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COMMUNICATION

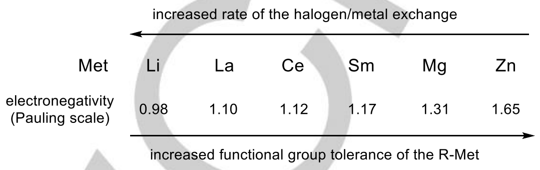
The Halogen-Samarium Exchange Reaction. Synthetic Applications and Kinetics

Lucile Anthore-Dalion+,a, Andreas D. Benischke+,a, Baosheng Wei+,a, Guillaume Berionni*b, Paul Knochel*,a

Fast I/Sm- and Br/Sm-exchanges take place when treating various aromatic or heterocyclic iodides and bromides with $n\text{Bu}_2\text{SmCl}\cdot4\text{LiCl}$ or $n\text{Bu}_3\text{Sm}\cdot5\text{LiCl}$ respectively. The resulting organosamarium reagents were efficiently quenched with aldehydes, ketones, and imines. Also, they undergo acylations when treated with *N*,*N*-dimethylamides leading to ketones. The rate of the Br/Sm-exchange on a typical aryl bromide was determined and showed that it was $8.5\cdot10^5$ faster than the Br/Mg-exchange, supporting that the rate of a metal-exchange is related to the ionic character of the carbon-metal bond and to the metal electronegativity.

Organometallics are key nucleophilic reagents for organic synthesis,[1] and their efficient preparation is an important synthetic task. Besides the oxidative addition[2] of a metal to an organic halide, the halogen-metal exchange reaction[3-5] is one of the most important synthetic routes to aryl and heteroaryl organometallics. The halogen/lithium-exchange[3] is certainly the most used in synthesis, however the functional group tolerance of aryllithiums is rather moderate.[4] As an alternative, the halogen/magnesium-exchange[5] is compatible with large number of functional groups, nevertheless this exchange reaction is considerably slower than the halogen/lithium exchange.[6] Further the iodine/zinc exchange proceeds at an even slower rate.[7] Besides ate-metal reagents such as manganates[8] and cuprates[9] undergo an exchange, but the atom economy[10] of these reactions is moderate.

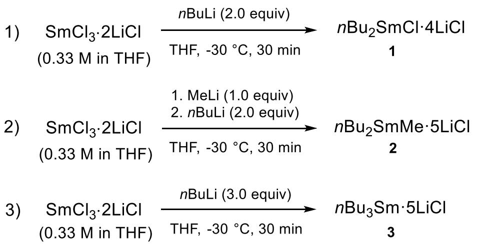
Recently, we have reported a new halogen/lanthanum exchange reaction and have found that this exchange is at least 10^6 faster than the halogen/magnesium exchange. Also the I/La- or Br/La-exchange displays a better functional group tolerance than the halogen/lithium exchange.[11] This led us to postulate that the rate of the halogen/metal exchange depends on the ionic character of the carbon-metal bond of the exchange reagent, and that the functional group compatibility also depends on this ionic character and therefore on the electronegativity[12] of the metal (Scheme 1).



Scheme 1. Relationship between the Pauling electronegativity[12] of the metal and the rate of the exchange reaction.

For proving this relation, we turned our attention to samarium which has an electronegativity of 1.17 compared to 1.10 for lanthanum and therefore we predicted that the halogen/samarium exchange should be slower than the halogen/lithium, the halogen/lanthanum and the halogen/cerium exchanges, and that the functional group tolerance of the resulting arylsamarium(III)-reagent should be better than those of the corresponding lanthanum(III)-reagents. Moreover, organosamarium reagents already proved their utility as nucleophiles, but only few preparation methods of these organometallics have been reported.[13] A halogen/samarium-exchange will then provide a new access to these reagents.

