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Magnesium aryloxides: synthesis, structure, solution behavior and magnesiate ion formation

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The heteroleptic magnesium complexes $[\{Ar'OMgBu\}_2]$ **1** and $[\{Ar'OMgN(i\text{-}Pr)_2\}_2]$ **2**, where OAr′ = 2,6-di-*tert*-butylphenoxy, have been prepared and found to be dimeric in the solid state, with tri-coordinate metal centers. Complex **1** utilizes the aryloxide anions as bridging groups whereas the amido anions connect the metals in **2**. Addition of THF or TMEDA to hydrocarbon solutions containing **2** results in disproportionation and the exclusive precipitation of the homoleptic, solvated, complexes $[Mg(OAr')_2 \cdot 2THF]$ **3** or $[Mg(OAr')_2 \cdot TMEDA]$ **4**. Both **3** and **4** are monomeric in the solid state with tetra-coordinate magnesium centers. Solution NMR spectroscopic studies of **1** and **2** reveal that disproportionation to the homoleptic complexes is promoted in THF-d_8 but that the main component still appears to be the heteroleptic species. Dissolution of the unsolvated dimeric complex $[Mg(OAr')_2]$ **5** in THF-d_8 results in partial formation of the magnesiate complex $[Ar'OMg]^+[(Ar'O)_3Mg]^-$**10**, along with the monomer **3**. In contrast, no magnesiate is formed on dissolution of **3** in THF-d_8, indicating that magnesiate formation most likely proceeds *via* unsymmetrical cleavage of the dimer. *Ab initio* calculations (HF/6-31G*) have been used to investigate the possible structures of the magnesiate species.

Introduction

Magnesium alkoxides and aryloxides are used in a wide range of applications including as reagents in organic synthesis,[1] as additives in polyolefin catalysis[2] and as precursors in metal–organic chemical vapor deposition (MOCVD).[3] In comparison, the coordination chemistry of these species has received limited attention. Despite the relatively small number of structural studies carried out, a surprisingly diverse range of architectures has been characterized for even the simple homoleptic bis-alkoxides and aryloxides (Fig. 1).[2a,4–7] Various forms of monomers, dimers, trimers and tetramers have been revealed, where the metal has been found to assume coordination numbers anywhere between three and six, depending on the size of the anion and the influence of donor solvents.

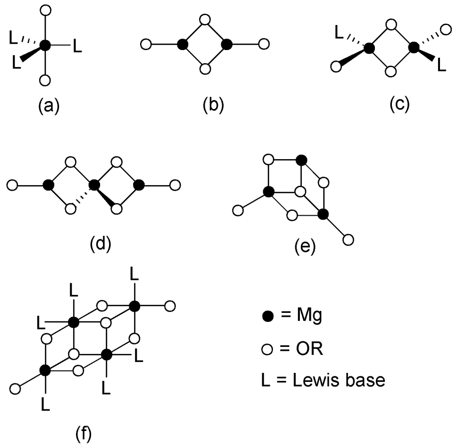


Fig. 1 Structurally characterized geometries of $(RO)_2Mg$ complexes.

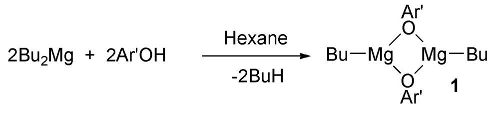
The characterization of these species has generally been accomplished through the use of sterically encumbered anionic ligands, in order to prevent further association into polymers. Nevertheless, the methoxide compound $[Mg(OMe)_2 \cdot 3.5THF]$,[8] which forms a complex polymeric network arrangement, and $[Mg(OMe)_2 \cdot 2THF]$,[9] which adopts a cubane structure with hexa-coordinated magnesium atoms, have both been successfully characterized in the solid state. In addition, there has been significant interest in the use of smaller magnesium alkoxides as components in mixed anion/mixed cation complexes to enable the dissolution of highly reactive alkali metal alkyl compounds for use in organic synthesis.[10,11]

As part of our ongoing studies into the development of new reagents in organic synthesis we have become interested in the use of alkoxide and aryloxide containing magnesium compounds.[12] Herein, we detail the synthesis and structural characterization of the tetra-coordinated, monomeric, magnesium bisaryloxides $[Mg(OAr')_2 \cdot 2THF]$ and $[Mg(OAr')_2 \cdot TMEDA]$, and the dimeric precursor heteroleptic compounds $[\{Ar'OMgBu\}_2]$ and $[\{Ar'OMgN(i\text{-}Pr)_2\}_2]$ (where OAr′ = 2,6-di-*tert*-butylphenoxy). Furthermore, the nature and stability of these complexes in arene and in polar media is discussed, and a pathway for the formation of the solvent separated magnesiate species $[Ar'OMg]^+[(Ar'O)_3Mg]^-$ from the parent bisaryloxide $[\{Mg(OAr')_2\}_2]$ is outlined.

Results and discussion

Syntheses

The alkylmagnesium aryloxide $[\{Ar'OMgBu\}_2]$, **1**, was readily prepared in high yield by the equimolar reaction between commercially available Bu_2Mg and 2,6-di-*tert*-butylphenol in hexane solution (Scheme 1). The reaction of *in situ* prepared **1** with one molar equivalent of diisopropylamine resulted in alkane elimination and formation of the amidomagnesium aryloxide $[\{Ar'OMgN(i\text{-}Pr)_2\}_2]$, **2** (Scheme 2). Both complexes **1** and **2** were deposited from solution as crystalline solids on allowing their reaction mixtures to stand at ambient temperature for several hours.



