Regioselective Metalations

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New In Situ Trapping Metalations of Functionalized Arenes and Heteroarenes with TMPLi in the Presence of $ZnCl_2$ and Other Metal Salts**

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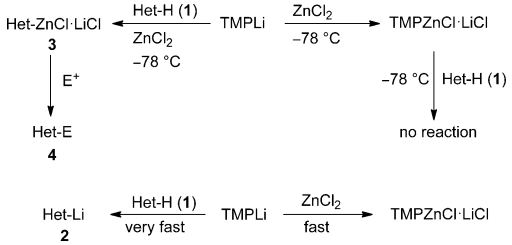
Abstract: *The addition of TMPLi to a mixture of an aromatic or heteroaromatic substrate with a metal salt such as $MgCl_2$, $ZnCl_2$, or CuCN at −78 °C first leads to lithiation of the arene followed by transmetalation with the metal salt to afford functionalized organometallic compounds of Mg, Zn, or Cu. This in situ trapping method allows an expedited metalation (−78 °C, 5 min) of a range of sensitive pyridines (bearing a nitro, ester, or cyano group) and allows the preparation of kinetic regioisomers of functionalized aromatic compounds or heterocycles not otherwise available by standard metalating agents, such as TMPMgCl·LiCl or TMPZnCl·LiCl.*

The lithiation of arenes and heteroarenes constitutes a powerful method[1] which is of great importance for various applications. TMPLi (TMP = 2,2,6,6-tetramethylpiperidyl)[2] has been used for the selective lithiation of arenes. Nevertheless, the scope of the lithiation of complex molecules with TMPLi is limited; highly reactive lithium derivatives are produced which often have little compatibility with sensitive functional groups (esters, cyano, or nitro groups), especially when attached to electron-deficient N heterocycles. A range of less-reactive bases of Mg and Zn have recently been developed to improve the reaction scope.[3] LiCl-complexed[4] metal amides, such as TMPMgCl·LiCl,[5] $TMP_2Mg{\cdot}2\,LiCl$,[6] TMPZnCl·LiCl,[7] and $TMP_2Zn{\cdot}2\,MgCl_2{\cdot}2\,LiCl$,[8] have proved to be especially useful.[9] Interestingly, it has been demonstrated that these powerful bases are compatible with several Lewis acids, which further increases their metalation scope.[10] Since lithium bases have been used in the presence of electrophiles such as boronic esters or Me_3SiCl (in situ trapping methods),[11] we envisioned metalations of functionalized N-heteroarenes and acceptor-substituted benzenes by the concomitant use of TMPLi and various metal salts such as $MgCl_2$, $ZnCl_2$, or CuCN. This new method would give a practical access to organometallic Mg, Zn, or Cu compounds.

The lithiation of functionalized carbocycles or heterocyclic arenes of type **1** with TMPLi would provide the unstable lithiated species **2**. The performance of this lithiation in the presence of $ZnCl_2$ (or $MgCl_2$ and CuCN) may result in an in situ trapping of the lithiated arene **2** to yield the zinc reagent **3**, which now has an excellent thermal stability and can be readily trapped with electrophiles, thereby leading to various products of type **4**. To be successful, such a method requires that the metalation of **1** with TMPLi is faster than the transmetalation of TMPLi to TMPZnCl·LiCl. It should be noted that TMPZnCl·LiCl is unreactive toward the metalation of **1** at −78 °C (Scheme 1). Herein, we report the realization of this in situ trapping method and demonstrate the advantages of this lithiation-transmetalation procedure for generating highly functionalized organozinc compounds that are otherwise difficult to prepare. We also show that these lithiations can be used to provide metalated intermediates with a different regioselectivity to the one produced with TMPZnCl·LiCl or $TMP_2Zn{\cdot}2\,LiCl$. This synthetic approach can be extended from $ZnCl_2$ to $MgCl_2$ or CuCN to produce valuable magnesium or copper intermediates.



Scheme 1. Reaction of a mixture of $ZnCl_2$ and an aromatic or a heterocyclic substrate **1** with TMPLi at −78 °C leads to zinc reagents of type **3** through a lithiation-transmetalation sequence.

First, we examined the metalation of 2,4-dichlorobenzonitrile (**1a**; Scheme 2). A calculation of the relative acidity of H3, H5, and H6 shows that H3 is about 10^6 times more acidic than H5 and H6.[12] Thus, the reaction of **1a** with a moderately powerful base such as TMPZnCl·LiCl only allows metalation at position 3, thus leading exclusively, after iodolysis, to the 3-iodinated benzonitrile **5a** in 78% yield.

