How to cite: Angew. Chem. Int. Ed. 2021, 60, 7626–7631
International Edition: doi.org/10.1002/anie.202016422
German Edition: doi.org/10.1002/ange.202016422

VIP **Alkoxides** **Very Important Paper**

Untangling the Complexity of Mixed Lithium/Magnesium Alkyl/Alkoxy Combinations Utilised in Bromine/Magnesium Exchange Reactions

*Leonie J. Bole, Neil R. Judge, and Eva Hevia**

In memory of Victor Snieckus

Abstract: *While it is known that the addition of Group 1 alkoxides to s-block organometallics can have an activating effect on reactivity, the exact nature of this effect is not that well understood. Here we describe the activation of sBu_2Mg towards substituted bromoarenes by adding one equivalent of LiOR (R = 2-ethylhexyl), where unusually both sBu groups can undergo efficient Br/Mg exchange. Depending on the substitution pattern on the bromoarene two different types of organometallic intermediates have been isolated, either a mixed aryl/alkoxide $[\{LiMg(2\text{-}FG\text{-}C_6H_4)_2(OR)\}_2]$ (FG = OMe; NMe_2) or a homoaryl $[(THF)_4Li_2Mg(4\text{-}FG\text{-}C_6H_4)_4]$ (FG = OMe, F). Detailed NMR spectroscopic studies have revealed that these exchange reactions and the formation of their intermediates are controlled by a new type of bimetallic Schlenk-type equilibrium between heteroleptic $[LiMgsBu_2(OR)]$, alkyl rich $[Li_2MgsBu_4]$ and $Mg(OR)_2$, with $[Li_2MgsBu_4]$ being the active species performing the Br/Mg exchange process.*

Typified by the LIC-KOR superbase reagent, adding (or more accurately, co-complexing) Group 1 alkoxides to s-block organometallics can cause profound reactivity enhancement of the latter, enabling unique chemical profiles.[1] These type of reagents, have proved to be exceptionally powerful bases for the deprotonative metallation of organic substrates.[2] Interestingly, despite their numerous applications, the constitution(s) and structure(s) of these bimetallic species in solution have remained concealed for over five decades, being a matter of intrigue and debate.[3] Shedding important light in this matter, recent seminal work by Klett has revealed that in the case of LiNp/KO*t*Bu combinations (Np = neopentyl), complicated aggregates are formed where the alkyl group coordinates in a unique manner to both Li and K, leading to hybrid Li/K−C bond polarity.[4] Within Group 1/Group 2 bimetallic combinations, early work by Screttas showed that the addition of magnesium alkoxides to alkyl/aryl sodium (or potassium) compounds induces the solubilisation of the heavier alkali organyl in non-polar solvents, a benefit attributed to the formation of mixed-metal aggregates.[5] Furthermore, Richey Jr has also found that aryl bromides and iodides react with equimolar mixtures of dialkylmagnesium reagents (R_2Mg) and alkali-metal alkoxides to furnish the desired products of Mg-halogen exchanges; whereas R_2Mg reagents on their own are inert towards these substrates.[6] While the formation of alkali-metal magnesiates has been postulated in some of these studies, tangible information on the constitution of these species is limited.

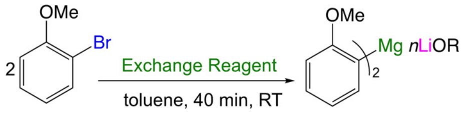
Expanding the synthetic potential of these bimetallic combinations, recently we reported $sBu_2Mg{\cdot}2\,LiOR$ (R = 2-ethylhexyl) enables fast regioselective Mg/Br exchange of dibromo(hetero)aromatics[7] as well as exchanges of less activated aryl chlorides.[8]

Removing some of the mystery in this chemistry, here we report our findings assessing the constitution of these bimetallic alkyl/alkoxide combinations and their reactivity towards bromoarenes, uncovering a complex equilibrium between different bimetallic species where the final composition of the Br/Mg exchange intermediates appears influenced by the substitution pattern in the aromatic substrate.

We started our studies by reassessing the reactivity of 2-bromoanisole (**1a**) towards different combinations of Li and Mg alkyl/alkoxide mixtures (Table 1).

Using our originally reported combination of sBuLi and $Mg(OR)_2$ in a 2:1 ratio[8] led to the full magnesiation of two equivalents of **1a** after 40 minutes at room temperature

Table 1: Screening of Mg/Br-exchange capabilities of magnesium reagents towards 2-bromoanisole (**1a**).



