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A practical *ortho*-rearrangement of silyl group of *ortho*-bromophenyl silyl ethers using magnesium(0)

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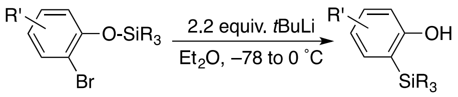
ABSTRACT

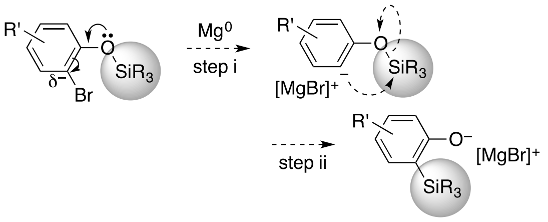
A practical synthesis of *ortho*-silyl-substituted phenol from *ortho*-bromophenyl silyl ethers without using RLi is described. Various *ortho*-bromophenyl silyl ethers are treated with commercially available Mg turnings, which are easy to handle in air, and transfer of the silyl group to the *ortho*-position occurs in good to high yields. Selective mono-magnesiation of 2,6-dibromophenyl silyl ether is observed even in the presence of excess Mg, and *ortho*-bromo-6-silylphenol is obtained as the predominant product. The obtained *ortho*-silyl-substituted phenol is formylated with $(CH_2O)_2/MgCl_2/Et_3N$, and then condensation with a diamine leads to a silyl-substituted salen-type ligand in a good yield. This scheme is suitable for the large scale synthesis of silyl-substituted salen-type ligands bearing imine groups.

Development of useful catalysts for novel and selective transformations has been an important topic over the past several decades, and one of the most successful prototypes is a family of salen–metal complexes. A variety of efficient processes by them including Al,[1] Cr,[2] Mn,[3] Ru,[4] Co,[5] Ti,[6] Fe,[7] Zr,[8] etc., has been developed. Bulky substituents on aromatic rings are required in some cases to secure desirable functions such as controlled reactivity, regio-, stereo-, and enantioselectivities, and some reports introduced bulky silyl-substituents on salen ligands.[9] Phenols with an *ortho*-silyl-substituent are precursors for the synthesis of silyl-substituted salen ligands and are efficiently synthesized from *ortho*-bromophenyl silyl ether by *ortho*-lithiation generally using RLi via the *retro*-Brook rearrangement.[10] *n*BuLi (~1.1 equiv.) at 0 ˚C is used in some cases, but the most general procedure is using *t*BuLi (~2.2 equiv.) from –78 to 0 ˚C because of its high applicability of the substrates (eq. 1). Although the method is clean, convenient, and suitable for lab-scale synthesis, it is not practical to apply to scale-up syntheses due to the high costs of the expensive reagents and also of the harsh reaction conditions at –78 ˚C as well as the pyrophoric nature of *t*BuLi. Na^0 was also used for this purpose,[11] while Na^0 is still reactive toward moisture and O_2 in air. We now report a practical *ortho*-silyl-rearrangement of *ortho*-bromophenyl silyl ethers using commercially available and generally air-stable Mg at/over rt.



(eq. 1)

Mg is rather inexpensive and generally easy to handle in air due to a thin layer of impermeable MgO.[12] The Grignard reagent obtained from the reaction of Mg^0 with R–X or Ar–X (X = Cl, Br, or I) has arguably been one of the most useful and versatile anionic reagents over the past century. However, there are no reports in which the *retro*-Brook rearrangement of *ortho*-halophenyl silyl ethers was systematically examined via Grignard reagent-formation to the best of our knowledge.[13] Considering the values of the standard electrode potentials (SEPs) of Li^+/Li^0, Na^+/Na^0 and Mg^{2+}/Mg^0 (E^0_{Li} = –3.04 V; E^0_{Na} = –2.71 V; E^0_{Mg} = –2.37 V),[14] we expected that the *ortho*-silyl rearrangement could proceed via the *ortho*-magnesiation of the *ortho*-halophenyl silyl ethers. At this point, there are two issues to be considered (Scheme 1): (i) the higher SEP value of Mg^0 may be insufficient for reduction of the electron-rich Ar–Br to form Ar^- $[MgBr]^+$,[15] especially with a bulky and electron-donating *ortho*-R_3SiO-substituent (step i) and (ii) the lower nucleophilicity of RMgX than that of RLi may cause a poor yield for the R_3Si-transfer reaction (step ii).



Scheme 1. Two possible issues for *ortho*-R_3Si rearrangement using Mg^0

We examined a typical reaction of *ortho*-halophenyl *tert*-butyldimethylsilyl (TBS) ether with Mg^0 (1.3 equiv.) in THF. To our delight, the reaction proceeded in good yield in either case as expected (eq 2).