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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

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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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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)<sub>2</sub>·4H<sub>2</sub>O 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 fivemembered 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 5hydroxypyrazoline 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 <sup>i</sup>PrZnBr 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 <sup>i</sup>PrZnBr to form 4isopropylanisole 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 CF<sub>3</sub> groups reduce the catalytic abilities of the complex, while with the <sup>t</sup>Bu 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 <sup>i</sup>PrZnBr 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  $^{
m i}$ PrZnBr demonstrating excellent yields of >99% after 24 h at 70  $^{\circ}$ 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 <sup>i</sup>PrZnBr the produced chlorobenzene was to some extend converted to benzene.

More recently the group of Glorius studied the nickel-catalyzed cross coupling of arvl bromides with tertiary Grignard reagents [7f]. Along with the desired coupling products to some extend 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 <sup>1</sup>PrZnBr 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 <sup>i</sup>PrZnBr 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.



**Fig. 3.** Molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–N1: 1.8513 (19), Ni2–N3: 1.8487(18), Ni1–O1: 1.8453(15), Ni2–O4 1.8375(16), Ni1–O2: 1.8229 (15), Ni2–O3: 1.8297(15), Ni1–P1: 2.2419(7), Ni2–P2: 2.2304(6), O1–Ni1–O2: 176.61(7), O3–Ni2–O4: 176.80(7), N1–Ni1–P1: 174.74(6), N3–Ni2–P2: 174.74(6).

(Table 3, entries 5 and 6). Importantly, for the substrates containing nitrile and thioether functions to some extend the hydrodecyanation or hydrodesulfurization was observed as side reaction (Table 3, entries 5 and 8). Probably the C-CN or C-S bond is activated by coordination to the nickel center [13]. Interestingly, the application of bromobenzene- $d_5$  (**19**) as substrate showed an excellent selectivity of the catalyst for the carbon halogen bond, while no scrambling of the deuterium atoms was noticed (Table 3, entry 9). Moreover, to some extent defluorination was performed with the described system (Table 3, entries 16 and 17). Furthermore, alkyl based halides were dehalogenated (Table 3, entries 18 and 20).

For studying the influence of the leaving group a mixture of 4-iodoanisole (**7**), 4-bromoanisole (**8**), 4-chloroanisole (**9**), and 4-fluoroanisole (**25**) was reacted with stepwise increasing amounts of *tert*-butylmagnesium chloride in the presence of pre-catalyst **2a** (Fig. 4). The obtained results are in accordance to the bond dissociation energies of the leaving groups:  $C-I (\sim 270 \text{ kJ/mol}) < C-Br (\sim 340 \text{ kJ/mol}) < C-CI (\sim 400 \text{ kJ/mol}) < C-F (\sim 490 \text{ kJ/mol}) [14].$ 

#### Table 1

4

5

6

Nickel-catalyzed dehalogenation of 4-iodoanisole (7).<sup>a</sup> 2.5-5 mol% pre-catalyst 1.5 equiv. <sup>i</sup>PrZnBr THF, 24h MeO MeO 7a Yield [%]<sup>b</sup> Entry Ni-source (mol%)  $T[^{\circ}C]$ 70 1 <1 6 (5.0) 70 87 2 3 1a (5.0) 70 < 1

<sup>a</sup> Reaction conditions: **7** (1.0 mmol), pre-catalyst (2.5–5.0 mol%), <sup>i</sup>PrZnBr (1.5 equiv., 0.5 M in THF), 40–70 °C, 24 h.

70

70

40

40

68

66

<sup>b</sup> Determined by GC-MS and <sup>1</sup>H NMR.

