nucleophilic alkylation of benzene by Hill, Maron and co-workers and the facile deprotonation of benzene by a potassium diboryllithiate by Lin, Yamashita, Nozaki and co-workers. That said, in both of these examples (amongst several others), the aromatic s-block interactions exist as part of transient intermediates and/or transition states, which due to their highly reactive nature, cannot be isolated.

Recently, however, the groups of Harder and Hill have reported a range of mono-cationic magnesium and calcium π-arene complexes, which have been isolated and crystallographically characterised. These include [(BDI)Mg(η$^6$-C$_6$H$_4$R$_2$)]$^+$ [B(C$_6$F$_5$)$_4$] Ia–c, [(BDI)Mg(η$^6$-C$_6$H$_3$Me$_3$)][B(C$_6$F$_5$)$_4$] II, [(BDI)Mg(η$^6$-C$_6$H$_2$R)][Al(OC(CF$_3$)$_3$)$_3$]$^+$ (R = H, Me) IIIa–c, [(BDI)Ca(η$^6$-C$_6$H$_3$Ar)][Al(OC(CF$_3$)$_3$)$_3$]$^+$ IV, [(BDI)Ca(η$^6$-C$_6$H$_6$)][B(C$_6$F$_5$)$_4$] V, and [(ArN═C(Bu)NAr)Ca(η$^6$-C$_6$H$_6$)][B(C$_6$F$_5$)$_4$] VI (Fig. 1; BDI = CH[N(C(R)NAr)$_2$]). All of these complexes show coordination of the arene through its π-system to the Lewis acidic group 2 centre. In the case of V, Harder and co-workers found that this simple coordination of

![Fig. 1](image-url)
benzene to the cationic calcium centre was sufficient to allow facile reduction of the benzene by an AlIII species, which on its own shows no reactivity towards simple aromatic molecules.\textsuperscript{10}

In contrast to solely hydrocarbon-based arenes (as seen in compounds I–VI), halogenated arenes favour coordination to cationic magnesium and calcium centres through the halogen. This can been seen in complexes such as \([\text{BDI}][\text{Mg}((\text{FPh})_2)]\), \([\text{B}(\text{CaF}_3)_2]\)\textsuperscript{VII,11} \([\text{BDI}][\text{Mg}((p\text{DFB})_2)]\)\textsuperscript{[Al(OC(F)\textsubscript{3})\textsubscript{3}]}\textsuperscript{VIII} (Fig. 1; pDFB = p-difluorobenzene) amongst a handful of others.\textsuperscript{6,9,10,12,13} This clearly shows a preference for these lighter, cationic group 2 centres to interact with hard donors, rather than the softer \(\pi\) system.

The chemistry of arene coordination to cationic group 2 complexes has gained significant attention over the past few years, as can be seen by the plethora of complexes shown in Fig. 1.\textsuperscript{6–11} That said, intramolecular arene coordination to neutral group 2 complexes, which can be more reminiscent of the intermediates/transition states seen in many synergistic reactions,\textsuperscript{3,4} are far less developed. Recently, we have reported the use of the bulky xanthene-based diamido ligand NON (NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tertbutyl-9,9-dimethyl-xanthene) in the stabilisation of a range of highly reactive group 13 complexes.\textsuperscript{14} Here we extend our investigations with the NON ligand to group 2, and show this ligand can also stabilise a range of low-coordinate neutral group 2 complexes, some featuring unprecedented bonding motifs with arenes.

Group 2 NON complexes were initially targeted by salt metathesis reactions between the previously reported dipotassium salt of the ligand \(\text{K}_2[\text{NON}]\textsuperscript{15}\) and magnesium/calcium iodide. These reactions were performed in diethyl ether and stirred for 1–2 days at room temperature, which resulted in the formation of etherate complexes.

Complexes 1 and 2 were crystallised from toluene and benzene, respectively, and their solid-state structures determined by X-ray crystallography (Fig. 2). The biggest difference between the solid-state structures of 1 and 2 is that the Mg centre in 1 is 4-coordinate, with one molecule of diethyl ether coordinating to the Mg centre, whereas the Ca centre in 2 is 5-coordinate, with two molecules of diethyl ether bound to the metal centre. This is presumably due to the larger ionic radius of calcium in comparison to magnesium (114 pm vs. 86 pm),\textsuperscript{16} allowing for an additional coordination site in 2. The larger size of calcium can also be seen in the ‘hinging’ of the ligand’s xanthene backbone, with the backbone in 2 hinging by 24.8° from planar, compared to the greater 42.9° in 1. This hinging is a consequence of the rigidity of the NON ligand; the ligand has to hinge more to accommodate a smaller metal to bring the two amido donors closer together.

Diethyl ether is crucial in the synthesis of 1 and 2, as stirring solutions of \(\text{K}_2[\text{NON}]\) with MgI/Cal in non-coordinating solvents such as toluene or benzene does not lead to a reaction, even at elevated temperatures (\textit{e.g.} 110 °C in toluene). This is presumably due to the low solubility of the metal halide salts in these solvents. Unfortunately, the coordinated diethyl ether molecules in 1 and 2 do block potential metal coordination sites for arene molecules. These diethyl ether ligands cannot simply be exchanged with arenes by refluxing the complexes in common aromatic solvents such as benzene or toluene, demonstrating that the coordination of the harder ether donors is preferred to the softer arene interactions.