Herein, we report the preparation of halogen/samarium exchange reagents and their use for performing efficient I/Sm- and Br/Sm-exchanges. We describe also the reaction of these new aryl- and heteroarylsamarium reagents with various electrophiles and provide an approximate rate for the Br/Sm-exchange. Thus, we have first prepared $\text{SmCl}_3\cdot2\text{LiCl}$ starting from $\text{SmCl}_3\cdot6\text{H}_2\text{O}$ in analogy to the preparation of $\text{LaCl}_3\cdot2\text{LiCl}$.[14] Similar concentration of $\text{SmCl}_3\cdot2\text{LiCl}$ in THF (0.33M) was obtained. After extensive screening, we identified three useful exchange reagents with the tentative formulas $n\text{Bu}_2\text{SmCl}\cdot4\text{LiCl}$ (**1**), $n\text{Bu}_2\text{SmMe}\cdot5\text{LiCl}$ (**2**) and $n\text{Bu}_3\text{Sm}\cdot5\text{LiCl}$ (**3**) obtained by the reaction of $\text{SmCl}_3\cdot2\text{LiCl}$ with the appropriate amounts of *n*BuLi and MeLi (Scheme 2).



Scheme 2. Preparation of alkylsamarium reagents **1**, **2** and **3**.

First, $n\text{Bu}_2\text{SmCl}\cdot4\text{LiCl}$ (**1**) proved to undergo efficient exchange reactions with aryl iodide of type **4**.[15] Aryl iodides **4a-d** bearing fluorinated or chlorinated substituents were converted into the

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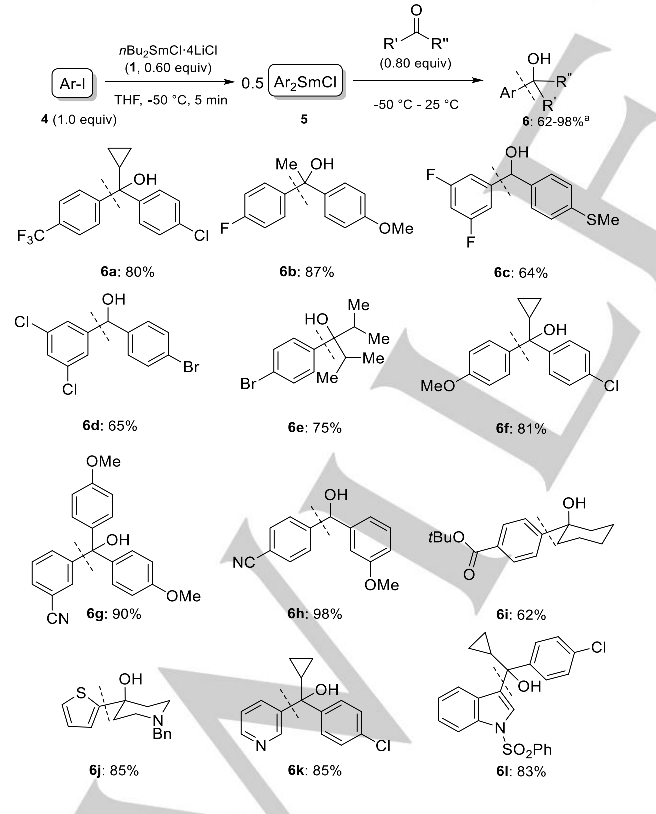
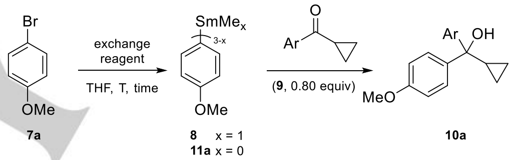
corresponding diarylsamarium chlorides **5a-d** within only 5 min at −50 °C in THF. Subsequent trapping reactions with carbonyl derivatives led to alcohols **6a-d** in 65-87% yield. Similarly, 1-bromo-4-iodobenzene (**4e**) underwent a selective I/Sm-exchange with *n*Bu$_2$SmCl·4LiCl (**1**, 0.60 equiv) under those conditions producing bis(4-bromophenyl)samarium(III) chloride (**5e**) in ca. 90% GC-yield, and its reaction with 2,4-dimethylpentan-3-one led to alcohol **6e** in 75% yield. Remarkably, no products resulting from a competitive Br/Sm-exchange was detected. Aryl iodides bearing electron-donating groups such as *p*-anisyl iodide (**4f**) also reacted under those conditions, to give after trapping with a ketone the tertiary alcohol **6f** in 81% yield. More sensitive groups such as nitriles or *tert*-butyl esters were also tolerated as exemplified by the reaction of 3-iodobenzonitrile (**4g**), 4-iodobenzonitrile (**4h**) and *t*-butyl 4-iodobenzoate (**4i**) which, after the I/Sm-exchange followed by trapping reactions with carbonyl derivatives, led to alcohols **6g-i** in 62-98% yield. The result with the iodo-ester derivative **4i** is particularly instructive, since such substituents were not tolerated in the case of the halogen-lanthanum exchange showing that organosamariums are compatible with more sensitive functional groups compared to the corresponding organolanthanum derivatives.[11] This observation is a strong argument in favor of a dependence of the functional group compatibility on the ionic character of the carbon-metal bond. Finally, 2-iodothiophene (**4j**) and 3-iodopyridine (**4k**) and indole (**4l**) reacted with *n*Bu$_2$SmCl·4LiCl (**1**, 0.60 equiv), furnishing diheteroarylsamarium derivatives **5j-l** which were further transformed into alcohols **6j-l** in 83-85% yield (Scheme 3).