Scheme 1

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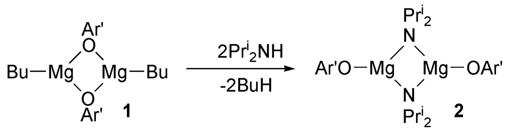
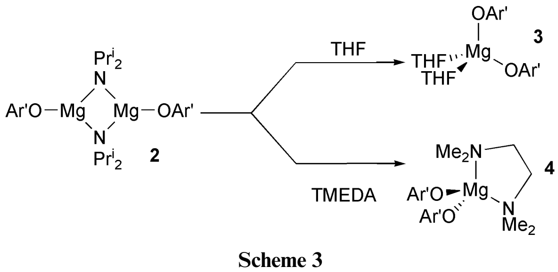


Scheme 2

On analysis of **1** by ^{1}H NMR spectroscopy we were interested to find the main alkyl component was the *n*-butyl anion with only trace quantities of *s*-butyl present, despite the starting material Bu_2Mg containing a mixture of *n*- and *s*-butyl groups.[13] Strohmann similarly noted the exclusive retention of the *n*-butyl group on reaction of Bu_2Mg with two different (aminomethyl)silanes, whereas Raston found that reaction of Bu_2Mg with one equivalent of the secondary amine hexamethyldisilazane resulted in the precipitation of the *s*-butyl containing alkylmagnesium amide [{*s*-BuMgN$(SiMe_3)_2$}$_2$].[14] In other cases, reaction of one molar equivalent of an amine with Bu_2Mg results in mixtures of complexes containing *n*- and *s*-butyl groups.[15] Also, addition of TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) to heptane solutions of Bu_2Mg results in the preferential precipitation of the monomeric bisalkyl complex [(*s*-Bu)$_2$Mg·TMEDA].[16] Therefore, the reactivity of Bu_2Mg cannot be predicted from simple thermodynamic or kinetic concerns,[17] rather the alkane eliminated from the organometallic appears to be dependant on other factors such as the nature of the reactive substrate.

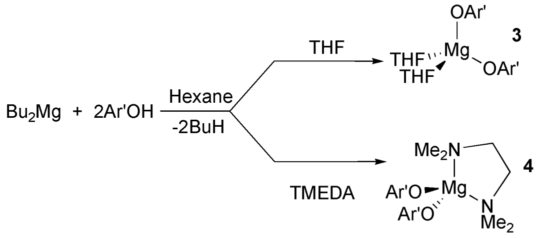
In an attempt to form solvated derivatives of **1** and **2**, either THF (one or two molar equivalents) or TMEDA (one molar equivalent) was added to hydrocarbon solutions of the complexes. Precipitates recovered from the reactions involving **1** were found to be complex mixtures, and were not analyzed further. However, the sole products isolated as solids from the reactions involving **2** were the homoleptic bisaryloxides [Mg(OAr′)$_2$·2THF] **3** and [Mg(OAr′)$_2$·TMEDA] **4** (Scheme 3).

These reactions indicate that a solvent induced disproportionation is occurring and that the magnesium bisamide is retained in solution. We have previously observed such disproportionation reactions for a variety of alkylmagnesium amides containing a 2-pyridyl amido anion.[15,18] In these instances the reactions are driven by a formal increase in the coordination number at the metal center. Also, very recently Chang and coworkers have reported that a similar disproportionation process occurs on the addition of the strong Lewis base HMPA (hexamethylphosphoramide) to the solvated alkylmagnesium amides [RMgNPh$_2$·2THF], to yield the homoleptic bisamide complexes [Mg(NPh$_2$)$_2$·2HMPA] (where R = Et or *i*-Pr).[19]



Scheme 3

Alternatively, complexes **3** and **4** can be prepared by reaction of two equivalents of the phenol with Bu_2Mg to form the bisaryloxide [{Mg(OAr′)$_2$}$_2$] **5**, followed by addition of the appropriate Lewis base (Scheme 4).[4]



Scheme 4

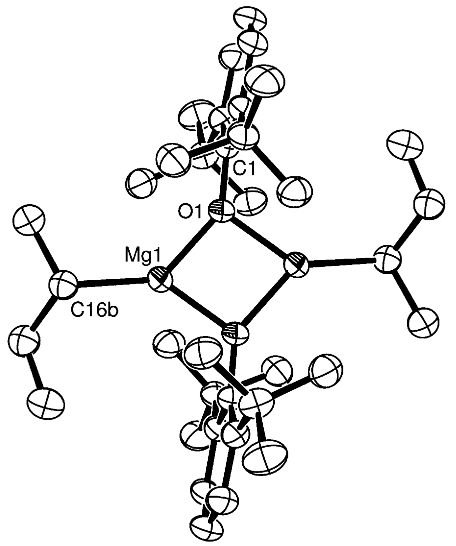


Fig. 2 Molecular structure of **1** with hydrogen atoms omitted for clarity.

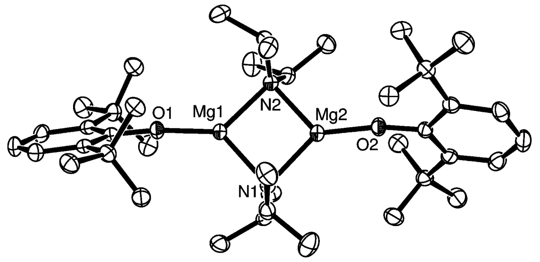


Fig. 3 Molecular structure of **2** with hydrogen atoms omitted for clarity.

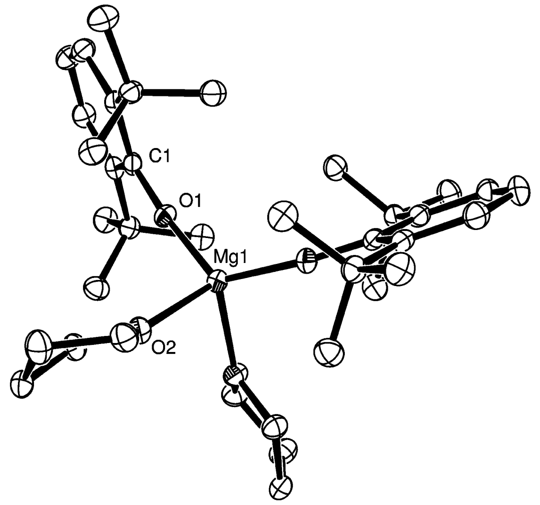


Fig. 4 Molecular structure of **3** with hydrogen atoms omitted for clarity.