Since the cyano group is a good *ortho*-directing group,[13] a kinetic metalation of **1a** at position 6 is expected when using

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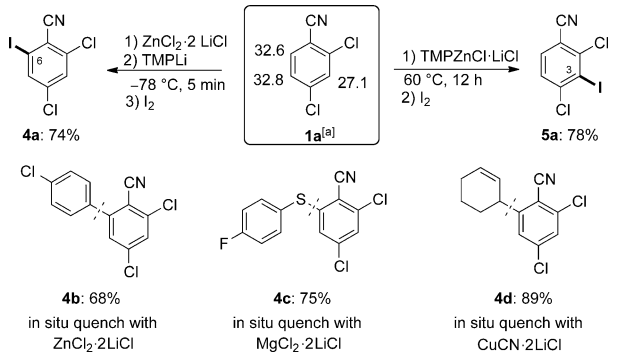
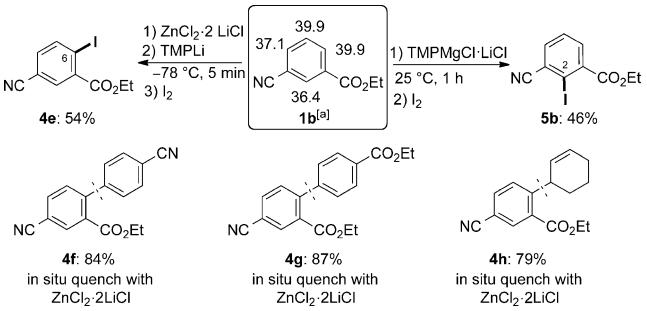


Scheme 2. Regioselectivity switch in the metalation of **1a** by TMPLi in the presence of metal salts or TMPZnCl·LiCl. [a] Calculated pK_a values for H3, H5, and H6.



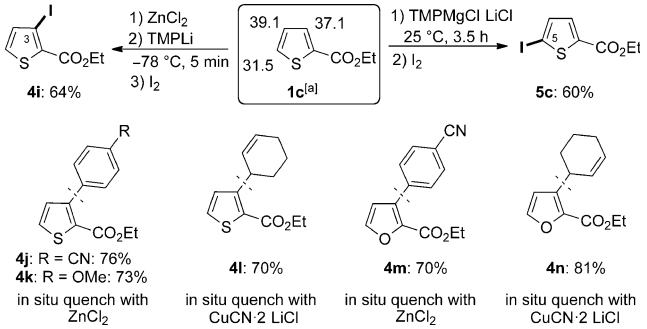
Scheme 3. Regioselectivity switch in the metalation of **1b** by TMPLi in the presence of metal salts or TMPMgCl·LiCl. [a] Calculated pK_a values for H2, H4, H5, and H6.

a very strong lithium base. Thus, a mixture of **1a** and $ZnCl_2$·2 LiCl (1.1 equiv) was treated with a solution of TMPLi (1.5 equiv, ca. 0.6 M) in THF at −78 °C. After 5 min, the metalation of **1a** is complete, and iodolysis furnishes the 6-iodobenzonitrile **4a** in 74 % yield. The complexation of $ZnCl_2$ with LiCl enhances the solubility and often increases the reaction yields by about 10–20 %. The regioselectivity of the metalation is excellent (ca. 95:5) and is complementary to the metalation with TMPZnCl·LiCl, which proceeds at position 3. Independently generated TMP_2Zn·2 LiCl or "$(TMP)_3ZnLi$·2 LiCl"[14] either does not metalate **1a** at −78 °C or metalates with low regioselectivity (C3/C6 = 4:1) and with only 29 % conversion after 10 min. Competition experiments show that the reaction of TMPLi with **1a** is more than six times faster than the reaction of TMPLi with $ZnCl_2$·2 LiCl (see the Supporting Information). Besides iodolysis, the resulting arylzinc compound derived from **1a** was submitted to a Negishi cross-coupling with 1-chloro-4-iodobenzene (0.9 equiv), which afforded the biphenyl **4b** in 68 % yield. All of the in situ trapping reactions favor the metalation at position 6.

Although this new in situ trapping is very satisfactory using $ZnCl_2$·2 LiCl, we have extended our method to the preparation of some other useful organometallic intermediates. Thus, mixing **1a** with $MgCl_2$·2 LiCl (1.1 equiv) and adding TMPLi (1.5 equiv, −78 °C, 5 min) produces the corresponding magnesium reagent, which on reaction with $ArSSO_2Ph$ (Ar = *p*-FC_6H_4) affords the thioether **4c** in 75 % yield. An in situ quench with CuCN·2 LiCl is also possible and produces valuable copper intermediates. Thus, performing the metalation of **1a** with TMPLi in the presence of CuCN·2 LiCl (1.1 equiv) provides the corresponding copper(I) intermediate, which reacts smoothly with 3-bromocyclohexene (0.9 equiv) to afford **4d** in 89 % yield.