In an attempt to synthesise ether-free NON group 2 complexes, more soluble group 2 starting materials were sought. As such, a solution of \(n\)-butyl-sec-butylmagnesium (0.7 M in hexane) was added to a solution of the protonated ligand \(\text{H}_2[\text{NON}]\) in benzene, sealed in a J. Young’s reaction vessel and heated to 95 °C for 3 days. After cooling and concentrating the reaction solution, large colourless crystals of the solvent-free magnesium dimer \([\text{Mg}[\text{NON}]]_2\) were isolated in high yield (Scheme 1). An analogous dialkylcalcium starting material is not readily available,\textsuperscript{17} but an ether-free NON calcium complex was accessible by heating a crystalline sample of 2 to 150 °C under high vacuum (\(1 \times 10^{-2}\) mbar) for 1 hour. This reaction proceeded with an obvious visible change in the material, from a colourless crystalline solid to a bright yellow powder. This was accompanied by a clear spike in the vacuum pressure.

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![Fig. 2](image)

**Fig. 2** Molecular structures of 1 (left) and 2 (right) as determined by X-ray crystallography. Displacement ellipsoids set at the 50\% probability level. Key bond lengths (Å) (for 1): Mg1–N2 2.0236(11), Mg1–N2 2.0281(11), Mg1–O1 2.0307(9), Mg1–O2 2.0159(10); (for 2): Ca1–N1 2.3295(11), Ca1–N2 2.3345(11), Ca1–O1 2.3348(9), Ca1–O2 2.3477(12), Ca1–O3 2.3531(12).

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![Scheme 1](image)

**Scheme 1** Synthesis of the ether-free complexes 3 and 4.
when the solid was heated above 120 °C, signalling the release of diethyl ether. After heating under vacuum, the bright yellow powder was dissolved in boiling benzene, which was then slowly cooled to room temperature overnight to give (NON)Ca (C₆H₅)₂ 4 as large yellow crystals (Scheme 1).

Compounds 3 and 4 have been characterised by X-ray crystallography (Fig. 3). Both compounds are ether-free group 2 NON complexes, crystallised from the same solvent (benzene) but have remarkably different solid-state structures. Compound 3 crystallises as a dimer, with the structure held together by the two Mg centres forming interactions with a Dipp group of the neighbouring NON ligand. This structure is reminiscent of the dicatonic magnesium dimers recently reported by Harder and coworkers. However, in the reported complexes, the dimers are held together by η¹-arene interactions between flanking aryl rings of the ligand and the Mg centres. In contrast, the interactions in 3 appear to be between the Mg centres and a meta C–H bond of the flanking Dipp group (Mg⋯C = 2.432(2)/2.494(2) Å, Mg⋯H = 2.31/2.32 Å (ref. 18)). The short Mg⋯C interaction are structurally more reminiscent of covalent agostic interactions commonly encountered in transition metal chemistry than the more commonly observed η¹ and/or η² interactions seen in the Mg cationic complexes, but the interaction with s⁵-Mg(n) is thought to be electrostatic/ionic in nature.

In contrast, compound 4 crystallises from benzene as a monomer, with two molecules of benzene coordinating to the calcium centre. One of these benzene molecules is coordinat- ing in an η⁶-fashion (Ca⋯C interactions range from 2.921(6) to 2.954(7) Å). Harder and Hill have recently reported a range of cationic η⁶-arene calcium complexes (Fig. 1, IV–VI), but neutral calcium complexes to exhibit this type of interaction are still rare. The calcium⋯η⁴-benzene distance in 4 is almost identical to that seen that in the cationic η-arene Ca complexes IV–VI (Ca⋯C(avg) = 2.94 Å; 2.93 Å IV; 2.93 Å V; 2.92 Å VI), suggesting a similar strength Ca⋯η⁴-benzene electrostatic interaction in 4 as in the cationic complexes. A distinctive coordination of the second benzene molecule in 4 is observed – possibly due to steric factors. The second benzene molecule displays bonding more akin to that seen in 3, with two “agostic-like” interactions between adjacent C–H bonds of the benzene molecule and the Ca centre. We believe this to be the first example of a group 2 complex to display this bonding mode with benzene. To gain a more accurate picture of the Ca⋯H–C distances in 4, the compound was also analysed by single crystal neutron diffraction (see ESI† for further details). From combined analysis of X-ray and neutron diffraction data, the two short Ca⋯H interactions (2.96(5), 3.01(4) Å) were found to be identical (within error) to the Ca⋯C distances (3.04(4), 3.053(7) Å), supporting the description as C–H coordination over a η-arene complex.