Solid state studies

The molecular structures of compounds **1**–**4** are shown in Fig. 2–5, and selected bond lengths and angles are given in Table 1. Firstly, regarding the structure of alkylmagnesium alkoxide **1**, although the alkyl units are disordered they appear to consist solely of *s*-butyl groups. Presumably this is a consequence of the better crystallization properties of these units compared with the more abundant *n*-butyl groups. In any event, a dimer is formed with the oxygen atoms of the aryloxide bridging

Table 1 Selected bond lengths (Å) and angles (°) for compounds **1**–**4**

For **1**			
Mg(1)–O(1)	1.9668(12)	Mg(1)–O(1*)	1.9708(12)
Mg(1)–C(16A)	2.133(5)	Mg(1)–C(16B)	2.126(3)
O(1)–C(1)	1.9708(12)		
O(1)–Mg(1)–O(1*)	84.12(5)	O(1)–Mg(1)–C(16A)	132.74(14)
O(1)–Mg(1)–C(16B)	133.99(9)	O(1*)–Mg(1)–C(16A)	143.10(13)
O(1*)–Mg(1)–C(16B)	137.05(10)	Mg(1)–O(1)–Mg(1*)	95.88(5)
Mg(1)–O(1)–C(1)	143.25(10)	Mg(1*)–O(1)–C(1)	120.83(10)
For **2**			
Mg(1)–O(1)	1.8292(11)	Mg(1)–N(1)	2.1139(14)
Mg(1)–N(2)	2.0878(14)	Mg(2)–O(2)	1.8223(11)
Mg(2)–N(2)	2.0791(14)	Mg(2)–N(1)	2.0882(14)
O(1)–C(13)	1.3415(18)	O(2)–C(27)	1.3373(18)
O(1)–Mg(1)–N(1)	131.77(6)	O(1)–Mg(1)–N(2)	134.65(5)
N(1)–Mg(1)–N(2)	92.88(5)	O(2)–Mg(2)–N(1)	137.64(6)
O(2)–Mg(2)–N(2)	128.23(6)	N(1)–Mg(2)–N(2)	93.88(5)
Mg(1)–O(1)–C(13)	172.05(10)	Mg(2)–O(2)–C(27)	175.48(11)
Mg(1)–N(1)–Mg(2)	85.67(5)	Mg(1)–N(2)–Mg(2)	86.58(5)
For **3**			
Mg(1)–O(1)	1.8639(10)	Mg(1)–O(2)	2.0627(11)
O(1)–C(1)	1.3389(16)		
O(1)–Mg(1)–O(2)	101.53(4)	O(1)–Mg(1)–O(1*)	122.85(7)
O(2)–Mg(1)–O(1*)	118.95(4)	O(2)–Mg(1)–O(2*)	88.71(6)
Mg(1)–O(1)–C(1)	170.99(9)		
For **4**			
Mg(1)–O(1)	1.8803(8)	Mg(1)–O(2)	1.8817(9)
Mg(1)–N(1)	2.2625(11)	Mg(1)–N(2)	2.2695(11)
O(1)–C(1)	1.3337(13)		
O(1)–Mg(1)–O(2)	118.41(4)	O(1)–Mg(1)–N(1)	103.39(4)
O(2)–Mg(1)–N(1)	121.81(4)	O(1)–Mg(1)–N(2)	121.96(4)
O(2)–Mg(1)–N(2)	105.30(4)	N(1)–Mg(1)–N(2)	81.41(4)
Mg(1)–O(1)–C(1)	165.23(8)		

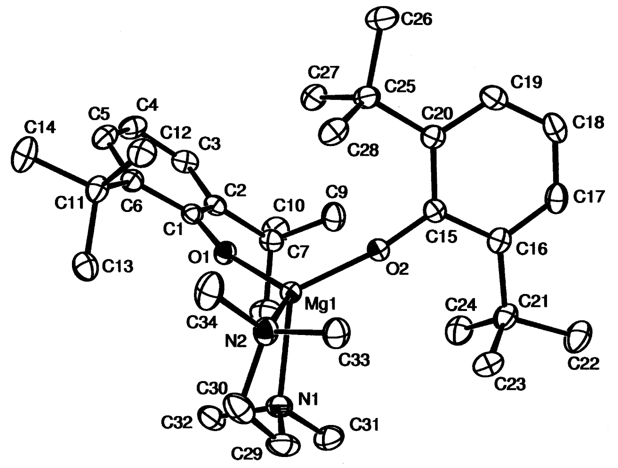


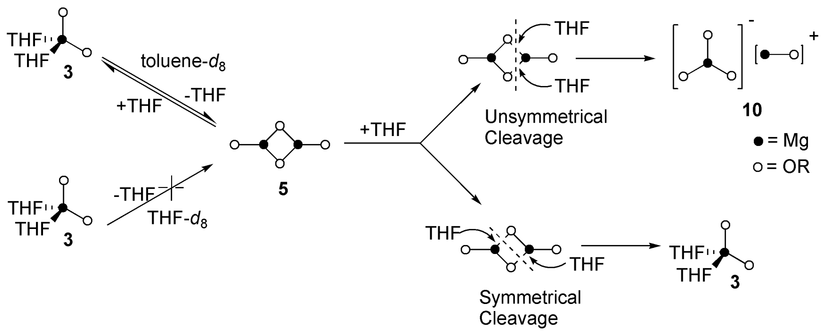
Fig. 5 Molecular structure of **4** with hydrogen atoms omitted for clarity.

between the metals. Rather surprisingly, there are very few compounds in the Cambridge Structural Database that can be used to compare directly with **1**.[20] The only other structurally characterized compound where magnesium covalently binds simultaneously to both alkoxide and alkyl anions is the product derived from the cleavage reaction of 2,1,1-cryptand by dineopentylmagnesium.[21] Although the ligand set is much more complex in this compound, it is again essentially a dimer bridging through anionic oxygen atoms and possessing terminal alkyl groups, similar to **1**. The preference for alkoxide bridges in both these complexes is consistent with the expected superior bridging ability of oxygen over carbon for electropositive metals.[22] Also, the aryl rings are essentially orthogonal to the strictly planar central Mg_2O_2 ring but do not symmetrically bisect the ring, rather they are skewed to one side with Mg–O–C angles of 120.83(10)° and 143.25(10)°.

