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Aryl and Heteroaryl Magnesium Reagents in Toluene via a Br/Mg- or a Cl/Mg-Exchange

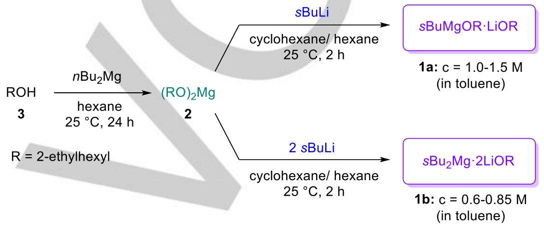
Dorothée S. Ziegler, Konstantin Karaghiosoff, and Paul Knochel*[a]

Dedication ((optional))

Abstract: *The alkylmagnesium alkoxide sBuMgOR·LiOR (R = 2-ethylhexyl) prepared as a 1.5* M *solution in toluene undergoes very fast Br/Mg-exchanges with aryl and heteroaryl bromides, producing aryl and heteroaryl magnesium alkoxides (ArMgOR·LiOR) in toluene. These Grignard reagents react with a broad range of electrophiles, including aldehydes, ketones, allyl bromides, acyl chlorides, epoxides and aziridines in good yields. Remarkably, the related reagent* $sBu_2Mg\cdot 2LiOR$ *(R = 2-ethylhexyl) allows a Cl/Mg-exchange with various electron-rich aryl chlorides in toluene producing diorganomagnesium species of type* $Ar_2Mg\cdot 2LiOR$*, which react well with aldehydes and allyl bromides.*

Organomagnesium halides are key intermediates in organic synthesis.[1] They are usually prepared by a direct insertion of magnesium turnings,[2] Rieke magnesium,[3] or magnesium powder, and lithium chloride[4] to organic halides. The heterogenous nature of this reaction complicates scale-up and industrial use.[2] A deprotomagnesiation of arenes or heteroarenes can also be accomplished using soluble hindered magnesium amides.[5] Alternatively, various organomagnesium halides can be prepared via a halogen-magnesium exchange by treating aryl or heteroaryl iodides or bromides with an alkylmagnesium halide[6] or better with *i*PrMgCl·LiCl (*turbo*-Grignard).[7] Furthermore, synthetically useful reagents for halogen-metal exchange are lithium organomagnesiates (R_3MgLi).However, in this case, lithium triorgano magnesiates are produced. [8] All these preparation methods provide Grignard reagents in ethereal solvents such as diethyl ether or THF and only a few methods have been reported describing the preparation of magnesium organometallics in non-polar solvents.[9] The synthesis of Grignard reagents in hydrocarbons or toluene is of great interest, since these weakly-coordinated Grignard reagents may display an original and unusual reactivity. Also, Grignard reagents in hydrocarbons or toluene are industrially friendly reagents, as such solvents improve aqueous extraction during work-ups.[10]

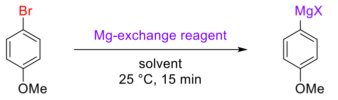
Herein, we report new halogen-magnesium exchange reagents *s*BuMgOR·LiOR (**1a**) and $sBu_2Mg\cdot 2LiOR$ (**1b**) (R = 2-ethylhexyl), that allow very fast Br/Mg-exchanges and, for the first time, a Cl/Mg-exchange on various electron-rich aryl chlorides. First, a convenient synthesis of **1a** and **1b** was developed. Thus, the magnesium alkoxide **2** was prepared by treating nBu_2Mg (0.7 M in hexane) with 2-ethylhexanol (**3**, 2.0 equiv) at 25 °C for 24 h.[11,12] The addition of one or two equivalents of *s*BuLi (1.2 M in cyclohexane) to the colorless gel (**2**) at 25 °C for 2 h provided slightly yellow solutions of **1a** and **1b**. Removal of the solvent in vacuo produced a foam which readily dissolves in toluene, affording a 1.0-1.5 M solution of **1a** and a 0.6-0.85 M slightly yellow solution of **1b** (Scheme 1).



Scheme 1. Preparation of the new exchange reagents **1a** and **1b**.

Both **1a-b** are very powerful exchange reagents, which for the first time, allow the synthesis of arylmagnesium reagents in toluene.[13] In preliminary experiments, the Br/Mg-exchange on 4-bromoanisole (**4a**) was examined (Table 1).

Table 1. Br/Mg-exchange for 4-bromoanisole (**4a**) using various magnesium-exchange reagents at 25 °C.