Entry	Exchange reagent[a]	n	Yield [%][b]
1	2 sBuLi + $Mg(OR)_2$	2	99
2	2 LiOR + sBu_2Mg	2	99
3	**LiOR + sBu_2Mg**	**1**	**99**
4	LiOR′ + sBu_2Mg	1	20
5	sBu_2Mg	0	5
6	LiOR + sBu_2Mg + 1.5 $Mg(OR)_2$	2[c]	0

[a] R = 2-ethylhexyl and R′ = $CH_2CH_2N(Me)CH_2CH_2NMe_2$. [b] Yields have been determined by GC analysis of reaction aliquots after an aqueous quench using hexamethylbenzene as internal standard. Formation only of anisole and unreacted 2-bromoanisole were observed. [c] n = 2 LiOR + 1.5 $Mg(OR)_2$. Optimized conditions highlighted in bold.

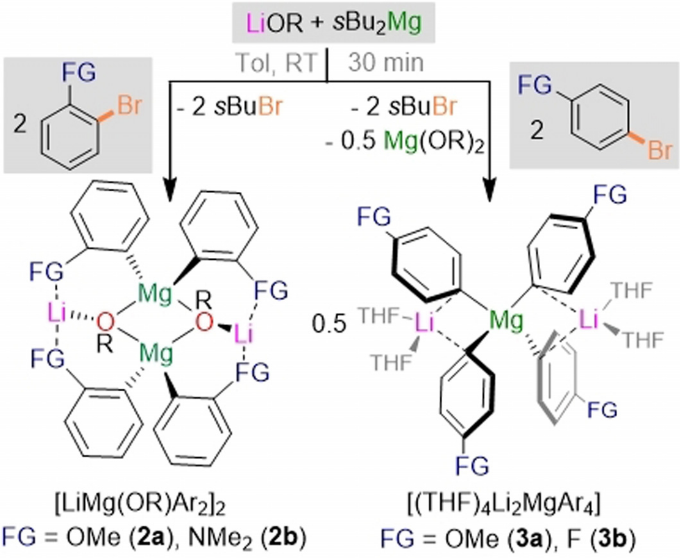
---

[*] Dr. L. J. Bole, N. R. Judge, Prof. Dr. E. Hevia
Department für Chemie und Biochemie, Universität Bern
3012 Bern (Switzerland)
E-mail: eva.hevia@dcb.unibe.ch

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.202016422.

(entry 1). The same conversion was observed when mixing *s*Bu_2Mg with two equivalents of LiOR, hinting at the formation of the same type of active mixed-metal organometallic species, which contrasts with the almost total lack of reactivity of *s*Bu_2Mg towards **1a** (5% yield, entry 5). Interestingly, **1a** can also undergo quantitative Br/Mg exchange when using a 1:1 mixture of *s*Bu_2Mg and LiOR (entry 3). This observation is consistent with our previous work where [{LiMg(2-anisyl)$_2$(OR)}$_2$] (**2a**) and LiOR are quantitatively formed as products of the reaction of **1a** with a 2:1 mixture of *s*BuLi and Mg(OR)$_2$ in toluene.[7] Exposing the key role of the alkoxide employed to mediate this transformation, using the relevant LiOR′ derived from 2-{[2-(dimethylamino)ethyl]methylamino}ethanol (dmem(H)) only a modest 20% yield of the magnesiation product was observed.[9] Studies using different combinations of Li and Mg alkoxides also revealed that when 1.5 equiv of Mg(OR)$_2$ were added to the initial LiOR/*s*Bu_2Mg combination the Br/Mg exchange totally shutdown (entry 6, Table 1).

Intrigued by these findings we next tested the reactivity of equimolar amounts of *s*Bu_2Mg and LiOR with several substituted bromoarenes (Scheme 1). ^{1}H NMR monitoring studies showed that the reaction with 2-bromoanisole led to the quantitative formation of **2a**. Similarly, when 2-bromodimethylaniline was employed [{LiMg(2-NMe$_2$-C$_6$H$_4$)$_2$-(OR)}$_2$] (**2b**) was obtained which could be isolated in a 46% yield as a solid.[10] X-ray crystallographic studies established the bimetallic dimeric constitution of **2b**, akin to that reported for **2a** (Figure 1).[7] Featuring a centrosymmetric four-membered {MgOMgO} ring, in **2b** each Mg binds to the *ipso* C of two aryl groups, occupying the position previously filled by a Br atom. In contrast, each Li coordinates to one alkoxide bridge in addition to two NMe$_2$ groups.



