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# Completion of a catalytic cycle of zirconium-catalyzed alkylation of silanes by addition of organic halides

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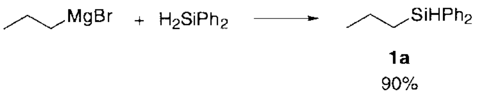
**A catalytic cycle in zirconium-catalyzed alkylation of silanes with secondary Grignard reagents was completed by addition of organic halides which were not incorporated in the products.**

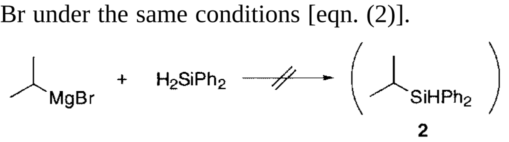
We have found and reported catalytic cycles containing a Zr(II) species and zirconacycles in carbon–carbon bond formation by the reaction of olefins and/or acetylenes with Grignard reagents.[1–5] One principle of the Zr(II)-mediated or -catalyzed reactions is the use of facile interchange of its oxidation states, II and IV. The zirconium(II) species is known to be of good $\pi$-electron accepting ability and oxidatively couples two unsaturated organic molecules. During the coupling reaction, the Zr(II) species is converted into Zr(IV). On these bases, zirconium(II)-catalyzed reactions have been developed involving olefins[1–4] and, in some cases, acetylenes.[5] We also reported not only unsaturated substrates but also dihydrogen[2] or silanes[3] as partners of unsaturated compounds such as olefins. During our investigations of zirconium-mediated alkylation reactions of silanes, we found that addition of organic halides led to a catalytic cycle in which the organic halides were not incorporated in the products. Herein, we report a novel type of catalytic cycle in alkylation of silanes with secondary Grignard reagents using zirconium.

It is well known that when $H_2SiPh_2$ is treated with $Pr^nMgBr$ in THF at room temperature, a nearly quantitative yield of $Pr^nSi(H)Ph_2$ **1** is obtained [eqn. (1)].[6] It is interesting that



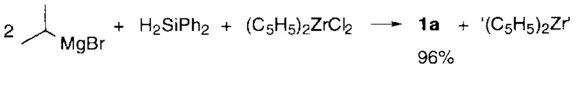
(1)

$H_2SiPh_2$ does not react at all with the more sterically hindered $Pr^iMgBr$ under the same conditions [eqn. (2)].



(2)

However, we found that when a stoichiometric amount of $(C_5H_5)_2ZrCl_2$ was added in the presence of a two-fold amount of $Pr^iMgBr$, the reaction of $H_2SiPh_2$ with $Pr^iMgBr$ proceeded to give **1a**, instead of the expected product $Pr^iSi(H)Ph_2$ **2** [eqn. (3)]. A stoichiometric amount of $(C_5H_5)_2ZrCl_2$ is required

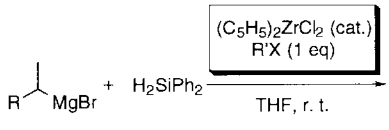


(3)

since the outcome of the reaction is explained by the total conversion to **1a**, '$(C_5H_5)_2Zr$,' $n$-$C_3H_8$ and 2 equiv. of $MgX_2$. Since the $Pr^i$ group was changed to an $Pr^n$ group in the product, it is reasonable to consider that the $Pr^i$ group is converted into propene on zirconium and then reacts with silane to afford $Pr^nSi(H)Ph_2$ and the Zr(II) species.

In order to extend this stoichiometric reaction to a catalytic reaction, oxidation of the built-up Zr(II) species was investigated. We found that certain organic halides were suitable for oxidation of the '$(C_5H_5)_2Zr$' species *via* oxidative addition[7–9] and tolerate the reaction conditions.