4a **5a**

entry	Mg-exchange reagent	equiv	solvent	yield(%)[a]
1	*i*PrMgCl·LiCl	1.2	THF	1 [0][b]
2	$sBu_2Mg\cdot 2LiCl$	0.6	THF	13 [0][b]
3	*s*BuMgOR·LiOR (**1a**)	1.2	toluene	85
4	*s*BuMgOR·LiOR (**1a**)	1.2	toluene	99[c]
5	*s*BuMgOR·LiOR (**1a**)	1.2	THF	14[c]

[a] Yield of **5a** determined by GC-analysis of water quenched reaction aliquots. [b] Yield obtained in toluene. [c] Yield obtained in the presence of TMEDA (1.2 equiv).

In THF, *i*PrMgCl·LiCl[7] required 27 h at 25 °C to complete the exchange reaction and produced the desired arylmagnesium halide **5a** (X = Cl). However, less than 1% of **5a** was formed with this exchange reagent after 15 min reaction time (entry 1).[14] The currently most powerful available exchange reagent $sBu_2Mg\cdot 2LiCl$[7b] led to 13% of **5a** (X = 4-anisyl) after 15 min (entry 2). A full conversion with this reagent required 8 h reaction time. Switching to toluene showed, that both of these reagents were unreactive. However, the addition of the new reagent *s*BuMgOR·LiOR (**1a**) to **4a** in toluene provided **5a** (X = OR·LiOR) in 85% yield within 15 min reaction time (entry 3). The addition of TMEDA (*N,N,N´,N´*-tetramethylethylenediamine; 1.2 equiv)

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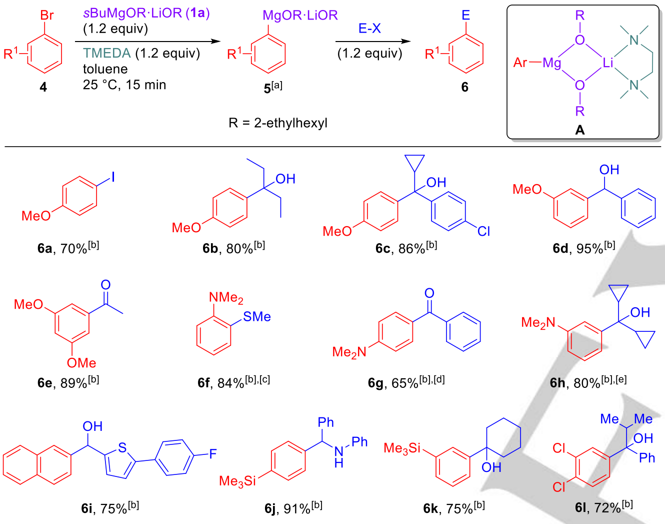
further improved the reaction conversion to 99% (entry 4).[15] The addition of TMEDA to *i*PrMgCl·LiCl[7] or *s*Bu_2Mg·2LiCl[7b] had no effect. Interestingly, the rate of the Br/Mg-exchange using **1a** in THF instead of toluene was considerably decreased and only a conversion of 14% was observed (entry 5). This showed, that there is a real advantage for carrying out the Br/Mg-exchange in non-polar solvents such as toluene.

Quenching of **5a** (X = OR·LiOR·TMEDA) with iodine furnished the aryl iodide **6a** in 70% yield (25 °C, 30 min; Scheme 2). Usually, arylmagnesium reagents do not add well to ketones.[16,17] However, trapping **5a** in toluene with ketones furnished the tertiary alcohols **6b-c** in 80-86% yield (25 °C, 2 h). Related aryl bromides such as 3-bromoanisole (**4b**) or 1-bromo-3,5-dimethoxybenzene (**4c**) underwent a complete Br/Mg-exchange by treatment with **1a** (25 °C, 15 min). These Grignard reagents were added to PhCHO or were acylated with a Weinreb amide[18], furnishing the desired products **6d** and **6e** in 89-95% yield (25 °C, 1 h).

