



Nickel-catalyzed hydrodehalogenation of aryl halides

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ABSTRACT

In the present study, the nickel-catalyzed dehalogenation of aryl and alkyl halides with *iso*-propyl zinc bromide or *tert*-butylmagnesium chloride has been examined in detail. With a straightforward nickel complex as pre-catalyst good to excellent yields and chemoselectivities were feasible for a variety of aryl and alkyl halides.

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1. Introduction

The transformation of carbon–halogen to carbon–hydrogen bonds is of importance for organic synthesis as well as industry [1]. Especially, the conversion of chlorinated arenes is a central matter, due to the negative impact of such chlorinated compounds (e.g., persistent organic pollutants) on the environment and human health [2]. On the other hand halides have been applied as protecting and directing groups in organic synthesis (Fig. 1) [3]. Commonly, after the halide functionalities have fulfilled their obligations a removal is needed to create the final product [2a,4]. Based on this issues efficient and straightforward hydrodehalogenation reactions are highly requested. Until now numerous methodologies have been reported for the hydrodehalogenation of aryl and alkyl halides [5,6]. In this regard, excellent performances have been exhibited by the application of metal-based catalysts. For instance various homogeneous and heterogeneous nickel catalysts in combination with hydrogen sources (e.g., borohydride, alkoxides, NaH) have been demonstrated for an efficient removal of halide functions under mild reaction conditions [6,7]. Especially, nickel complexes modified by N-heterocyclic carbenes (NHCs) or phosphanes have been proven to catalyze such transformations [6,7].

Recently, we have studied the nickel-catalyzed cross coupling of aryl halides with organometallic zinc reagents (Fig. 2) [8]. As

pre-catalysts the well-defined nickel complexes **1** and **2** have been found to be active in supporting this transformation. Interestingly, in case of *iso*-propyl zinc bromide as reagent to some extent dehalogenation processes have been observed. Based on that, we report herein our studies on the nickel-catalyzed dehalogenation of organic halides applying organometallic zinc and Grignard reagents.

2. Results and discussion

The 1-benzoyl-5-hydroxypyrazoline ligand **5** was synthesized in accordance to the procedure reported in the literature (Scheme 1) [8a,b,9]. Benzohydrazide (**4**) was reacted with equimolar amounts of 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (**3**) and refluxed for 24 h in ethanol. After work-up the desired ligand **5** was obtained as colorless crystalline compound. Interestingly, the condensation reaction was highly selective, while the isomer with the trifluoromethyl function next to the hydroxyl group was not isolated. With this ligand in hand we examined the coordination to nickel salts (Scheme 1). In agreement to our previously established protocol a methanol solution of the ligand and an excess of triphenylphosphane (2.0 equiv.) was added to a solution of Ni(OAc)₂·4H₂O in methanol at room temperature [8b]. After stirring overnight, all volatiles were removed to obtain a brown powder, which was extracted with ethanol and purified by crystallization to obtain brown crystals. Crystals suitable for X-ray measurements were grown from ethanol by slow evaporation of the solvent at room temperature. The solid-state structure of complex **6** has been

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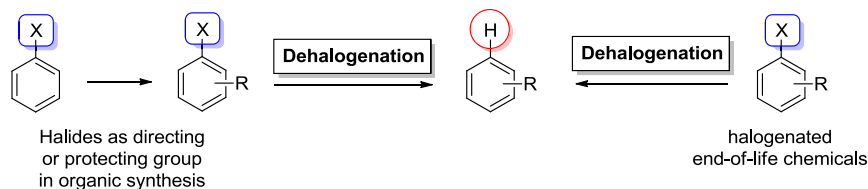


Fig. 1. Reasons for dehalogenation reactions.

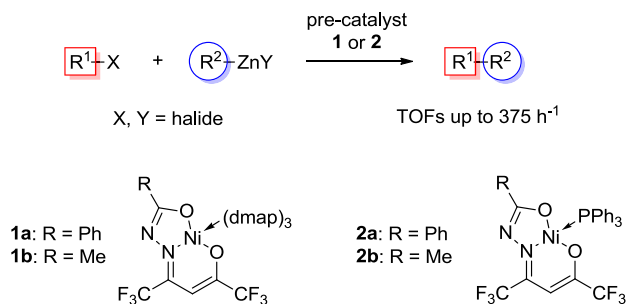


Fig. 2. Application of complexes **1** and **2** in cross coupling reactions (DMAP = 4-dimethylamino pyridine).

characterized by single crystal X-ray diffraction analysis. Thermal ellipsoid plots selected bond lengths and angles are shown in Fig. 3. The tridentate ligand is coordinated in a *O,N,O'*-mode creating a five-membered as well as a six-membered ring system and therefore shielding one side of the metal. The triphenylphosphane ligand is *cis*-positioned to the oxygen donors, while the nitrogen of the 5-hydroxypyrazoline ligand is connected to the nickel centre in the *trans*-position. A similar square planar motif was observed by Joshi and co-workers and more recently by us when applying ammonia instead of triphenylphosphane as additional ligand, while with DMAP an octahedral structure was achieved [8b,10,11]. The Ni–N1, Ni–O1, and Ni–O2 bond lengths are found in a similar range of those observed in nickel (II) complexes having the same coordinating atoms.