Analogous switches of regioselectivity were observed for several aromatic systems. The calculated pK_a values of the different positions of ethyl 3-cyanobenzoate (**1b**) show that H2 is the most acidic proton (Scheme 3). A deprotonation with TMPMgCl·LiCl leads, after iodolysis, to the 2-iodinated ethyl benzoate **5b** in 46 % yield. Treatment of **1b** with TMPLi in the presence of $ZnCl_2$·2 LiCl allows lithiation at the sterically less hindered position, namely position 6, which is adjacent to the most powerful directing group (the ethyl ester moiety). The metalation of **1b** is complete after 5 min at −78 °C, and furnishes, after iodolysis, the aryl iodide **4e** accompanied by about 20 % of the iodide **5b**. These aryl iodides can be readily separated to provide the pure iodide **4e** in 54 % yield. The use of $ZnCl_2$·2 LiCl for the in situ trapping allows functionalization of position 6 by subsequent Negishi cross-coupling reactions; after chromatographic separation from small quantities of regioisomers, the pure 6-arylated products **4f** and **4g** were isolated in 84 and 87 % yield, respectively. Similarly, a CuCN·2 LiCl catalyzed allylation with 3-bromocyclohexene (0.7 equiv) provides the 3-cyanobenzoate **4h** in 79 % yield (Scheme 3).[15]

The new in situ quench procedure has also been applied to the metalation of heterocyclic ring positions, which are notoriously difficult to metalate. Thus, as expected, thiophene derivative **1c** undergoes a smooth magnesiation at position 5 with TMPMgCl·LiCl (Scheme 4). Metalation at this position



Scheme 4. Regioselectivity switch in the metalation of **1c** by TMPLi in the presence of metal salts or TMPMgCl·LiCl and metalation of **1d** with TMPLi in the presence of metal salts. [a] Calculated pK_a values for H3, H4, and H5.

is favored for thermodynamic reasons, since H5 is the most acidic hydrogen atom in the molecule. This high tendency to metalate position 5 can be overcome by an in situ quench with $ZnCl_2$ and TMPLi. The metalation of **1c** is complete within 5 min at −78 °C, thereby producing the C3-zincated thiophene as the major regioisomer (C3/C5 = 75:25). Interestingly, the complexation of $ZnCl_2$ with additional LiCl lowers this regioselectivity. After iodolysis, the thienyl iodide **4i** is

Table 1: Synthesis of products **7** by metalation with TMPLi in the presence of $MgCl_2$, $ZnCl_2$, or CuCN and quenching with electrophiles.

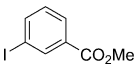
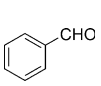
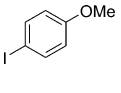
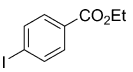
Entry	Substrate	Electrophile	Product[a]
1	**6a**	R = CO_2Me	**7a**: 90%[b,f]
2	**6a**	R = CF_3	**7b**: 77%[b,f]
3	**6a**	TMSCl	**7c**: 96%[c]
4	**6a**		**7d**: 96%[e]
5	**6b**		**7e**: 84%[b,f]
6	**6c**		**7f**: 79%[b,f]
7	**6d**		**7g**: 94%[d]
8	**6d**		**7h**: 86%[b,f]
9	**6d**		**7i**: 86%[e]
10	**6d**		**7j**: 94%[e]
11	**6e**	R = CF_3	**7k**: 80%[b,f]
12	**6e**	R = CN	**7l**: 70%[b,f]
13	**6f**	I_2	**7m**: 87%[c]

Table 1: (Continued)

Entry	Substrate	Electrophile	Product[a]
14	**6f**		**7n**: 80%[b,f]

[a] Yield of analytically pure product. [b] $ZnCl_2$·2 LiCl was added. [c] $MgCl_2$·2 LiCl was added. [d] $MgCl_2$ was added. [e] CuCN·2 LiCl was added. [f] Obtained by a palladium-catalyzed cross-coupling with 2% $[Pd(dba)_2]$ and 4% P(2-furyl)$_3$.

obtained in 64% yield. The addition of $ZnCl_2$ allows Negishi cross-coupling reactions with electron-poor iodides, such as 4-iodobenzonitrile, as well as electron-rich iodides, such as 4-iodoanisole, to give, after chromatographic separation, 2,3-disubstituted thiophenes **4j** and **4k** in yields of 76 and 73%, respectively. Performing the in situ trapping with CuCN·2 LiCl allows an allylation with 3-bromocyclohexene (0.7 equiv) to furnish **4l** in 70% yield.