Moving on to consider the structure of **2**, a dimeric arrangement is found again but in this instance the amide residues adopt bridging positions and the aryloxides are terminally bound. The preference for the amide bridges in **2** is somewhat unexpected and is most likely a consequence of the large steric bulk of the aryloxide anion reducing its effectiveness as a bridging group. A similar situation was found in the bimetallic complex $[Me_2Al\{\mu\text{-}N(i\text{-}Pr)_2\}_2MgOAr'']$ **6** (where OAr″ = O-2,6-$^tBu_2$-4-Me-C_6H_2) where the aryloxide resides in a terminal position and the amido anions bridge between the two metal centers.[23] All of the other structurally characterized heteroleptic dimers of the form $[\{ROMgNR_2\}_2]$ are found to adopt geometries with bridging oxygen atoms and terminal amide units.[24] However, when there is no alternative connecting group present the OAr′ anion has been found to bridge between metals such as lithium,[25] sodium,[26] magnesium,[4] or zinc in aggregated complexes.[27]

Since the local environment for the magnesium atoms in **2** and **6** both involve binding to a pair of bridging diisopropylamido anions and a terminal aryloxide, their bond lengths and angles involving the metals are similar. For example, the Mg–O distances are 1.826 Å (mean) and 1.808(3) Å, the Mg–N distances are 2.092 Å (mean) and 2.110 Å (mean) for **2** and **6** respectively.[28] Also, the bond angles around the distorted trigonal planar magnesium atoms in the two compounds are similar and range between 92.88(5)° and 137.64(6)° for **2**, and between 86.1(1)° and 142.5(1)° for **6**.

Rather surprisingly, compounds **3** and **4** are the first reported examples of tetra-coordinated, monomeric, magnesium bisalkoxides or aryloxides. The closely related complexes



Scheme 5 Solution behavior of the bisaryloxide species.

[Mg{OC$_6$H$_3$(2,6-*i*-Pr)$_2$}$_2$·3THF] **7**, [Mg{OC$_6$H$_2$(2,4,6-Cl)$_3$}$_2$·3THF] **8**, and [Mg{OC$_6$H$_3$(2,6-Me)$_2$}$_2$·3py] **9** all adopt trigonal bipyramidal geometries, with five-coordinate metal centers.[6a] It appears that the large *t*-Bu groups in **3** and **4** preclude donation from a third donor atom as found in **7**–**9**. The coordination difference at the metals is reflected in the slightly shorter Mg–O(Ar′) distances of 1.875 Å (mean), range 1.8639(10) to 1.8817(9) Å, found in **3** and **4** compared with those of 1.894 Å (mean), range 1.879(2) to 1.914(2) Å, for **7**–**9**.[6a] Although the average of the angles around the metals in **3** and **4** are similar (108.01 and 108.71° respectively), the small bite angle demanded by chelation of the TMEDA molecule results in the narrow N(1)–Mg(1)–N(2) angle of 81.41(4)° in **4**, whereas the two THF molecules adopt a wider O(2)–Mg(1)–O(2*) angle of 88.71(6)° in **3**.

Solution studies

The ^{1}H and ^{13}C NMR spectra in toluene-d_8 of the heteroleptic alkylmagnesium aryloxide **1** display only one set of resonances for the alkyl and aryloxide anions suggesting that the solid state structure, the aryloxy bridged dimer, is retained in solution. When complex **1** was dissolved in THF-d_8, again a single set of resonances was observed in the ^{1}H NMR spectrum. However, a second minor component was discernible from the ^{13}C NMR spectrum run from this solution. This was determined to be the solvated bisaryloxide **3**, by identification of the small but characteristic methyl signal at 32.24 ppm.[29] From these results it appears that the polar solvent media THF promotes disproportionation of **1**, albeit to a very limited extent.

The ^{1}H and ^{13}C NMR spectra of amidomagnesium aryloxide **2** in toluene-d_8 again show the presence of a single solution aggregate, consistent with the presence of the amido bridged dimer found in the solid state. However, when complex **2** was dissolved in THF-d_8 the solvated bisaryloxide **3** could be identified as a minor species (approximately 5%) in both the ^{1}H and ^{13}C NMR spectra, again indicating that an equilibrium is established between the heteroleptic and homoleptic complexes in polar media. Since the sole solid product isolated from the reaction of **2** with THF was the solvated bisaryloxide **3**, and no amide containing species was precipitated, it can be assumed that **3** is the least soluble species in solution leading to its preferential crystallization despite it being present in only relatively small proportions.

Next, we moved on to re-examine the nature of the previously prepared unsolvated bisaryloxide **5** in solution.[4] In toluene-d_8 **5** is clearly present as a dimer, as evidenced by the two sets of resonances of equal intensity, representing the bridging and terminal anions. However, an unusual pattern is observed when **5** was dissolved in THF-d_8, where three sets of resonances are displayed, rather than sole formation of the disolvated monomer **3** as may have been expected. Ittel noted a similar pattern when pyridine-d_5 was added to benzene-d_6 solutions of the magnesium bisaryloxide derived from butylated hydroxytoluene.[4] The signals were attributed to a bisaryloxy monomer, and the formation of a charge separated magnesiate species. Our studies confirm this assignment, where a pair of signals in a 3 : 1 ratio represent the magnesiate complex [Ar′OMg]$^+$-[(Ar′O)$_3$Mg]$^-$ **10**, and the third set of resonances arise from the disolvated monomer **3**.

Seminal studies by Richey established that magnesiate ions could be prepared by the action of crowns or cryptands on organomagnesium compounds.[30,31] More recently, Harder has described the facile preparation of completely charge separated magnesiate complexes through the use of stabilized anions such as fluorenyl$^-$ and Ph$_4$B$^-$.[32] However, all attempts to isolate solids from the solutions containing complex **10** resulted in the precipitation of monomer **3**. Hence the definitive structural characterization of the magnesiate has eluded us thus far.