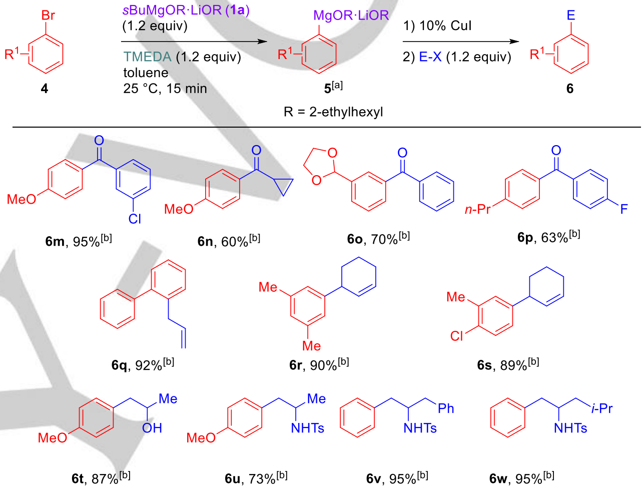


[a] TMEDA has been omitted for the sake of clarity. [b] Yield of analytically pure isolated product. [c] The reaction time was 1 h. [d] The reaction time was 4 h [e] The reaction time was 2 h.

Scheme 2. Br/Mg-exchange for aryl bromides of type **4** leading, via intermediate organomagnesiums of type **5**, to functionalized arenes of type **6**.

Also, bromoanilines **4d-f** which are very reluctant to undergo a Br/Mg-exchange with previously known exchange reagents,[7b-d] were converted to the corresponding arylmagnesium alkoxides within 1-4 h at 25 °C in toluene. Their trapping with $MeSO_2SMe$, morpholino(phenyl) methanone[19] or dicyclopropyl ketone produced the polyfunctional aniline derivatives **6f-h** in 65-84% yield (25 °C, 1-2 h). 2-Bromonaphthalene (**4g**) was converted within 15 min to the Grignard reagent and its addition to a thienylaldehyde, led to the alcohol **6i** in 75% yield (25 °C, 1 h). Similar electron-rich aryl bromides such as **4h** and **4i** were converted to the Grignard reagents and were quenched with cyclohexanone or *N*-Benzylideneamine, leading to **6j** and **6k** in 75-91% yield (25 °C, 2 h). Finally, electron-poor aryl bromide **4j** underwent the Br/Mg-exchange at 25 °C within 15 min and gave, after quenching, **6l** in 72% yield (25 °C, 2 h). These results demonstrated, that arylmagnesium alkoxides of type **5** complexed with LiOR and TMEDA are superior nucleophiles, since they react smoothly with various ketones. The structure of the magnesium reagents **5** were tentatively proposed to be **A** (Scheme 2).

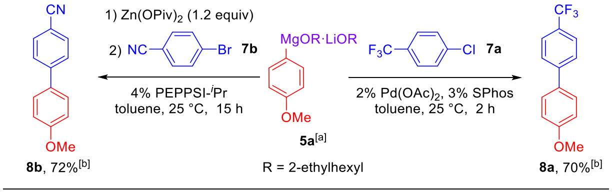
Furthermore, the Grignard reagents **5** (X = OR·LiOR·TMEDA) underwent a range of copper-catalyzed reactions such as acylations with various acyl chlorides in toluene leading to ketones **6o-6p** in 60-95% yield (10% CuI, 0 °C, 1 h; Scheme 4). Also, allylations of arylmagnesium alkoxides were realized at 25 °C with allylic bromides, providing products **6q-6s** in 89-92% yield. The opening of epoxides and aziridines with arylmagnesium reagents is also a challenging reaction, that often required Lewis acids or harsh reaction conditions.[20] We found, that epoxides or aziridines were opened under mild conditions (25 °C, 4-10 h), leading to the expected products **6t-6w** in 73-95% yield.



[a] TMEDA has been omitted for the sake of clarity. [b] Yield of analytically pure isolated product.

Scheme 3. Br/Mg-exchange for aryl bromides of type **4** leading, via intermediate organomagnesiums of type **5**, to functionalized arenes of type **6** in the presence of 10% CuI.

The arylmagnesium alkoxides of type **5** (X = OR·LiOR·TMEDA) also participate in Pd-catalyzed cross-couplings (Scheme 4).



[a] TMEDA has been omitted for the sake of clarity. [b] Yield of analytically pure isolated product.

Scheme 4. Cross-couplings of organomagnesium intermediate **5a**.