In contrast, the corresponding furan derivative **1d** is always metalated predominantly at position 3. The use of the in situ quench procedure furnishes the 3-metalated furan with superior regioselectivity and higher conversion, and gives the 3-substituted furans **4m** and **4n** in yields of 70 and 81%, respectively, after allylation or cross-coupling (Scheme 4).

This in situ quench method also allows the smooth metalation of sensitive heterocycles. The direct magnesiation or lithiation of 2-chloro-3-cyanopyridine (**6a**) is difficult. Attempts to use TMPLi, TMP_2Mg·2 LiCl, or TMPMgCl·LiCl for deprotonation led to decomposition. Only TMP_2Zn·2 $MgCl_2$·2 LiCl allows the zincation of **6a** in 48 h at 25 °C in good yield. In contrast, metalation with TMPLi in the presence of $ZnCl_2$·2 LiCl allows the same zinc species to be prepared within 5 min at −78 °C.[16] Negishi cross-coupling with methyl 4-iodobenzoate or 1-iodo-4-(trifluoromethyl)-benzene led to the 4-arylated pyridines **7a** and **7b** in 90% and 77% yield, respectively (Table 1, entries 1 and 2). The use of TMPLi in the presence of $MgCl_2$·2 LiCl allows a smooth silylation of **6a** with TMSCl to provide pyridine **7c** in 96% yield (entry 3). An in situ quench using CuCN·2 LiCl furnishes, after allylation, pyridine **7d** in 96% yield (entry 4). In the case of other cyano-, ester-, nitro-, or thioether-substituted pyridines such as **6b**,[17] and **6c**–**6f**, the lithiated derivatives of which are prone to decomposition and have to be handled at low temperature, the in situ quench with $MgCl_2$·2 LiCl, $ZnCl_2$·2 LiCl, or CuCN·2 LiCl and TMPLi offers a simple preparative alternative and furnishes directly within 5 min the corresponding organometallic intermediates, which undergo additions to aldehydes, Negishi cross-coupling reactions, allylations, or acylations in 70–94% yield (entries 5–14).

In summary, the faster deprotonation of arenes and heteroarenes with TMPLi compared to the transmetalation of TMPLi with Mg, Zn, or Cu halides has allowed us to develop an in situ quench method, in which functionalized aromatic or heteroaromatic substrates mixed with Mg, Zn, or Cu halides have been metalated within 5 min by TMPLi at

−78 °C, and lead after transmetalation to various functionalized Mg, Zn, or Cu derivatives. The method allows a range of functionalized pyridines and related heterocycles to be metalated smoothly, more efficiently, and in higher yields than conventional metalations. In several cases, a different regioselectivity of the metalation is observed than in standard metalation procedures, thereby providing previously unaccessible organometallic reagents. The scale-up of this in situ trapping procedure through continuous flow reactions is currently being investigated as well as other extensions of the method.

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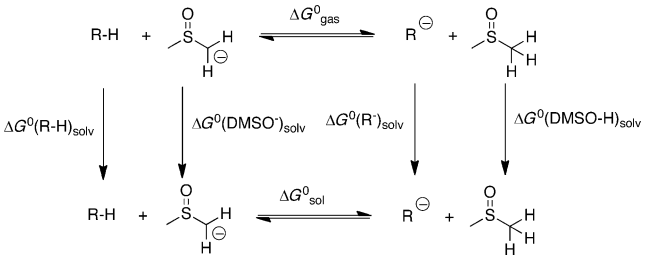
[12] C–H acidities have been calculated following the protocol proposed by Guo and co-workers,[18] which involves gas-phase free-energy calculations with the B3LYP hybrid functional in combination with the 6-311++G(2df,2p) basis set. Solvent effects were then determined through single-point calculations with the SMD continuum solvation model[20] for DMSO in combination with B3LYP/6-31G(d) theory. The best fit for a reference dataset with known pK_a values and hence the most reliable results were obtained using DMSO as reference with pK_a = +35.1.[19] Since almost all organometallic transformations are performed in THF solution, the obtained pK_a values in DMSO have been corrected to THF using Streitwieser's linear correlation[21] (see the Supporting Information). The thermochemical cycle for the pK_a calculation of a hydrocarbon R–H using DMSO anion as the reference base in DMSO solution is shown below:



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[15] The regioselectivity depends somewhat on the metal salt as well as on the electrophile used for the in situ quench; see the Supporting Information.

[16] ^{13}C NMR experiments showed the same zinc species for both experiments. For details see the Supporting Information.
[17] The use of TMPLi in the presence of $MgCl_2$ and quenching with iodine gives 2-cyano-3-iodopyridine in 72% yield; alternatively the use of TMPLi at −78°C and quenching with iodine gives a 53% yield of the product: T. Cailly, F. Fabis, S. Lemaître, A. Bouillon, S. Rault, *Tetrahedron Lett.* **2005**, *46*, 135.
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