Scheme 3. I/Sm-exchanges with aryl iodides and subsequent trappings. (a) Yields in our report are all calculated based on the amount of electrophile.

Then, we turned our attention to the Br/Sm-exchange involving the use of less expensive aryl bromides compared to aryl iodides. Whereas *n*Bu$_2$SmCl·4LiCl (**1**) was a suitable exchange reagent for I/Sm-exchange reactions, no Br/Sm-exchange with 4-bromoanisole (**7a**) took place under those conditions even after extended reaction time (Table 1, entry 1). In contrast, the mixed species *n*Bu$_2$SmMe·5LiCl (**2**, 0.70 equiv), inspired from our previous work on lanthanum,[11] reacted at −30 °C, leading to full conversion of 4-bromoanisole (**7a**) into the corresponding diaryl(methyl)samarium reagent **8** within 1 h. Subsequent reaction with ketone **9** provided the tertiary alcohol **10a** in 69% yield (Table 1, entry 2). Interestingly, we noticed that *n*Bu$_3$Sm·5LiCl (**3**) exchanged all its three butyl residues, whereas the related *n*Bu$_3$La·5LiCl was able to exchange only one butyl residue.[11a,c] Indeed, the exchange of *n*Bu$_3$Sm·5LiCl (**3**, 0.40 equiv) with **7a** led to full conversion into the corresponding triarylsamarium derivative **11a** within only 15 min at −30 °C. The trapping reaction with ketone **9** then furnished alcohol **10a** in 90% yield (Table 1, entry 3).[16] Interestingly, whereas the Br/La-exchange on **7a** was completed after less than 5 min at −50 °C,[11] the Br/Sm-exchange required 15 min at −30 °C, indicating a somewhat slower rate than the corresponding Br/La-exchange.[11]

Table 1. Optimization of alkylsamarium(III) species for Br/Sm-exchanges.