Thus, *p*-anisylmagnesium derivative (**5a**; X = OR·LiOR·TMEDA) underwent a Kumada cross-coupling[21] in the presence of 2% $Pd(OAc)_2$ and 3% SPhos[22] (25 °C, 2 h), producing the biphenyl **8a** in 70% yield. Transmetalation with $Zn(OPiv)_2$[23] in toluene led to a milky suspension which reacted with **7b** (25 °C, 15 h) via a Negishi cross-coupling using 4% of PEPPSI-^{i}Pr,[24,25] furnishing the desired product **8b** in 72% yield (Scheme 4). We also extended our method to the preparation of several heterocyclic magnesium alkoxides. Quenching with various electrophiles led to the desired products **11a-11g** in 60-75% yield. Interestingly, the treatment of 2,3,4,5-tetrachlorothiophene[26] (**9e**) with **1a** (2.4 equiv) led to a double Cl/Mg-exchange, providing a bis-

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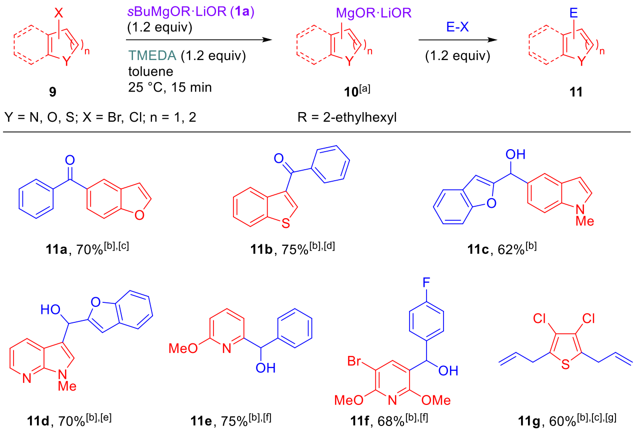
magnesium species, which after a copper-catalyzed allylation with allyl bromide, gave 2,5-bis-allylthiophene **11g** in 60% yield (Scheme 5).

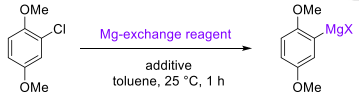


[a] TMEDA has been omitted for the sake of clarity. [b] Yield of analytically pure isolated product. [c] 10% CuI was added. [d] The reaction temperature was -10 °C. [e] The reaction time was 3 h. [f] The reaction time was 1 h at -30 °C [g] The reaction time was 4 h.

Scheme 5. Br/Mg-exchange for heteroaryl bromides and chlorides of type **9** leading, via intermediate organomagnesiums of type **10**, to functionalized heteroarenes of type **11**.

This excellent propensity of magnesium exchange reagent **1a** for undergoing Cl/Mg-exchanges led us to explore the scope of such an almost unknown Cl/Mg-exchange.[26] 2-Chloro-1,4-dimethoxybenzene (**12a**) was used as substrate and was submitted to various Grignard exchange reagents. We found that *i*PrMgCl·LiCl[7] or *s*Bu$_2$Mg·2LiCl[7b] did not react with **12a**, even in the presence of TMEDA or PMDTA (*N,N,N´,N´´,N´´*-pentamethyldiethylenetriamine).

Table 2. Cl/Mg-exchange on aryl chloride **12a** using various magnesium-exchange reagents.

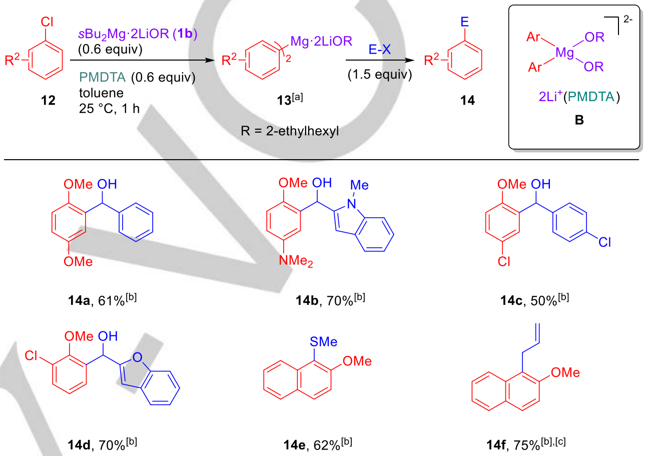


12a **13a**

entry	exchange reagent	equiv.	additive	yield (%)[a]
1	*i*PrMgCl·LiCl	1.2	PMDTA	0 [0][b]
2	*s*Bu$_2$Mg·2LiCl	0.6	PMDTA	0 [0][b]
3	*s*BuMgOR·LiOR (**1a**)	1.2	PMDTA	0 [0][b]
4	*s*Bu$_2$Mg·2LiOR (**1b**)	0.6	-	48
5	*s*Bu$_2$Mg·2LiOR (**1b**)	0.6	TMEDA	59
6	*s*Bu$_2$Mg·2LiOR(**1b**)	0.6	PMDTA	73 [20][c]

[a] Yield of **13a** determined by GC-analysis of water quenched reaction aliquots. [b] Yield obtained in the presence of TMEDA. [c] Yield obtained in THF.