2a (5.0)

6 (2.5)

6 (5.0)

Moreover, the potential of the complexes was evaluated in the hydrodechlorination of polychlorinated organic pollutant e.g., hexachlorobenzenze (**29**, Fig. 5). In more detail, catalytic amounts of complex **2a** were reacted with **29** with stepwise increasing amounts of *tert*-butylmagnesium chloride. The addition of 1 equiv. of *tert*-butylmagnesium chloride resulted in the formation of significant amounts of pentachlorobenzene, while increasing the amount showed a broad variety of products, including all possible compounds on the way to benzene. Noteworthy, for products **31**, **32** and **33** different isomers were detected. Moreover, to some extend the cross coupling of the chlorinated benzenes was observed, resulting after dechlorination in biphenyl **35**. Finally, after addition of 6 equiv. of *tert*-butylmagnesium chloride benzene **24a** was observed as major product.

For the understanding of the origin of the hydrogen atom of the created carbon-hydrogen bond the dehalogenation of 8 was performed in THF-d<sub>8</sub>, however, no incorporation of deuterium was detected. Moreover, the reaction was performed as described in Table 3 entry 2 and afterwards it was guenched with methanol- $d_4$ . Noteworthy, no incorporation of deuterium was monitored, excluding probably a transfer of the magnesium to the aryl halide. On the other hand, the reaction of **8** with EtMgBr- $d_5$  under standard conditions gave deuteroanisole in 51% yield, while as side reaction the cross coupling was observed (49%). Based on that, we assume the source of hydrogen should be the tert-butyl group of the Grignard reagent by  $\beta$ -hydride elimination as figured out for other catalytic system [5a,15]. On the other hand, for various nickel-catalyzed cross couplings radical species has been proposed as intermediates [16]. In order to probe the existence of radical species substrate **36** was applied (Scheme 2) [17]. In earlier studies it has been shown that the corresponding radical of 36 forms 1-methylindane (37) due to 5exo-trig cyclization with a rate constant of  $10^8 \text{ s}^{-1}$  [18]. Indeed, significant amounts of 37 were observed by GC-MS along with the desired dehalogenated product (38) and various undefined side products, indicating a radical based reaction mechanism. Moreover, the addition of 1 equivalent of TEMPO gives hint to a radical based process, because a diminished yield (17%) was noticed.

#### Table 2

Entry

Nickel-catalyzed dehalogenation with <sup>i</sup>PrZnBr - scope and limitations.<sup>a</sup>

5 mol% 6

X = I, Br, Cl

Substrate

н

Yield [%]<sup>b</sup>

Table 3

Entry

13

14

15

Nickel-catalyzed dehalogenation with tBuMgCl - scope and limitations.<sup>a</sup>

THF, r.t.-

 $T[^{\circ}C]$ 

Substrate

$$\frac{Cl}{+} R \frac{l}{l}$$

Conv. [%]<sup>b</sup>

>99

Yield [%]<sup>b</sup>

**7a**: >99<sup>c</sup>

1 7a: 87 1 r.t. MeC 2 **7a**: >99 2 Me **7a**: >99 3 3 Me 4 4 10a: 78 10 Br 5 11a: 10<sup>4</sup> 5 11 6 6 12a: 35 12 EtOO 7 7 **13a**: >99 13 Me 8 14a: 87<sup>d</sup> 8 14 MeS 9 **15a**: <1 9 15 R R **16a**: 75<sup>e</sup> 10 16 10 11 17a: 49 11 17 Br 12 18a: <1 12 18 ö

 $^{a}$  Reaction conditions: substrate (1.0 mmol), pre-catalyst  ${\bf 6}$  (5 mol%),  $^{i}PrZnBr$ (1.5 equiv., 0.5 M in THF), 70 °C, 24 h.

<sup>b</sup> Determined by GC-MS and <sup>1</sup>H NMR.

<sup>c</sup> As side product benzene (7%) was observed.

<sup>d</sup> As side product benzene (13%) was observed.

<sup>e</sup> As side product benzene (25%) was observed.