[LiMg(OR)Ar$_2$]$_2$
FG = OMe (**2a**), NMe$_2$ (**2b**)

[(THF)$_4$Li$_2$MgAr$_4$]
FG = OMe (**3a**), F (**3b**)

Scheme 1. Reactions of sBu_2Mg·LiOR (*R* = 2-ethylhexyl) with 2-bromo and 4-bromo-substituted arenes (25 °C, toluene, 30 min, using 2 equivalents of the relevant bromoarene). For **3a** and **3b** amounts of THF were introduced to facilitate their crystallisation.[10]

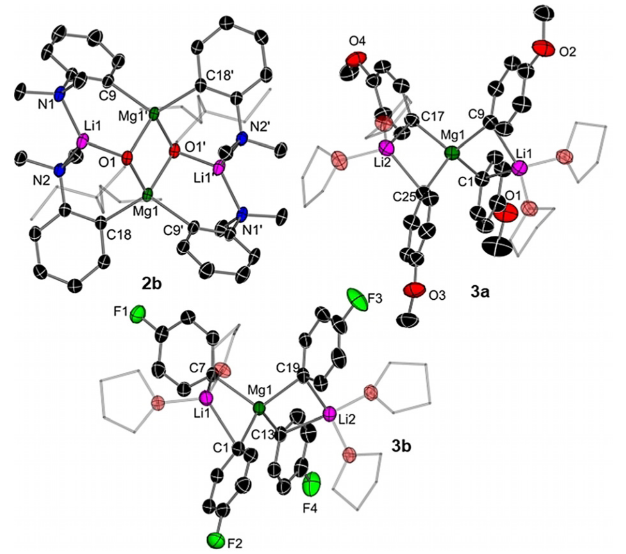
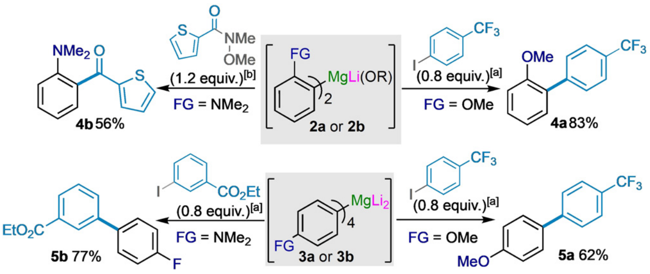


Figure 1. Molecular structures of **2b**, **3a** and **3b** with displacement ellipsoids at 50% probability, all H atoms omitted, and with C atoms in 2-ethylhexyl substituents and THF molecules drawn as wire frames for clarity. Equivalent atoms of **2b** generated by (1−*x*, 1−*y*, 1−*z*) symmetry operation.[20]

Adding further interest, when *s*Bu_2Mg and LiOR were reacted with two equivalents of 4-bromo-anisole and 4-bromo-fluorobenzene an entirely new type of mixed-metal product was obtained (Scheme 1), namely the homoleptic tetra(aryl)lithium magnesiates [(THF)$_4$Li$_2$MgAr$_4$] (Ar = 4-OMe-C$_6$H$_4$, **3a**; Ar = 4-F-C$_6$H$_4$, **3b**) in 74 and 60% isolated yields, respectively.[11] In this case the Br/Mg exchange reaction occurs with concomitant elimination of Mg(OR)$_2$ (determined by ^{1}H and ^{13}C NMR).[10] The molecular structures of **3a** and **3b** were established by X-ray crystallography (Figure 1). Diverging markedly from **2a** and **2b**, **3a** and **3b** exhibit a monomagnesium constitution, with a 2:1 Li:Mg ratio where all anionic groups are 4-substituted aryls resulting from Br/Mg exchange. Both structures contain a C4-coordinated Mg atom flanked by two THF-solvated Li cations. Unlike in **2a** and **2b**, here the lithium centres do not interact with the donor substituents on the aromatic rings, which are now located too remote, and instead they adopt a perpendicular disposition to the aromatic rings, binding to their *ipso* C in a similar manner as previously reported by Weiss for the higher order sodium magnesiate [(PMDETA)$_2$Na$_2$MgPh$_4$] (PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine).[12]

^{1}H NMR monitoring of the reactions of the LiOR/*s*Bu_2Mg bimetallic combination with these different bromoarenes showed that **2a**,**b** and **3a**,**b** are in each case the only organometallic product of the reaction and that their formation did not result from a disproportionation during the crystallisation process. It should also be noted that these species are the sole organometallic species present in solution when using the original 2*s*BuLi/Mg(OR)$_2$ combination, offering further support to the in situ formation of the same exchange reagent.[7]



Scheme 2. Comparative electrophilic interception studies of **2a**–**2b** and **3a**,**b** prepared in situ via Br/Mg exchange with 0.6 equiv of the 2sBuLi·Mg(OR)$_2$ combination. [a] ZnCl$_2$ (1.3 equiv), E$^+$ (0.8 equiv), Pd(OAc)$_2$ (4 mol%), SPhos (8 mol%). [b] E$^+$ (1.2 equiv), 25 °C, 12 h.[10]