Under catalytic conditions, typically 10 mol% of $(C_5H_5)_2ZrCl_2$ and 1 equiv. of an organic halide were employed [eqn. (4)]. The results of a comparison study using various



(4)

organic halides as additives are shown in Table 1 As a control experiment, when no organic halide was added, the reaction gave only 22% yield of $Pr^nSiHPh_2$ **1a**. When 1 equiv. of bromo- or iodo-propane was added, the desired product was obtained in 67 and 91% yield, respectively. This remarkable improvement clearly showed that a catalytic cycle was achieved. The best result of 99% yield was obtained when 1,3-dibromopropane was used as the additive. Though bromobenzene, bromopropane and iodopropane showed fairly good performances, iodobenzene showed a very poor effect on this reaction, which may be due to the readily occurring deiodination.[9] 1,3-Dibromopropane was the best choice by far as additive and the reaction proceeded with as little as 2 mol% of the catalyst. In the absence of $(C_5H_5)_2ZrCl_2$ **1a** was not formed.

Similarly, when $H_2SiPh_2$ was treated under the same conditions with 2 equiv. of $Bu^sMgCl$, $Bu^nSiHPh_2$ **1b** was obtained in 89% yield. In spite of our attempts, tertiary Grignard reagents such as $Bu^tMgCl$ or secondary Grignard reagents such as cyclohexylmagnesium bromide did not successfully promote this reaction owing, probably, to the instability of the corresponding disubstituted-olefin zirconium complexes.

To understand the role and the superiority of 1,3-dibromopropane, 2-benzyl-1,3-dibromopropane **3** was used as an

**Table 1** Reactions of $Pr^iMgBr$ with $H_2SiPh_2$ in the presence of a catalytic amount of $(C_5H_5)_2ZrCl_2$ and various organic halides[a,b]

| Entry | R′X | $Cp_2ZrCl_2$/eq | Time/h | Yield (%)[c] |
|---|---|---|---|---|
| 1 | — | 0.1 | 24 | 22 |
| 2 | 1-Bromopropane | 0.1 | 6 | 67 |
| 3 | 1-Iodopropane | 0.1 | 6 | 91 |
| 4 | 1,3-Dibromopropane | 0.1 | 3 | 99 |
| 5 | 1,3-Dibromopropane | 0.02 | 24 | 93 |
| 6 | 1,3-Dibromopropane | 0.01 | 18 | 41 |
| 7 | 1,3-Diiodopropane | 0.1 | 3 | 3 |
| 8 | Bromobenzene | 0.1 | 6 | 78 |
| 9 | Iodobenzene | 0.1 | 1 | 2[d] |
| 10 | 2-Bromopropene | 0.1 | 24 | 73 |

[a] R = Me, corresponding to eqn. (4). [b] Typical reaction conditions: $H_2SiPh_2$ (0.5 mmol), $(C_5H_5)_2ZrCl_2$ (as indicated), $Pr^iMgBr$ (1.5 mmol), R′X (0.5 mmol); room temp. [c] Yields were determined by GC. [d] PhI was consumed in 1 h and further reaction did not proceed.