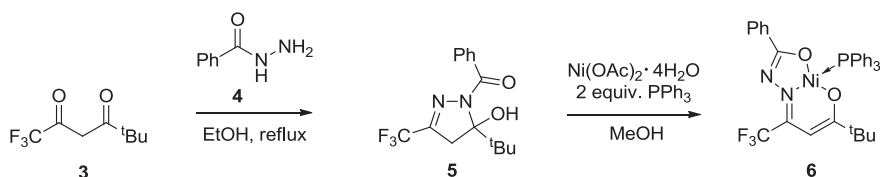
Initially, the dehalogenation of 4-iodoanisole (**7**) with ¹PrZnBr in THF was studied as a model reaction to explore appropriate conditions and to examine the influence of various reaction parameters (Table 1). As expected when performing the reaction in the absence of nickel complexes no product formation was monitored (Table 1, entry 1). However, when applying 5.0 mol% of **6** full conversion was realized after 24 h at 70 °C (Table 1, entry 2). The dehalogenated product **7a** was obtained in 87% yield, while as side product the homocoupling product 4,4'-dimethoxy biphenyl was detected.

Noteworthy, the coupling of **7** with ¹PrZnBr to form 4-isopropylanisole was not noticed. In addition, the complexes **1a** and **2a** were tested as dehalogenation pre-catalysts (Table 1, entries 3 and 4). Only in case of **2a** product formation (40%) was observed along with 7% heterocoupling. Probably, the electron-withdrawing effects of two CF₃ groups reduce the catalytic abilities of the complex, while with the ^tBu group in complex **6** a more basic metal

center is formed. Moreover, the benefit of the triphenylphosphane ligand in **2a** and **6** in comparison to the DMAP ligand can be the easier dissociation to create a more active complex as shown in earlier NMR studies [8]. Besides, the loading of the pre-catalyst was decreased to 2.5 mol%, resulting in a diminish of product **7a** (68%) (Table 1, entry 5). Additionally, the influence of the reaction temperature was studied. Here, the amount of **7a** is decreased at lower temperature (40 °C: yield 66%) (Table 1, entry 6).

Once the optimized reaction conditions were established, the scope and limitations of the nickel-catalyzed dehalogenation of aryl halides applying ¹PrZnBr as reagent were investigated. A number of aryl halides with various functional groups were converted (Table 2). In order to study the influence of the leaving halide function 4-bromo- (**8**) and 4-chloroanisole (**9**) were reacted with ¹PrZnBr demonstrating excellent yields of >99% after 24 h at 70 °C (Table 2, entries 1–3). In case of the bromobenzonitrile (**11**) the desired product was obtained in low yields along with benzene as side product, which is formed by removing the nitrile function under described conditions (Table 2, entry 5). In contrast, better results were realized for substrates containing ester, amino, and thioether functions (Table 2, entries 6–8). Noteworthy, thioanisole (**14a**) was obtained in 87%, while as minor product benzene was monitored. Furthermore, 1-bromo-4-chlorobenzene (**16**) was dehalogenated to the corresponding chlorobenzene (Table 2, entry 10). However, due to the excess of ¹PrZnBr the produced chlorobenzene was to some extent converted to benzene.

More recently the group of Glorius studied the nickel-catalyzed cross coupling of aryl bromides with tertiary Grignard reagents [7f]. Along with the desired coupling products to some extent dehalogenation was observed. In addition, in their recent work Jacobi von Wangelin and co-workers showed the efficient iron-catalyzed dehalogenation of aryl and alkyl halides applying Grignard reagents [5a]. Based on that, we studied the potential of *tert*-butylmagnesium chloride as dehalogenation reagent instead of ¹PrZnBr under same conditions (Table 3). Interestingly, in the absence of complex **6** aryl iodides were dehalogenated in good to excellent yields, probably via an iodine magnesium exchange and subsequent hydrolysis under work-up conditions (Table 3, entries 1 and 4). In contrast, for the dehalogenation of 4-bromo (**8**) and 4-chloroanisole (**9**) the presence of **6** was required to realize the product formation (Table 3, entries 2–3). Noteworthy, in various cases the corresponding homocoupling and cross coupling products were detected [12]. In comparison to ¹PrZnBr higher yields were obtained. For instance the substrates containing nitrile or ester functions were converted in good yields at room temperature



Scheme 1. Synthesis of the nickel complex **6**.

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