To ascertain whether the different composition of **2a**,**b** and **3a**,**b** could have an influence on their further functionalization, electrophilic interception studies were carried out (Scheme 2).[10]

Thus, transmetallation of **2a**, **3a** and **3b** with ZnCl$_2$ followed by Pd catalysed cross-coupling with 4-iodo-trifluoromethylbenzene or ethyl-3-iodobenzoate led to the formation of asymmetric bis(arenes) **4a**, **5a** and **5b** in good yields ranging from 62 to 83%. In addition, **2b** reacts with a Weinreb amide to form acylation product **4b** in a 56% yield. While these quenching studies demonstrate the synthetic utility of these mixed-metal complexes and their ability to undergo C–C bond forming processes, they also illustrate how on many occasions the constitution of the active organometallic species can remain concealed, limiting the understanding on how such bimetallic reagents operate. This is particularly relevant for these reactions, where using the same exchange reagent and same reaction conditions, produces different types of magnesium aryl species.

Puzzled by the contrasting compositions of **2a**,**b** versus **3a**,**b**, we next probed the constitution of the exchange reagent sBu$_2$Mg/LiOR in toluene solutions using a combination of NMR experiments including ^{1}H-DOSY NMR. These studies revealed the presence of two distinct organometallic species in solution containing sBu groups (Figure S1).[10] One species whose M-C*H* fragment of the sBu groups resonates at $\delta = 0.40$ ppm in the ^{1}H NMR spectrum (Figure 2a) belongs to a compound which also contains alkoxide ligands (both sets of resonances exhibit almost identical diffusion coefficients (D) by ^{1}H-DOSY NMR).[10] These data support the formation of co-complexation product [LiMgsBu$_2$(OR)] (**6**) (Figure 2a). The second species displays an upfield shifted multiplet at $\delta = -0.26$ ppm which is intermediate between those chemical shifts found for the single metal reagents sBuLi ($\delta = -1.09$ ppm) and sBu$_2$Mg ($\delta = 0.05$ ppm). Moreover, ^{1}H-DOSY NMR experiments indicate that this signal belongs to a species that contains only sBu groups,[10] which coupled with the homoleptic constitution of the exchange products **3a**–**3b**, suggest that this second species may be homoleptic tetra(alkyl) [Li$_2$MgsBu$_4$] (**7**) (Figure 2a). Further support for this interpretation was found when [Li$_2$MgsBu$_4$] (**7**) was prepared independently via co-complexation of two equivalents of sBuLi with sBu$_2$Mg which gave a colourless oil with its ^{1}H NMR spectrum showing a multiplet at $\delta = -0.26$ ppm, the same chemical shift as that found in the sBu$_2$Mg/LiOR mixture (Figure 2b).

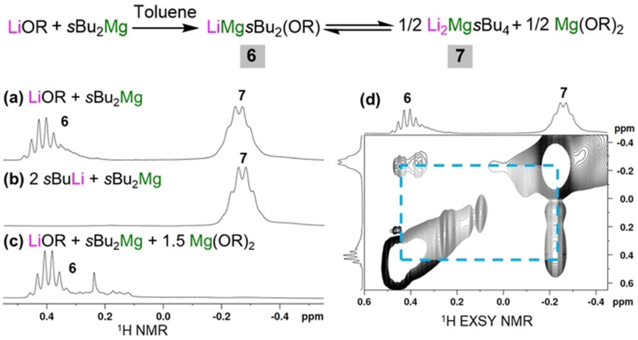


Figure 2. Proposed equilibrium of [LiMgsBu$_2$(OR)] (**6**) with [Li$_2$MgsBu$_4$] (**7**) and Mg(OR)$_2$. Section of ^{1}H NMR spectra (from 0.5 to −0.5 ppm) in [D$_8$]toluene of: a) LiOR + sBu$_2$Mg; b) 2 sBuLi + sBu$_2$Mg and c) LiOR + sBu$_2$Mg + 1.5 Mg(OR)$_2$. d) Section of ^{1}H-EXSY NMR spectrum of LiOR + sBu$_2$Mg in [D$_8$]toluene.