As the Mg⋯H–C interactions in 3 (responsible for holding together the dimeric structure) are expected to be weak, we probed whether this dimeric structure was retained in solution. A number of NMR experiments were carried out on a solution of 3 in d₈-toluene. Firstly, just simple observation of the 1D ¹H NMR spectrum acquired at 25 °C, shows a highly symmetric NON environment, with only one septet and two doublets for the Dipp isopropyl groups. This splitting arrangement is common for simple monomeric NON complexes with Cs symmetry, such as complexes 1 and 2. If the dimeric structure of 3 was retained in solution (at least for times comparable to that of the NMR timescale), a more complicated ¹H NMR spectrum would be expected. Collection of a second ¹H NMR spectrum at ~70 °C gave an almost identical spectrum, suggesting that this is not due to fluxional averaging at room temperature. Further evidence that the dimeric of nature of 3 does not persist in solution is provided by diffusion-ordered spectroscopy (DOSY) NMR measurements. Measurements recorded on a C₆D₆ solution of 3 at 298 K gave a hydrodynamic radius of 7.7 Å for the species in solution. This is considerably smaller than what would be consistent with a dimeric structure (the dialane [(NON)Al]₂ for example = 8.9 Å) and almost identical to that recorded for monomeric NON complex 1 (7.6 Å). As such, it is believed that 3 exists as a monomer in solution.

It was expected that the metal⋯arene interactions (both C–H and η⁶) observed in the solid-state structures of 3 and 4 would be weak and therefore easily broken/exchanged if the complexes were exposed to a harder/stronger donor. To investigate whether this was indeed the case, the reactivity of 3 and 4 was explored with respect to diethyl ether and fluorobenzene. The addition diethyl either to benzene solutions of either 3 (1 equiv.) or 4 (2 equiv.), resulted in almost instantaneous reactions, affording the diethyl ether adducts 1 and 2 in near quantitative yield. In a similar reaction, the dissolution of 3 or 4 in
fluorobenzene, followed by crystallisation from the reaction mixture leads to the neutral fluorobenzene adducts (NON)Mg (FPh)$_2$ and (NON)Ca(FPh)$_3$, in high crystalline yields.

Complexes 5 and 6 have been characterised by X-ray crystallography and their solid-state structures shown in Fig. 4. As with the diethyl ether adducts 1 and 2, both complexes are monomeric in the solid state, with the Ca compound 6 coordinating one more donor molecule than the Mg analogue 5 (two coordinating PhF molecules in 5 and three in 6). In both complexes, the fluorobenzene molecules coordinate to the metal centre solely through the fluorine atom, in a similar fashion to the PhF and pDBF cationic adducts previously reported by Hill and Harder (Fig. 1, VII and VIII)\(^8,11\) However, 5 and 6 represent the first crystallographically characterised examples of neutral fluorinated arene adducts of magnesium and calcium. Surprisingly, the Mg···F distances in the neutral adduct 5 (2.073(3) to 2.099(3) Å) are comparable to those observed in the cationic adducts VII and VIII (1.9513(8)/2.0019(8) Å; VII 2.073(4)/2.100(3) Å),\(^8,11\) indicating comparable interactions in all 3 complexes. The Ca···F distances in 6 range from 2.3873 (18) to 2.5082(18) Å. No simple fluoroarene adducts of cationic calcium complexes are reported for comparison, but the values are comparable to those found in the dicationic complex [Ca(HMB)(pDBF)$_2$]$^{2+}$ (2.415(7)–2.483(7) Å; HMB = hexamethylbenzene).\(^12\) Furthermore, the coordinated C···F bond lengths in 5 (1.376(4) and 1.394(5) Å) and 6 (1.389(4) to 1.394(3) Å) show a slight elongation compared to that in ‘free’ fluorobenzene (ca. 1.36 Å).\(^21\)

The lability of the PhF ligands in 5 and 6 were found to be markedly different. When crystals of 5 were dissolved in C$_6$D$_6$, it was evident that the adduct formation was retained in solution by noticeable shifts in the $^1$H and $^{13}$C($^1$H) NMR compared to those of 3. Furthermore, the $^{19}$F NMR showed a single resonance at −124.9 ppm, considerably shifted from that of ‘free’ fluorobenzene in C$_6$D$_6$. Dissolution of 6 in C$_6$D$_6$ led, by contrast to an immediate colour change, from colourless crystals to a bright yellow solution, which quickly deposited bright yellow crystals. Analysis of this product (by $^1$H NMR and X-ray crystallography) revealed reformation of the calcium benzene adduct 4. This clearly shows that 6 has a preference for the softer π-arene donor than the harder fluorine donors.

In summary, a series of neutral Mg and Ca complexes, which display a number of unprecedented coordination modes with aromatic substrates, including the η$^6$-coordination of benzene and ‘agostic-like’ M···C–H interactions in 3 and 4, have been isolated and crystallographically characterised. Rare neutral fluoroarene adducts of Mg and Ca have also been isolated by dissolution of 3 and 4 in fluorobenzene. We are currently investigating the reactivity of these group 2···arene complexes in synergistic reaction mechanisms.

Conflicts of interest

There are no conflicts to declare.

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