We were intrigued by the fact that isolating the disolvated monomer **3** as a pure material, followed by dissolution in either toluene-d_8 or THF-d_8 did not result in the formation of any magnesiate species. Rather, only a single set of resonances consistent with retention of the solvated monomeric structure was observed. This led us to speculate that formation of magnesiate **10** may occur through the unsymmetrical cleavage of a dimeric aggregate, a route which is perhaps not available for the disolvated monomer **3** in polar solvent media.[33] We tested this notion by carrying out variable temperature (V-T) ^{1}H NMR studies of toluene-d_8 and THF-d_8 solutions of **3** in order to detect the presence of any dynamic solution behavior. On progressively cooling a toluene-d_8 solution of complex **3** between 25 °C and −80 °C a notable shift in the position of the *p*-H occurred (6.19 to 6.23 ppm), consistent with a dynamic process occurring. In contrast, no discernable shifts for any of the anion signals were observed when the sample was run over the same temperature range in THF-d_8. These studies indicate the solvated monomer **3** is most likely the sole or at least dominant species present in THF solution, whereas aggregation back to the dimer **5**, presumably with loss of coordinated solvent, is possible for **3** in arene solution. The formation of the dimer allows the unsymmetrical cleavage process to occur on addition of excess polar solvent to form the magnesiate **10** (Scheme 5). In a similar vein, direct dissolution of dimeric **5** in THF-d_8 may result in unsymmetrical cleavage to give the solvent separated species.

An EXSY experiment on the THF-d_8 solution containing the magnesiate **10** and the monomer **3** indicated no exchange between any of the species present over the NMR timescale. Doping a THF-d_8 solution containing **10** with **3** resulted in no discernable increase in the relative concentration of the magnesiate (with reference to SiMe$_4$ as an internal standard). This again supports the assessment that no equilibrium is present between the magnesiate and the monomer in neat THF solution.

V-T studies of the dimer **5** in toluene-d_8 also showed some movement in the signals over the temperature range 80 °C to −80 °C. However, EXSY studies at both 300 K and 350 K indicated that no exchange occurs on the NMR timescale between the bridging and terminal anions. This suggests that the observed shifts are a consequence of movement of the

Table 2 Selected bond lengths (Å) and angles (°) for the geometry optimized structures **I**–**IV**

	I	**II**	**III**	**IV**
Mg–O(Ar′)	1.878	1.875	1.858	1.825
Mg–O(THF)	2.156	–	2.103/2.134 (eq) 2.242/2.243 (ax)	2.053 (mean)
O–C(Ar′)	1.324	1.312	1.328	1.333
Mg–O–C(Ar′)	171.4	179.8 (mean)	176.8	159.47
(Ar′)O–Mg–O(Ar′)	128.3	120.0	–	–

groups within the dimeric structure and not due to either any solution aggregation or scrambling of the anions within the dimer. This contrasts with the solution behaviour for bulky magnesium amides such as $[\{Mg(NSiMe_3)_2\}_2]$, where both intramolecular ligand exchange and temperature dependant solution aggregation are known to occur.[34]

Computational studies

Since we were unable to obtain X-ray structural data for the magnesiate species, an *ab initio* (HF/6-31G*) computational study was undertaken. Firstly, for comparative purposes the neutral disolvated monomer **I** was geometry optimized using the coordinates from the X-ray structure of **3** as a starting point for the calculation. Overall, very good agreement was found between the calculated and experimentally determined structures, with the averaged differences in bond lengths and angles involving the metals being only 0.05 Å and 2.8° respectively (see Table 2 for details). Next, due to the size of the 2,6-di-*tert*-butylphenoxy ligand it is likely that the anion $[(Ar'O)_3Mg]^-$, **II**, is a monomer similar to the structurally characterized $[(t\text{-}BuCH_2)_3Mg]^-$ anion, and this was the only species considered (Fig. 6).[21] Three possible monomeric cations, with either three-, four- or five-coordinated THF molecules, were investigated. Calculation of the hexa-coordinated, pseudo-octahedral cation $[Ar'OMg\cdot5THF]^+$ resulted in expulsion of a single THF molecule, presumably due to lack of space in the complex. However, reasonable geometries were found for both the penta-coordinate species $[Ar'OMg\cdot4THF]^+$, **III**, and the tetra-coordinate complex $[Ar'OMg\cdot3THF]^+$, **IV**. The structure of **III** appears to be the most likely candidate for the cation since the dissociation of a single THF molecule from **III** to **IV** was determined to be endothermic by 10.73 kcal mol^{-1}.

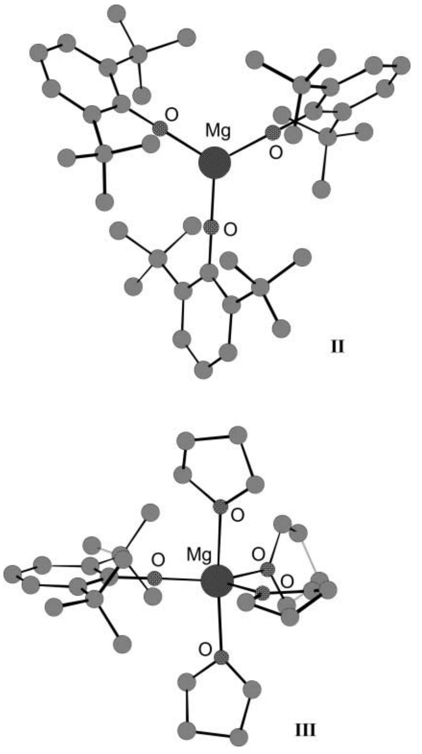


Fig. 6 Geometry optimized (HF/6-31G*) structures **II** and **III**.

Structure **II** has approximate C_3 symmetry with the aryl rings in a propeller-like arrangement. The same geometry for **II** was produced on starting the optimization from approximately D_{3h} symmetry, with the aryl rings perpendicular to the plane of the three oxygen centers. Model **III** displays a distorted trigonal bipyramidal geometry with the aryl ligand in an equatorial position, minimizing the steric repulsions in the system. This ligand arrangement is consistent with the experimentally determined structures of the trisolvated aryloxides **7**, **8** and **9**.[6a]

The effect of changing between a neutral, anionic and cationic species appears to only have a minor effect on the bond lengths within the complexes (Table 2). For example, the Mg–O(Ar′) and the O–C(Ar′) distances vary by only 0.020 Å and 0.016 Å respectively between the complexes. As expected, the shortest Mg–O(Ar′) distance, 1.858 Å, is found in the cation **III**. Also, the equatorial Mg–O(THF) distances in **III** are comparable with those in **I** (with mean distances of 2.118 Å and 2.125 Å), whereas longer distances are found for the more sterically encumbered axial sites (at 2.243 Å).