Furthermore, ^{1}H-EXSY NMR experiments indicate that lithium magnesiates **6** and **7** are in equilibrium with each other (Figure 2d). An explanatory possible equilibrium is depicted in Figure 2, with the combination of equimolar amounts of sBu$_2$Mg and LiOR forming mixed alkyl(alkoxide) co-complex [LiMgsBu$_2$(OR)] (**6**) which in turn is in equilibrium with tetra(alkyl) [Li$_2$MgsBu$_4$] (**7**) and Mg(OR)$_2$. Adding credence to this interpretation it was found that adding increasing amounts of Mg(OR)$_2$ to a sBu$_2$Mg/LiOR combination caused the gradual decrease of **7** in solution, until it disappears completely after 1.5 equiv of Mg(OR)$_2$ in total. This suggests that under these conditions the equilibrium lies towards the formation of **6**. While studies on homo(alkyl) alkali-metal magnesiates have described that higher and lower order species can be in equilibrium with each other,[14] the type of equilibrium depicted in Figure 2 for mixed alkyl/alkoxide species is, as far as we can ascertain, unknown in lithium magnesiate chemistry. It bears a strong resemblance with the well-established classical Schlenk equilibrium in Grignard reagent chemistry where heteroleptic RMgX reagents are in equilibrium with the homoleptic species, MgR$_2$ and MgX$_2$. Related to these findings, O'Hara has recently found that a sodium dialkyl magnesiate supported by a biphenolate ligand [Na$_2$Mg(biphen)Bu$_2$] is in equilibrium with all alkoxide sodium magnesiate [Na$_2$Mg(biphen)$_2$] along with Na$_2$MgBu$_4$ although, in this case, all species involved within the equilibrium have the same 2:1 alkali metal:magnesium ratio.[13]

The high solubility of [LiMgsBu$_2$(OR)] (**6**) and [Li$_2$MgsBu$_4$] (**7**) in hydrocarbon solvents precluded their crystallization. In the case of **6**, using the alkoxide LiOR′ [R′ = CH$_2$CH$_2$N(CH$_3$)CH$_2$CH$_2$N(CH$_3$)$_2$], which contains two amide groups, in a co-complexation reaction with one equivalent of sBu$_2$Mg led to the isolation of dimeric [LiMgsBu$_2$(OR′)]$_2$ (**8**) in a 35% crystalline yield (Figure 3). X-ray crystallographic studies revealed a step ladder motif for **8**, comprising outer Li-C rungs and inner Mg-O rungs.[15] Along the ladder edge, internal NMe$_2$ from the alkoxide ligands and another sBu group coordinate to Li and Mg,

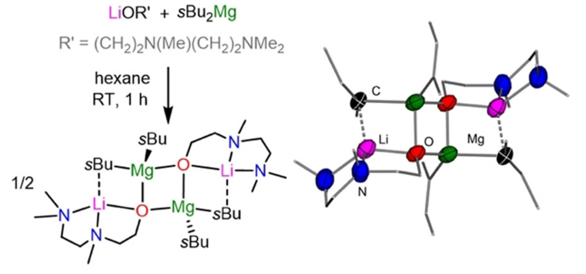


Figure 3. Left: Synthesis of [$LiMgsBu_2(OR')$] (**8**); [$R' = CH_2CH_2N(CH_3)CH_2CH_2N(CH_3)_2$] via co-complexation of LiOR′ with sBu_2Mg and Right: molecular structure of **8** with displacement ellipsoids at 30% probability, all H atoms omitted, and with C atoms drawn as wire frames (except for CH group of bridging sBu groups) for clarity.[20]

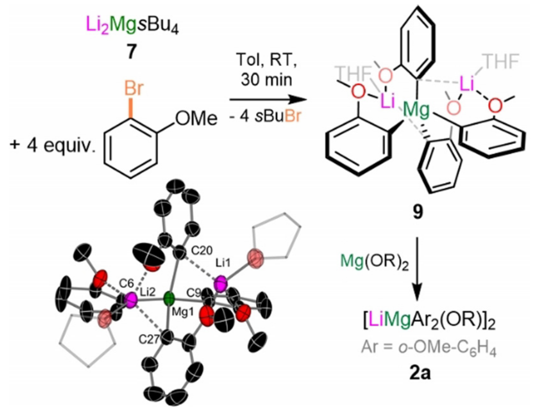
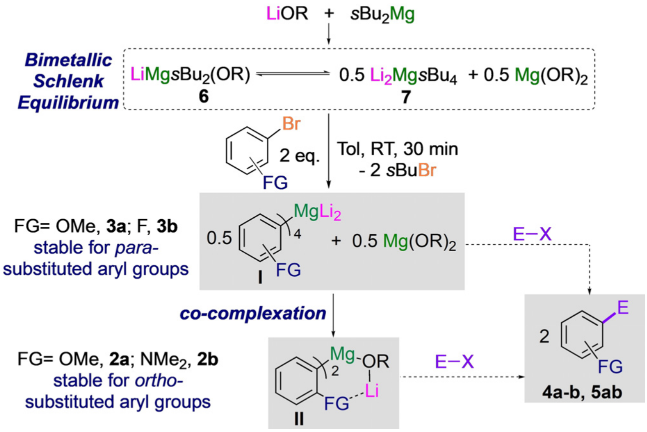