Also, *s*BuMgOR·LiOR (**1a**, R = 2-ethylhexyl) gave no exchange under various conditions (Table 2, entries 1-3). After extensive experimentations, we found, that *s*Bu$_2$Mg·2LiOR (**1b**, 0.6 equiv) led to 48% of a Cl/Mg-exchange affording a bis-magnesium reagent of type **13** after 1 h reaction time at 25 °C (entry 4). The addition of TMEDA (0.6 equiv) improved the conversion to 59% and the addition of PMDTA (0.6 equiv) instead of TMEDA further increased the conversion to 75% yield (entries 5 and 6). The addition of benzaldehyde (1.5 equiv) led to the alcohol **14a** in 61% yield (25 °C, 1 h). This Cl/Mg-exchange was extended to a range of aryl chlorides bearing a methoxy group[27,28] in *ortho*-position. For all these substrates the Cl/Mg-exchange was completed within 1 h at 25 °C and produced a diarylmagnesium species **13** of tentative structure **B**. Quenching with various electrophiles (1.5 equiv) furnished the expected products **14b-14f** in 50-75% yield (Scheme 7).



[a] PMDTA has been omitted for the sake of clarity. [b] Yield of analytically pure isolated product. [c] 10% CuI was added.

Scheme 6. Cl/Mg-exchange for aryl chlorides of type **12** leading via intermediate organomagnesiums of type **13** to functionalized arenes of type **14**.

In conclusion, we have reported a method for preparing well soluble aryl and heteroaryl magnesium alkoxides complexed with one or two equivalents of lithium alkoxide, respectively, (LiOR; R = 2-ethylhexyl) in toluene using the new exchange reagents *s*BuMgOR·LiOR (**1a**) and *s*Bu$_2$Mg·2LiOR (**1b**).[29] These exchanges are ca. 30 times faster than the previous exchange reagent *s*Bu$_2$Mg·2LiCl[7b] and ca. 110 times faster than *i*PrMgCl·LiCl[7] (*turbo*-Grignard). Furthermore, the resulting Grignard reagent of type ArMgOR·LiOR (**5**) or HetArMgOR·LiOR (**10**) display an excellent reactivity in toluene adding well to ketones and opening epoxides and aziridines under mild conditions. Furthermore, *s*Bu$_2$Mg·2LiOR (**1b**) is able to trigger a Cl/Mg-exchange leading to diarylmagnesium species of the type **13** (ArMg$_2$·2LiOR). Further applications of these new aryl magnesium alkoxide reagents in toluene are currently studied in our laboratories.

Experimental Section

See Supporting Information.

Acknowledgements

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Keywords: Grignard reagent • halogen-magnesium exchange • lithium • magnesium • toluene

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[28] In the presence of a stronger directed metalation group (DMG) compared to MeO, the Cl/Mg-exchange proceeds faster (see SI; example **14g**).

[29] A patent application has been filed.

Entry for the Table of Contents (Please choose one layout)

Layout 2:

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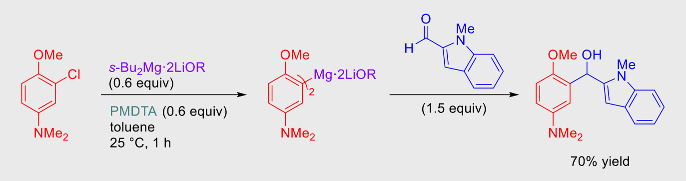

Grignard reagents in toluene: *s*BuMgOR·LiOR (R = 2-ethylhexyl) undergoes very fast Br/Mg exchanges producing aryl and heteroaryl magnesium alkoxides (ArMgOR·LiOR) in toluene (30-110 times faster than previous exchange reagents). Remarkably, these Grignard reagents react with a broad range of electrophiles. The related reagent *s*Bu$_2$Mg·2LiOR (R = 2-ethylhexyl) allows for the first time Cl/Mg-exchanges with aryl chlorides in toluene producing Ar$_2$Mg·2LiOR.

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