Since there is no direct change in translational entropy between **I** and **II**/**III** it appears that secondary interactions with the polar solvent media leads to the stabilization of the magnesiate. This is in agreement with the fact that the relative concentration of **10** is higher in the more polar solvent pyridine-d_5 compared with THF-d_8 (70% *versus* 35% of the integrated ligand intensity).

Finally, it is worth noting that it may have been reasonably assumed that dissolving the unsolvated complex **5** or the disolvated monomer **3** in THF-d_8 would have resulted in the formation of the same solution species. This is patently not the case, and since the reactivity of **3** and **10** will be expected to be significantly different from one another,[30] this highlights the importance of considering the method of preparation adopted if such compounds were to be used as reagents in synthesis.

Experimental

All manipulations were carried out under a protective argon atmosphere using standard Schlenk techniques.[35] All solvents were distilled over sodium/benzophenone until blue, degassed and stored over 4 Å molecular sieves prior to use. The phenol was purchased from Aldrich, recrystallized twice from hexane, dried under vacuum and stored in a desiccator over KOH before use. All glassware was flame-dried under vacuum before use. Bu_2Mg was purchased from Aldrich as a 1 M solution in hexane and was standardized by titration with salicylaldehyde phenylhydrazone directly before use.[36] Deuteriated solvents for NMR studies were stored over 4 Å molecular sieves under an argon atmosphere. The NMR spectra were recorded on a Bruker AMX 400 spectrometer at 25 °C unless otherwise stated. All ^{13}C assignments were determined using HMQC experiments. Elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyzer.

[{Ar′OMgBu}$_2$] (1)

Dibutylmagnesium (10 mmol in hexane) was syringed into a Schlenk tube under argon, then 5 mL of hexane and 5 mL of toluene were added, and the solution was left to stir for five min. One equivalent (10 mmol, 2.06 g) of 2,6-di-*tert*-butylphenol was then added *via* a solids addition tube. The resulting mixture was left to stir for five min, and the clear solution was then allowed to stand to allow crystallization. Colorless blocks of **1** precipitated on standing the solution for several hours at ambient temperature. Yield: 1.30 g, 90.91%. Mp: 229–231 °C (Found C, 75.4; H, 8.8%. $C_{18}H_{30}OMg$ requires C, 75.5; H, 10.5%). ^{1}H NMR (400.13 MHz, toluene-d_8, 300 K): δ −0.10 (m, 2H; CH_2, Bu), 0.87 (t, 3H; CH_3, Bu), 1.22 (m, 2H; CH_2, Bu), 1.53 (s, 18H; CH_3, *t*-Bu), 1.53 (s, 2H; CH_2, Bu), 6.82 (t, 1H; *p*-H, Ph), 7.21 (d, 2H; *m*-H, Ph). ^{13}C NMR (100.63 MHz, toluene-d_8, 300 K): δ 7.06 (CH_2, Bu), 14.20 (CH_3, Bu), 31.03 (CH_2, Bu), 31.31 (CH_2, Bu), 32.80 (CH_3, *t*-Bu), 35.14 (C, *t*-Bu), 120.84 (*p*-C, Ph), 126.32 (*m*-C, Ph), 139.62 (*o*-C, Ph), 156.52 (*i*-C, Ph). ^{1}H NMR (400.13 MHz, THF-d_8, 300 K): δ −0.47 (m, 2H; CH_2, Bu), 0.85 (t, 3H; CH_3, Bu), 1.25 (m, 2H; CH_2, Bu), 1.37 (s, 18H; CH_3, *t*-Bu), 1.53 (m, 2H; CH_2, Bu), 6.18 (t, 1H; *p*-H, Ph), 6.89 (d, 2H; *m*-H, Ph). ^{13}C NMR (100.63 MHz, THF-d_8, 300 K): δ 8.67 (CH_2, Bu), 14.55 (CH_3, Bu), 31.12 (CH_3, *t*-Bu), 32.92 (CH_2, Bu), 33.96 (CH_2, Bu), 35.64 (C, *t*-Bu), 112.84 (*p*-C, Ph), 124.74 (*m*-C, Ph), 137.97 (*o*-C, Ph), 164.37 (*i*-C, Ph). Note: the ^{13}C THF-d_8 NMR spectrum displayed a weak signal at +32.24 ppm consistent with the presence of trace quantities of **3**.

[{Ar′OMgN(*i*-Pr)$_2$}$_2$] (2)

Dibutylmagnesium (5 mmol in hexane) was syringed into a Schlenk tube under argon and 10 mL of hexane was added and the solution was left to stir for five min. One equivalent (5 mmol, 0.7 mL) of diisopropylamine was added and the mixture stirred for 5 min followed by the addition of one equivalent (5 mmol, 1.03 g) of 2,6-di-*tert*-butylphenol *via* a solids addition tube. The mixture was then allowed to stir for a further ten min, after which a white solid precipitated. The solvent was then removed *in vacuo* and replaced by 5 mL of toluene and 2 mL of hexane. The mixture was heated gently until all the solid redissolved. After cooling to ambient temperature and standing overnight clear cube shape crystals of **2** were deposited. Yield: 0.56g, 34.04%. Mp: 166–168 °C (Found: C, 71.6; H, 10.7; N, 4.1%. $C_{20}H_{35}NOMg$ requires C, 73.0; H, 10.6; N, 4.3%). ^{1}H NMR (400.13 MHz, toluene-d_8, 300 K): δ 1.18 (d, 12H; CH_3, *i*-Pr), 1.56 (s, 18H; CH_3, *t*-Bu), 3.20 (sept, 2H; CH, *i*-Pr), 6.81 (t, 1H; *p*-H, Ph), 7.33 (d, 2H; *m*-H, Ph). ^{13}C NMR (100.63 MHz, toluene-d_8, 300 K): δ 27.05 (CH_3, *i*-Pr), 31.81 (CH_3, *t*-Bu), 35.36 (C, *t*-Bu), 46.90 (CH, *i*-Pr), 115.68 (*p*-C, Ph), 125.36 (*m*-C, Ph), 137.48 (*o*-C, Ph), 161.09 (*i*-C, Ph). ^{1}H NMR (400.13 MHz, THF-d_8, 300 K): δ 1.02 (d, 12H; CH_3, *i*-Pr), 1.42 (s, 18H; CH_3, *t*-Bu), 3.19 (sept, 2H; CH, *i*-Pr), 6.19 (t, 1H; *p*-H, Ph), 6.92 (d, 2H; *m*-H, Ph). ^{13}C NMR (100.63 MHz, THF-d_8, 300 K): δ 27.20 (CH_3, *i*-Pr), 32.02 (CH_3, *t*-Bu), 35.96 (C, *t*-Bu), 50.08 (CH, *i*-Pr), 113.08 (*p*-C, Ph), 125.05 (*m*-C, Ph), 138.33 (*o*-C, Ph), 164.46 (*i*-C, Ph). Note: the THF-d_8 spectra also contained approximately 5% of **3** but the exact quantity could not be determined due to significant but not complete overlapping of the signals.