Figure 4. Synthesis of [$(THF)_2Li_2Mg(2\text{-}OMe\text{-}C_6H_4)_4$] (**9**) via Br/Mg exchange of four equivalents of **1a** with [Li_2MgsBu_4] (**7**) and subsequent conversion in **2a** via co-complexation with $Mg(OR)_2$. Molecular structure of **9** with displacement ellipsoids at 50% probability, all H atoms omitted, and with C atoms in THF molecules drawn as wire frames for clarity.[20]

respectively to complete the dimer. Alternatively, **8** can be viewed as two dinuclear {LiOMgC} rings which combine laterally through the Mg-O edges to form a tetranuclear ladder.

While these findings shed light on the constitutions of these mixed alkyl/alkoxide mixtures in solution, it was still not clear why two completely different types of aryl lithium magnesiates form during the Br/Mg exchange process with substituted bromoarenes (Scheme 1). At first glance, it appeared that **2a**,**b** resulting from the reaction with 2-bromo substituted substrates could be the products if the exchange process was effected by [$LiMg\textit{s}Bu_2(OR)$] (**6**). In contrast, homoleptic **3a**,**b** seemed more likely to be formed via [$Li_2Mg\textit{s}Bu_4$] (**7**). In order to establish if both systems, **6** and **7**, could be active towards Mg/Br exchange, we first carried out the reaction of **7** with four equivalents of 2-bromoanisole (**1a**) in toluene to produce tetra(aryl) lithium magnesiate [$(THF)_2Li_2Mg(2\text{-}OMe\text{-}C_6H_4)_4$] (**9**) in a 90% isolated yield (Figure 4) (GC analysis confirmed quantitative conversion of **1a**).[10] Exhibiting a contacted ion pair magnesiate structure reminiscent to that of **3a**, **9** displays a distorted tetrahedral with Mg bonded to four *ortho*-metallated molecules of anisole, while Li interacts with OMe groups of two anisyl groups as well as a THF ligand. To maximise these Li-OMe contacts the Li⋯Mg⋯Li vector in **9** is significantly more bent than in **3a** [88.15(11) *vs* 159.05(8)°], while the lengths of the Mg–C bonds in both complexes are almost identical [average values, 2.223 and 2.2313 Å for **9** and **3a**, respectively]. Considering the alkyl-rich constitution of higher order magnesiate **7**,[16] coupled with its ability to quantitatively promote Br/Mg exchange of **1a**, the selective formation of **2a** when **1a** was reacted with the LiOR/$\textit{s}Bu_2Mg$ combination became even more puzzling. In an attempt to mimic the reaction conditions when using this mixed alkyl/alkoxide reagent, one molar equivalent of $Mg(OR)_2$ (which is the other product observed from disproportionation of **6** into **7**) was introduced to a suspension of **9** in toluene which led to the quantitative formation of **2a** (Figure 4).

Adding a new layer of complexity, these results set at least two different scenarios to explain the formation of mixed alkyl/alkoxides **2a**,**b** during the exchange reactions. On one hand, in situ generated tetra(alkyl) magnesiate **7** could be responsible for the Br/Mg exchange in all cases, furnishing [Li_2MgAr_4] (**I**) intermediates that in the case of *ortho*-substituted Ar groups can undergo co-complexation with the concomitantly generated $Mg(OR)_2$ furnishing **2a**,**b** (as depicted in Scheme 3). Alternatively the more kinetically activated *ortho*-substituted bromoarenes[17] could react preferentially with mixed(alkyl) alkoxide magnesiate **6** whereas, for less reactive 4-substituted substrates, the exchange may occur via tetra(alkyl) magnesiate **7**. However, this second option seems less likely as using isolated crystals of related mixed(alkyl) alkoxide magnesiate **8** towards **1a** led to significantly lower conversions (20%, see Supporting Information), a behaviour that we have also noticed in Zn/I exchange reactions using [$LiZnEt_2(OR')$].[9] Especially revealing was the fact that when an excess of 1.5 equiv of $Mg(OR)_2$ was added to the equimolar mixture LiOR and $\textit{s}Bu_2Mg$ (pushing the bimetallic Schlenk equilibrium depicted in Scheme 3 towards the exclusive formation of **6** in solution, Figure 2c), the exchange process is completely suppressed with no conversion seen after 40 minutes (entry 6, Table 1 and Supporting Information).[18]



Scheme 3. Proposed organometallic species involved in lithium alkoxide mediated Mg/Br exchange of bromoarenes.