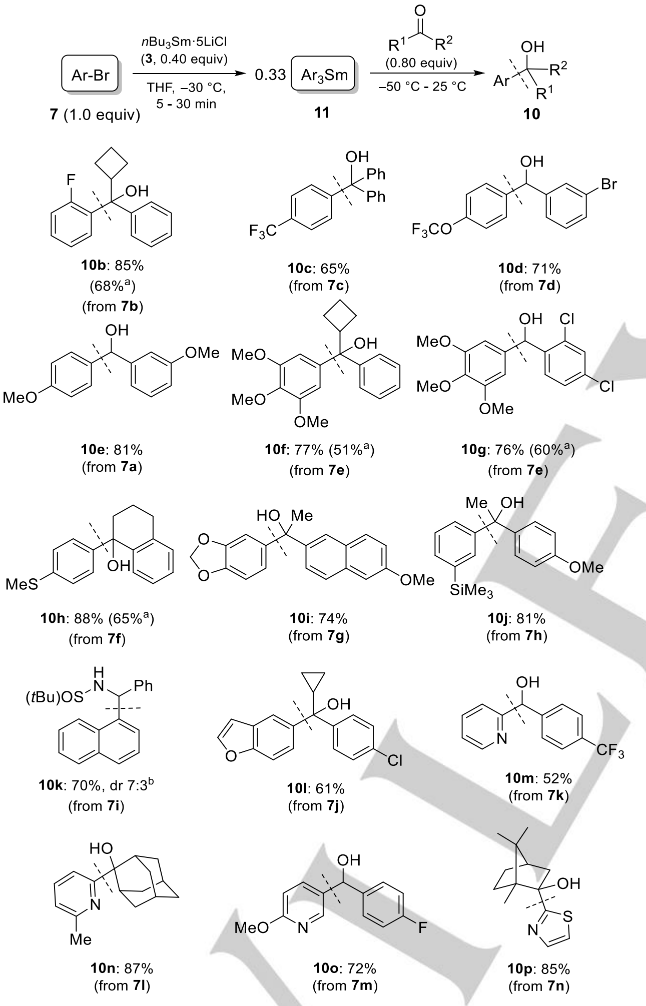


Entry	Exchange reagent	Conditions	Conversion of **7a** (%)	Yield (%)
1	*n*Bu$_2$SmCl·4LiCl (**1**, 0.6 equiv)	>1 h −50 °C	0	-
2	*n*Bu$_2$SmMe·5LiCl (**2**, 0.70 equiv)	1 h −30 °C	>95	69
3	*n*Bu$_3$Sm·5LiCl (**3**, 0.40 equiv)	15 min −30 °C	>95	90

Ar = 4-chlorophenyl

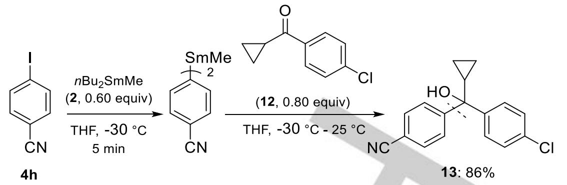
The exchange reagent *n*Bu$_3$Sm·5LiCl (**3**) was then used to explore the scope of the Br/Sm-exchange. First, 1-bromo-2-fluorobenzene (**7b**), underwent an exchange within 5 min at −30 °C, furnishing triarylsamarium derivative **11b**, and subsequent trapping with a ketone provided the tertiary alcohol **10b** in 85% yield. Interestingly,[11a] the same reaction with *n*BuLi led only to degradation of aryl bromide **7b**. Other fluorinated aryl bromides **7c-d** furnished the corresponding organosamarium compounds **11c-d**, and their reaction with a ketone or 3-bromobenzaldehyde, provided alcohols **10c-d** in 65-71% yield. Similarly, the exchange on electron-rich aryl bromides such as 4-bromoanisole (**7a**), 3,4,5-trimethoxybromobenzene (**7e**), 4-bromothioanisole (**7f**), 4-bromo-1,2-(methylenedioxy)benzene (**7g**) and 1-bromo-3-trimethylsilylbenzene (**7h**) with *n*Bu$_3$Sm·5LiCl (**3**, 0.40 equiv) proceeded efficiently to form triarylsamarium compounds **11a** and **11e-h**, although longer reaction times of up to 30 min were required. After trapping with aldehydes or ketones, alcohols **10e-j** were obtained in 74-88% yield. Ellman *tert*-butyl sufinamide reacted with *tris*(1-naphthyl)samarium (**11i**), resulting from the Br/Sm-exchange on 1-bromonaphthalene (**7i**), to furnish the amine derivative **10k** in 70% (dr=7:3). Finally, heteroaryl bromides **7j-m** underwent the Br/Sm-exchange providing tri(heteroaryl)samarium derivatives **11j-m**. These reacted with either ketones or aldehydes, and alcohols **10l-o** were obtained in 52-87% yields.