[Mg(OAr′)$_2$·2THF] (3)

This compound was prepared by a variety of routes, including the addition of stoichiometric amounts (1–2 molar equivalents) of THF to solutions of *in situ* prepared **1**. However, it was most simply made through direct solvation of the bisaryloxide. Dibutylmagnesium (5 mmol in hexane) was syringed into a Schlenk tube under argon, 5 mL of hexane was added and the mixture was allowed to stir for five min. Two equivalents (10 mmol, 2.06 g) of 2,6-di-*tert*-butylphenol was added to the solution *via* a solids addition tube followed by the addition of 2 equivalents (10 mmol, 0.81 mL) of THF. The clear mixture was then stirred for a further ten min and then left to stand at ambient temperature. After several hours, small white crystals of **3** formed. Yield: 1.80g, 62.3%. Mp: 184–186 °C (Found: C, 73.8; H, 9.9%. $C_{36}H_{58}O_4Mg$ requires C, 74.7; H, 10.0%). ^{1}H NMR (400.13 MHz, toluene-d_8, 300 K): δ 1.25 (m, 8H; CH_2, THF), 1.55 (s, 36H; CH_3, *t*-Bu), 3.64 (m, 8H; OCH_2, THF), 6.73 (t, 2H; *p*-H, Ph), 7.33 (d, 4H; *m*-H, Ph). ^{13}C NMR (100.63 MHz, toluene-d_8, 300 K): δ 24.86 (CH_2, THF), 31.88 (CH_3, *t*-Bu), 35.53 (C, *t*-Bu), 70.75 (OCH_2, THF), 114.22 (*p*-C, Ph), 125.25 (*m*-C, Ph), 137.57 (*o*-C, Ph), 163.17 (*i*-C, Ph). ^{1}H NMR (400.13 MHz, THF-d_8, 300 K): δ 1.37 (s, 36H; CH_3, *t*-Bu), 1.77 (m, 8H; CH_2, THF), 3.62 (m, 8H; OCH_2, THF), 6.23 (t, 2H; *p*-H, Ph), 6.92 (d, 4H; *m*-H, Ph). ^{13}C NMR (100.63 MHz, THF-d_8, 300 K): δ 26.59 (CH_2, THF), 32.24 (CH_3, *t*-Bu), 36.01 (C, *t*-Bu), 68.44 (OCH_2, THF), 113.80 (*p*-C, Ph), 125.32 (*m*-C, Ph), 138.20 (*o*-C, Ph), 163.92 (*i*-C, Ph).

[Mg(OAr′)$_2$·TMEDA] (4)

As for **3**, this compound could also be prepared by directly solvating the bisaryloxide. However, for brevity only the disproportionation reaction will be outlined. Dibutylmagnesium (5 mmol in hexane) was syringed into a Schlenk tube under argon, followed by 5 mL of hexane and the mixture was allowed to stir for five min. One equivalent (5 mmol, 1.03 g) of 2,6-di-*tert*-butylphenol was added to the solution *via* a solids addition tube. The mixture was left to stir for five min before the addition of one equivalent (5 mmol, 0.70 mL) of diisopropylamine. This was stirred for a further five min and then one equivalent (5 mmol, 0.76 mL) of TMEDA was added. The reaction mixture was then heated to reflux for one hour and left to cool to ambient temperature. High quality colorless crystals of **4** were deposited on standing the solution for several hours at ambient temperature. Yield: 1.06g, 77.1%. Mp: 264–266 °C (Found: C, 73.1; H, 10.6; N, 5.3%. $C_{34}H_{58}O_2N_2Mg$ requires C, 74.1; H, 10.2; N, 5.1%). ^{1}H NMR (400.13 MHz, toluene-d_8, 300 K): δ 1.55 (s, 40H; CH_3, *t*-Bu; and CH_2, TMEDA), 2.05 (s, 12H; CH_3, TMEDA), 6.71 (t, 2H; *p*-H, Ph), 7.33 (d, 4H; *m*-H, Ph). ^{13}C NMR (100.63 MHz, toluene-d_8, 300 K): δ 32.53 (CH_3, *t*-Bu; CH_2, TMEDA), 35.83 (C, *t*-Bu), 57.18 (CH_3, TMEDA), 114.28 (*p*-C, Ph), 125.57 (*m*-C, Ph), 137.48 (*o*-C, Ph), 163.05 (*i*-C, Ph). ^{1}H NMR (400.13 MHz, THF-d_8, 300 K): δ 1.41 (s, 36H; CH_3, *t*-Bu), 2.15 (s, 12H; CH_3, TMEDA), 2.30 (s, 4H; CH_2, TMEDA), 6.25 (t, 2H; *p*-H, Ph), 6.94 (d, 4H; *m*-H, Ph). ^{13}C NMR (100.63 MHz, THF-d_8, 300 K): δ 32.23 (CH_3, *t*-Bu), 36.00 (C, *t*-Bu), 46.40 (CH_3, TMEDA), 59.15 (CH_2, TMEDA), 113.80 (*p*-C, Ph), 125.32 (*m*-C, Ph), 138.20 (*o*-C, Ph), 163.92 (*i*-C, Ph).