Collectively our study confirms that addition of LiOR kinetically activates the two alkyl groups on *s*Bu_2Mg to effectively undergo Br/Mg exchange.[6,7] However this activation is not due to the formation of a more reactive alkyl/alkoxide lithium magnesiate as initially thought, but better to the presence of a bimetallic Schlenk equilibrium which generates in situ a much more reactive species, namely higher order tetra(alkyl) lithium magnesiate **7** (Scheme 3). It is important to note that under the conditions of this study we do not observe the disproportionation of **7** in solution to its lower order derivative LiMg*s*Bu_3 and *s*BuLi (a process that has been reported for related sodium tetra(alkyl) derivatives Na_2MgR_4 (R = *n*Bu, CH_2SiMe_3)), hinting that the choice of alkali-metal adds to the complexity of this s-block heterobimetallic systems.[19] Thus, the four alkyl groups on **7** are active towards the exchange to form tetra(aryl) intermediates [Li_2MgAr_4] (**I**) which have been trapped and structurally authenticated for Ar = 4-OMe-C_6H_4, **3a**; Ar = 4-F-C_6H_4, **3b**. However, for 2-substituted aryls (Ar = 2-OMe-C_6H_4, 2-NMe_2-C_6H_4), upon formation of **I**, co-complexation with $Mg(OR)_2$ (which is also present in the reaction media as a consequence of the Schlenk equilibrium referred above) can ensue, furnishing mixed-metal, mixed-ligand intermediate [$LiMgAr_2(OR)$] (**II**) (Scheme 3). Comparing the structures of **2a**,**b** vs. **3a**,**b**, the preferred formation of **II** can be attributed to the unique Lewis donor stabilisation achieved by Li through simultaneous coordination to the donor *ortho*-substituents on the aryl group and the oxygens of the alkoxide ligand. This coordination environment is not available for *para*-substituted arenes. Nevertheless, both intermediates **I** and **II** undergo electrophilic interception as shown in Scheme 3 affording in all cases the relevant functionalized substituted arene **4a**,**b**, **5a**,**b**.

To conclude, by combining reactivity studies with detailed NMR and structural studies, the mist surrounding the complex constitutions of intermediates involved in lithium alkoxide mediated Br/Mg exchange processes has begun to clear.

The participation of several distinct lithium magnesiates, exhibiting not only different ligand sets, but also different Li:Mg ratios has been established, advancing understanding of the *modus operandi* of these mixtures thus paving new paths towards further synthetic applications.

Acknowledgements

We thank Professor Paul Knochel and Alexandre Desaintjean (Ludwig-Maximilians-Universität München) for their helpful discussions which inspired this work and for performing the electrophilic interception studies which furnished **4a**,**b** and **5a**,**b**. We also thank the Swiss National Science Foundation (200021_188573) and the University of Bern for the generous financial support of this research.

Conflict of interest

The authors declare no conflict of interest.

Keywords: alkoxides · bromine/magnesium exchange · lithium · magnesium · mixed-aggregates

---

[1] a) M. Schlosser, *J. Organomet. Chem.* **1967**, *8*, 9; b) L. Lochmann, J. Pospišil, D. Lim, *Tetrahedron Lett.* **1966**, *7*, 257.

[2] a) L. Lochmann, *Eur. J. Inorg. Chem.* **2000**, 1115; b) F. Mongin, A. Harrison-Marchand, *Chem. Rev.* **2013**, *113*, 7563; c) L. Lochmann, M. Janata, *Cent. Eur. J. Chem.* **2014**, *12*, 537.

[3] a) M. Schlosser, S. Strunk, *Tetrahedron Lett.* **1984**, *25*, 741; b) W. Bauer, L. Lochmann, *J. Am. Chem. Soc.* **1992**, *114*, 7482; c) S. D. Robertson, M. Uzelac, R. E. Mulvey, *Chem. Rev.* **2019**, *119*, 8332; d) J. Klett, *Chem. Eur. J.* **2021**, *27*, 888.

[4] a) P. Benrath, M. Kaiser, T. Limbach, M. Mondeshki, J. Klett, *Angew. Chem. Int. Ed.* **2016**, *55*, 10886; *Angew. Chem.* **2016**, *128*, 11045; b) B. Jennewein, S. Kimpel, D. Thalheim, J. Klett, *Chem. Eur. J.* **2018**, *24*, 7605.