The difference of reactivity between $n\mathrm{Bu_2SmMe{\cdot}5LiCl}$ (**2**) and $n\mathrm{Bu_3Sm{\cdot}5LiCl}$ (**3**) already observed with 4-bromoanisole (**7a**) (Table 1) was confirmed in the case of substrates **7b,e-f**. Their reaction with **2** proceeded with 10-20% lower yields than with **3**. This difference is mainly explained by the formation of side-products when $n\mathrm{Bu_2SmMe{\cdot}5LiCl}$ (**2**) is used as exchange reagent, namely the Ar-Me coupling product as well as an alcohol resulting from the methyl attack onto the ketone (Scheme 4).



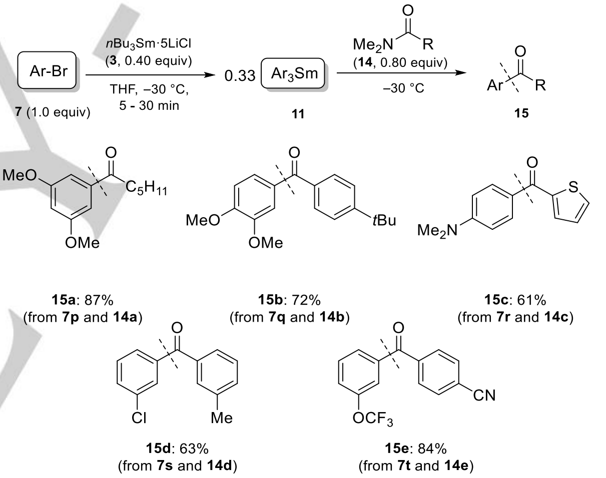
Scheme 4. Br/Sm-exchanges with aryl iodides and subsequent trapping reactions. (a) $n\mathrm{Bu_2SmMe{\cdot}5LiCl}$ (0.70 equiv) was used. (b) the corresponding Ellman *tert*-butyl sufinyl imine was used as trapping reagent.

Unfortunately, the Br/Sm-exchange was too slow compared to the corresponding I/Sm-exchange, to tolerate either nitriles or esters. Indeed, a faster I/Sm-exchange reaction on 4-iodobenzonitrile (**4h**) at −30 °C with $n\mathrm{Bu_2SmMe{\cdot}5LiCl}$ (**2**) was possible and led, after trapping with ketone **12** to the tertiary alcohol **13** in 86% yield (Scheme 5).



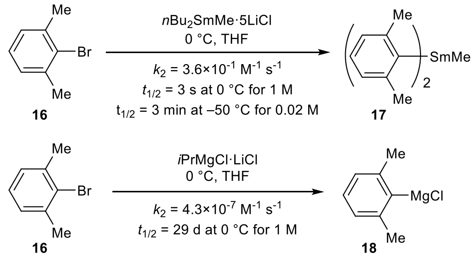
Scheme 5. I/Sm-exchange on 4-iodobenzonitrile (**4h**) with **2** at −30 °C

Finally, we wish to report the addition of triarylsamarium derivatives of type **11** on *N*,*N*-dimethylamides of type **14** led selectively to ketones of type **15**, with only trace amounts of the overaddition alcohol.[11,17] This acylation was applied to various aryl bromides and furnished, after Br/Sm-exchange followed by addition to benzamides **14a-d**, ketones **15a-d** in 61-87% yields. Interestingly, the reaction of *tris*(3-(trifluoromethoxy)phenyl)-samarium (**11f**), obtained *via* an exchange reaction of aryl bromide **7d** and $n\mathrm{Bu_3Sm{\cdot}5LiCl}$ (**3**), with 4-cyano-*N*,*N*-dimethylbenzamide (**14e**) led selectively to ketone **15e.** No addition on the nitrile group was detected (Scheme 6).



Scheme 6. Acylation of $\mathrm{Ar_3Sm}$ **13** with *N*,*N*-dimethylamides of type **14**.