[{(Ar′O)$_2$Mg}$_2$] (5)

This compound was prepared by a slightly modified version of Ittel's synthesis.[4] Dibutylmagnesium (5 mmol in hexane) was syringed into a Schlenk tube under argon, followed by 10 mL of hexane and the solution was left to stir for five min. Two equivalents of 2,6-di-*tert*-butylphenol (10 mmol, 2.06 g) were then added to the solution by a solids addition tube. The reaction mixture was then left to stir for ten min at ambient temperature followed by gentle heating to dissolve any precipitate. White needle like crystals of **5** formed upon cooling to room temperature over several hours. Yield: 1.06g, 48.8%. ^{1}H NMR (400.13 MHz, toluene-d_8, 300 K): δ 1.20 (s, 18H; CH_3, *t*-Bu), 1.58 (s, 18H; CH_3, *t*-Bu), 6.69 (t, 1H; *p*-H, Ph), 6.76 (t, 1H; *p*-H, Ph), 7.09 (d, 2H; *m*-H, Ph), 7.21 (d, 2H; *m*-H, Ph). ^{13}C NMR (100.63 MHz, toluene-d_8, 300 K): δ 31.92, 34.13 (CH_3, *t*-Bu), 35.07, 36.06 (C, *t*-Bu), 115.78, 121.74 (*p*-C, Ph), 125.21, 127.84 (*m*-C, Ph), 138.03, 138.43 (*o*-C, Ph), 155.88, 160.61 (*i*-C, Ph). ^{1}H NMR (400.13 MHz, THF-d_8, 300 K): δ 1.41, 1.40, 1.37 (s, CH_3; *t*-Bu), 6.14, 6.23, 6.32 (t, *p*-H; Ph),

Table 3 Crystallographic parameters for **1**, **2**, **3** and **4**

Compound	**1**	**2**[a]	**3**	**4**
Formula	$C_{36}H_{60}Mg_2O_2$	$C_{47}H_{78}Mg_2N_2O_2$	$C_{36}H_{58}MgO_4$	$C_{34}H_{58}MgN_2O_2$
M	573.46	751.73	579.13	551.13
Crystal size/mm	0.40 × 0.35 × 0.25	0.45 × 0.30 × 0.08	0.70 × 0.18 × 0.10	0.70 × 0.55 × 0.12
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$Pccn$	$P21/c$
a/Å	11.9509(3)	12.88850(10)	20.0212(6)	11.6257(2)
b/Å	10.4326(2)	15.4780(2)	9.8738(2)	15.3910(2)
c/Å	14.2307(3)	22.8343(3)	16.6859(5)	18.7651(3)
β/°	90.392(1)	90	90	96.118(1)
V/Å^3	1774.23(7)	4555.17(9)	3298.56(15)	3338.54(9)
Z	2	4	4	4
No. reflections collected	7848	52199	7089	13620
No. independent reflections	4036	10408	3769	7604
R_{int}	0.0198	0.046	0.0539	0.0182
D_{calc}/g cm^{-3}	1.073	1.096	1.166	1.097
μ/cm^{-1}	0.095	0.090	0.090	0.083
R	0.0498	0.0388	0.0437	0.0379
R_w	0.1464	0.0809	0.1002	0.0959

[a] Crystals contained one molecule of toluene per dimer of **2**.

6.85, 6.92, 7.02 (d, *m*-H; Ph). ^{13}C NMR (100.63 MHz, THF-d_8, 300 K): δ 32.17, 32.22, 32.37 (CH_3, *t*-Bu), 35.94, 36.00 (C, *t*-Bu), 112.68, 113.78 (*p*-C, Ph), 124.54, 125.30, 126.61 (*m*-C, Ph), 138.19, 138.51 (*o*-C, Ph), 163.92 (*i*-C, Ph). Complete assignment of the magnesiate peaks in the ^{13}C NMR spectrum was complicated due to overlapping and/or weak signals.

For comparison the chemical shift positions for the free phenol, 2,6-di-*tert*-butylphenol, are given: ^{1}H NMR (400.13 MHz, toluene-d_8, 300 K): δ 1.43 (s, 18H; CH_3, *t*-Bu), 4.87 (s, 1H; OH), 6.80 (t, 1H; *p*-H, Ph), 7.12 (d, 2H; *m*-H, Ph). ^{13}C NMR (100.63 MHz, toluene-d_8, 300 K): δ 30.38 (CH_3, *t*-Bu), 34.36 (C, *t*-Bu), 120.30 (*p*-C, Ph), 125.24 (*m*-C, Ph), 136.02 (*o*-C, Ph), 151.26 (*i*-C, Ph). ^{1}H NMR (400.13 MHz, THF-d_8, 300 K): δ 1.42 (s, 18H; CH_3, *t*-Bu), 6.02 (s, 1H; OH), 6.71 (t, 1H; *p*-H, Ph), 7.09 (d, 2H; *m*-H, Ph). ^{13}C NMR (100.63 MHz, THF-d_8, 300 K): δ 30.89 (CH_3, *t*-Bu), 35.36 (C, *t*-Bu), 120.73 (*p*-C, Ph), 125.53 (*m*-C, Ph), 138.29 (*o*-C, Ph), 155.21 (*i*-C, Ph).

X-Ray crystallography

Single crystal diffraction data were recorded by a Nonius Kappa CCD diffractometer at 123 K using graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å). The structures were refined by full-matrix least-squares and against F^2 to convergence using the SHELXL-97 program.[37] Specific crystallographic data and refinement parameters are given in Table 3.

CCDC reference numbers 200471–200474.

See http://www.rsc.org/suppdata/dt/b2/b212608g/ for crystallographic data in CIF or other electronic format.

Computational details

The Gaussian 98 series of programs were used for the calculations.[38] No symmetry constraints were imposed and the molecules were allowed to freely optimize at the HF/6-31G* level of theory.[39] The crystal structure data were used as the starting point for the calculation of **I**.

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