[5] a) C. G. Screttas, B. R. Steele, *Appl. Organomet. Chem.* **2000**, *14*, 653; b) C. G. Screttas, M. Micha-Screttas, *Organometallics* **1984**, *3*, 904; c) C. G. Screttas, M. Micha-Screttas, *J. Organomet. Chem.* **1985**, *290*, 1; d) C. G. Screttas, M. Micha-Screttas, *J. Organomet. Chem.* **1986**, *316*, 1; e) M. Micha-Screttas, C. G. Screttas, B. R. Steele, G. A. Heropoulos, *Tetrahedron Lett.* **2002**, *43*, 4871.

[6] J. Farkas, S. J. Stoudt, E. M. Hanawalt, A. D. Pajerski, H. G. Richey, *Organometallics* **2004**, *23*, 423.

[7] A. Desaintjean, T. Haupt, L. J. Bole, N. R. Judge, E. Hevia, P. Knochel, *Angew. Chem. Int. Ed.* **2021**, *60*, 1513; *Angew. Chem.* **2021**, *133*, 1536.

[8] D. S. Ziegler, K. Karaghiosoff, P. Knochel, *Angew. Chem. Int. Ed.* **2018**, *57*, 6701; *Angew. Chem.* **2018**, *130*, 6811.

[9] M. Balkenhohl, D. S. Ziegler, A. Desaintjean, L. J. Bole, A. R. Kennedy, E. Hevia, P. Knochel, *Angew. Chem. Int. Ed.* **2019**, *58*, 12898; *Angew. Chem.* **2019**, *131*, 13030.

[10] See Supporting Information for details.

[11] ^1H NMR analysis of these reactions showed almost quantitative conversions to these bimetallic species which are the only organometallic species formed from the solution along with $Mg(OR)_2$.

[12] a) M. Geissler, J. Kopf, E. Weiss, *Chem. Ber.* **1989**, *122*, 1395; b) E. Weiss, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1501; *Angew. Chem.* **1993**, *105*, 1565.

[13] a) J. Francos, P. C. Gros, A. R. Kennedy, C. T. O'Hara, *Organometallics* **2015**, *34*, 2550; b) C. Yeardley, A. R. Kennedy, P. C. Gros, S. Touchet, M. Fairley, R. McLellan, A. J. Martínez-Martínez, C. T. O'Hara, *Dalton Trans.* **2020**, *49*, 5257.

[14] For selected examples see: a) L. M. Seitz, T. L. Brown, *J. Am. Chem. Soc.* **1966**, *88*, 4140; b) S. E. Baillie, W. Clegg, P. Garcia-Alvarez, E. Hevia, A. R. Kennedy, J. Klett, L. Ruso, *Chem. Commun.* **2011**, *47*, 388; c) S. E. Baillie, W. Clegg, P. Garcia-Alvarez, E. Hevia, A. R. Kennedy, J. Klett, L. Ruso, *Organometallics* **2012**, *31*, 5131.

[15] For selected references on ring laddering in *s*-block organometallics see: a) R. E. Mulvey, *Chem. Soc. Rev.* **1991**, *20*, 167; b) A. Downard, T. Chivers, *Eur. J. Inorg. Chem.* **2001**, 2193; c) A. D. Bond, *Cryst. Growth Des.* **2005**, *5*, 755; d) W. Clegg, S. H. Dale, D. V. Graham, R. W. Harrington, E. Hevia, L. M. Hogg, A. R. Kennedy, R. E. Mulvey, *Chem. Commun.* **2007**, 1641.

[16] a) R. E. Mulvey, F. Mongin, M. Uchiyama, Y. Kondo, *Angew. Chem. Int. Ed.* **2007**, *46*, 3802; *Angew. Chem.* **2007**, *119*, 3876, and references therein; b) L. Davin, A. Hernán-Gómez, C. McLaughlin, A. R. Kennedy, R. McLellan, E. Hevia, *Dalton Trans.* **2019**, *48*, 8122.

[17] L. Shi, Y. Chu, P. Knochel, H. Mayr, *J. Org. Chem.* **2009**, *74*, 2760.

[18] After 24 h at room temperature 60% conversion was observed, while after 48 h the reaction was complete.

[19] T. X. Gentner, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2021**, https://doi.org/10.1002/anie.202010963; *Angew. Chem.* **2021**, https://doi.org/10.1002/ange.202010963.

[20] Deposition Number(s) 2049361 (**2b**), 2049362 (**3a**), 2049363 (**3b**), 2049364 (**8**) and 2049365 (**9**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Manuscript received: December 10, 2020
Accepted manuscript online: January 6, 2021
Version of record online: February 26, 2021