These results indicated clearly that the Br/Sm-exchange is slower than the Br/La-exchange and confirm our intuition[18] that the rate of a halogen/metal-exchange is related to the ionic character of the carbon-metal bond (and therefore related to the metal electronegativity). To confirm this, we have quantitatively determined the rate of the Br/Sm-exchange reaction. Thus, absolute rate constant of Br/Sm-exchange reaction of 2,6-dimethylbromobenzene **16** with $n\mathrm{Bu_2SmMe{\cdot}5LiCl}$ **2** at 0 °C in THF (Scheme 7) was calculated with the Eyring equation by extrapolation of kinetic measurements performed between –40 and –60 °C (see the SI). The very small activation enthalpy $\Delta H^{\ddagger}$ of a few $\mathrm{kJ.mol^{-1}}$ indicated that the reaction is entropy-controlled.



Scheme 7. Comparison of the kinetics of Br/Sm and Br/Mg exchange reactions in THF at 0 °C for 1 M solutions of reagents.

Quantitative comparison with the second-order rate constant of Br/Mg exchange with the turbo-Grignard reagent *i*PrMgCl·LiCl with **16** (Scheme 7) revealed that the Br/Sm exchange proceeds 8.5 × 10^5 faster.[19] The Br/La exchange kinetics on **16** with the reagent *n*Bu_2LaMe·5LiCl could not previously be measured even in highly diluted solutions at -50°C because the exchange reaction proceeded in only a few seconds. The $t_{1/2}$ for Br/Sm-exchange on **16** is equal to 3 min under the same experimental conditions (Figure S1 in SI), which led us to the conclusion that the Br/La proceeds much faster (factor 10 or greater) than the Br/Sm exchange for which only the lower limit is known.

In summary, we have reported a new I/Sm- and Br/Sm-exchange reaction on various aryl and heteroaryl iodides and bromides. The resulting organosamarium reagents proved to be very useful organometallic intermediates adding efficiently to aldehydes and ketones and undergoing acylations with *N,N*-dimethylamides. Compared to the corresponding aryllanthanum reagents prepared by a related exchange reaction,[11a-b] a better functional group tolerance was observed, an ester or an pyridyl ring being tolerated. Furthermore, a kinetic study allowed us to determine the rate of the Br/Sm-exchange, confirming that it is considerably faster than the Br/Mg-exchange (8.5 × 10^5 faster) but somewhat slower than the Br/La-exchange. This clearly supports that the metal electronegativity is an important factor for predicting the rate of a halogen/metal exchange.

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Keywords: halogen-samarium exchange • samarium • kinetics • functionalized organometallics • lanthanides

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[15] The rate of the I/Sm-exchange is much faster than the rate of the Br/Sm-exchange, therefore the optimum reagents for both exchanges are different. A summary of all samarium reagents prepared and tested are included as Table S1 in the SI.

[16] For a comparison with arylcerium reagent, see Table S2 in the SI.

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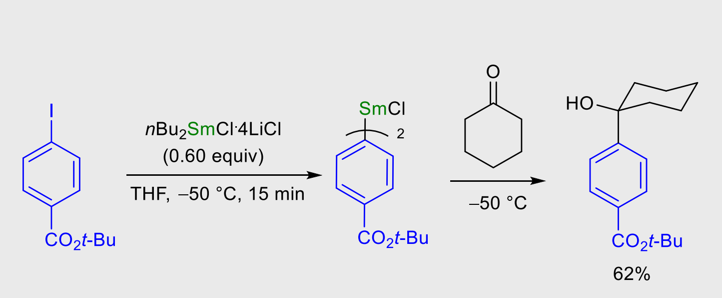

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The Halogen-Samarium Exchange Reaction. Synthetic Applications and Kinetics

Samarium stories. Aryl and heteroaryl iodides and bromides were converted to the corresponding samarium(III)-reagents *via* halogen-samarium exchanges using $n\mathrm{Bu_2SmCl}$ and $n\mathrm{Bu_3Sm}$ respectively. Remarkably, in contrast to the previously reported preparation of aryllanthanum species, samarium reagents tolerates more functional groups (such as an ester). This was explained by the higher electronegativity of samarium (compared to lanthanum) which leads to an organosamarium species with a less ionic carbon-metal bond. We found also that the Br/Sm-exchange is $8.5 \cdot 10^5$ faster than the Br/Mg-exchange.