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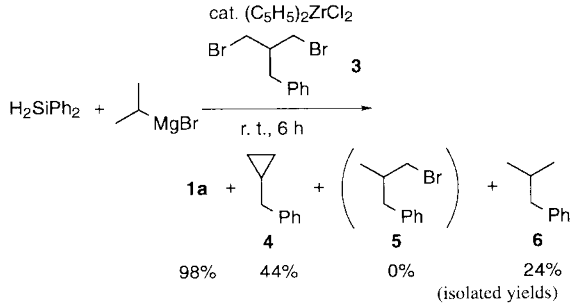
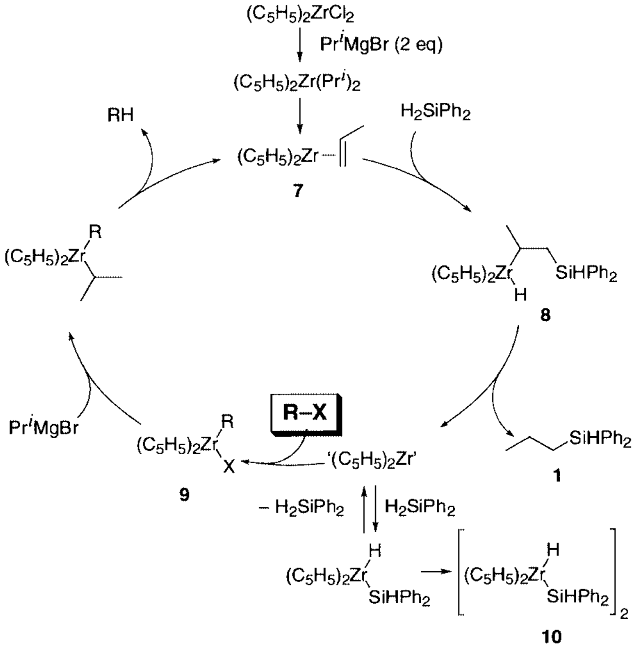
oxidation reagent and the catalytic reaction was carried out [eqn. (5)]. A mixture of three products, benzylcyclopropane **4** and reduction products **5** and **6** were obtained with **5** observed at an early stage. After completion of the reaction, two products, **4** and **6** were obtained in 44 and 24% yields, respectively. The formation of the major product **4** is explained by an oxidative addition of one carbon–bromine bond of **3** to the zirconium(II) species, followed by nucleophilic ring closure forming a cyclopropane ring and $(C_5H_5)_2ZrBr_2$.



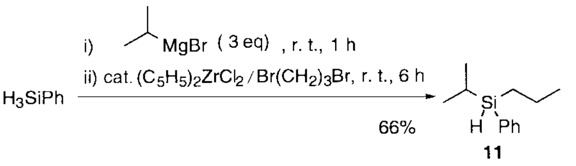
(5)

On the basis of these observations, the mechanism of Scheme 1 is proposed. Zirconium–olefin complex **7** is formed and reacts with $H_2SiPh_2$ (**7** ⟶ **8**). Reductive elimination of the silylated compound gives $Pr^nSiHPh_2$ **1**. The so-formed '$(C_5H_5)_2Zr$' reacts with an alkyl bromide (RX) to give **9**,[7] followed by ligand exchange with $Pr^iMgBr$ and β-hydride elimination to regenerate $(C_5H_5)_2Zr(C_3H_6)$ **7**. Alternatively, oxidation of '$(C_5H_5)_2Zr$' with alkyl bromides might afford $(C_5H_5)_2ZrX_2$ which is also converted into **7** by the reaction with $Pr^iMgBr$. An alkyl bromide plays an important role in reoxidizing the zirconium(II) species to zirconium(IV). In its absence, regeneration of the catalyst does not occur and '$(C_5H_5)_2Zr$' reacts with $H_2SiPh_2$ leading to the μ-hydride bridged dimer **10**.[3a]



**Scheme 1**

One-pot reaction of $H_3SiPh$ with 3 $Pr^iMgBr$ without a catalyst for 1 h followed by the addition of 10 mol% of $(C_5H_5)_2ZrCl_2$ and 1,3-dibromopropane selectively afforded $HSi(Pr^i)(Pr^n)Ph$ **11** in 66% yield [eqn. (6)]. An $Pr^i$ group was incorporated directly from the Grignard reagent in the absence of the catalyst, and an $Pr^n$ group was incorporated after the addition of the zirconium catalyst with 1,3-dibromopropane.



(6)

We conclude that a zirconium(II) species is efficiently oxidized by organic halides, which assists regeneration of the active catalyst. We believe this is the first example of a zirconium(II)-catalyzed reaction in which an oxidant is explicitly added to complete the catalytic cycle. Further studies to clarify the mechanism are in progress.

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