Based on the preliminary results we propose a reaction mechanism as presented in Scheme 3. First the triphenylphosphane ligand dissociates from complexes 2 or 6 to create open coordination sites. In an earlier NMR study the dissociation was monitored

Weo /			
MeO Br	70	>99	<b>7a</b> : 72
MeO 9	70	>99	<b>7a</b> : 60
Me 10	r.t.	52	<b>10a</b> : 52 <sup>c</sup>
NC Br	r.t.	>99	<b>11a</b> : 86 <sup>d</sup>
EtOOC Br	r.t.	>99	<b>12a</b> : 73
Me <sub>2</sub> N Br 13	r.t.	>99	<b>13a</b> : 61 <sup>e</sup>
MeS Br 14	70	90	<b>14a</b> : 58 <sup>f</sup>
D D D D D D D D D D	70	>99	<b>19a</b> : 62
CI Br 16	r.t.	>99	<b>16a</b> : 36 <sup>g</sup>
Br 17	70	>99	<b>17a</b> : 92
Br 20	70	>99	<b>20a</b> : 67
<sup>t</sup> Bu Br 21	r.t.	>99	<b>21a</b> : 65
Br S Br 22	70	>99	<b>22a</b> : 81
CI 23	70	>99	<b>23a</b> : 57

Table 3 (continued)

Entry	Substrate	T [°C]	Conv. [%] <sup>b</sup>	Yield [%] <sup>b</sup>
16	F 24	70	59	<b>24a</b> : 49
17	MeO F 25	r.t.	34	<b>7a</b> : 34
18	Br 26	r.t.	>99	<b>26a</b> : 70
19	Br 27	r.t.	>99	<b>27a</b> : 13
20		70	47	<b>28a</b> : 40
21 <sup>h</sup>	MeO Br	70	94	<b>7a</b> : 64
22 <sup>i</sup>	MeO Br	70	91	<b>7a</b> : 76

<sup>a</sup> Reaction conditions: substrate (1.0 mmol), pre-catalyst **6** (5 mol%), <sup>t</sup>BuMgCl (1.5 equiv., 2.0 M in diethyl ether), THF (2.0 mL), r.t -70 °C, 24 h.

<sup>b</sup> Determined by GC–MS and <sup>1</sup>H NMR.

<sup>c</sup> Without catalyst.

<sup>d</sup> As side product benzene (6%) was observed.

<sup>e</sup> As side product benzene (6%) was observed.

<sup>f</sup> As side product benzene (7%).

<sup>g</sup> As side product benzene (23%) was observed.

<sup>h</sup> Toluene was used as solvent.

<sup>i</sup> 1.5 equiv. EtMgBr (3.0 M in *n*-hexane).

by <sup>31</sup>P NMR and the free coordinations sites were occupied by the solvent THF to form the complex **A** [8]. The complex **A** reacts with the Grignard reagents to create complex **B**, which contains a 4-membered ring system [19]. After  $\beta$ -hydride elimination ethylene is formed and the nickel-magnesium hydride species **C**. The organic halide approaches the coordination sphere of the nickel and



**Fig. 4.** Reactivity study of different anisole halides and pre-catalyst **2a** (reaction conditions: substrates **7**, **8**, **9**, **25** (each 1.0 mmol), pre-catalyst **2a** (1.25 mol%), <sup>t</sup>BuMgCl (1.2 equiv., 0.5 M in THF, every 24 h), 70 °C. Determined by GC–MS applying *n*-dodecane as internal standard).



**Fig. 5.** Hydrodechlorination of hexachlorobenzene **29** (reaction conditions: substrate **29** (1.0 mmol), pre-catalyst **2a** (5 mol%), <sup>t</sup>BuMgCl (1.0 equiv., 0.5 M in THF, every 24 h), 70 °C. Determined by GC–MS. For **31**, **32**, and **33** the sum of isomers is shown).

33 16a 24a 35

mediates a single electron transfer (SET) to oxidize the complex and produce a radical [16]. The one-electron oxidized complex can on the one hand oxidized at the metal center or on the other hand the electron can be stored in the ligand (non-inocent ligand). Subsequently, MgX<sub>2</sub> is eliminated and the radical recombines with the nickel species to form the species **E**. Finally, an elimination of Ar–H occurs to regenerate complex **A**.

## 3. Conclusion

50

0

29 30 31 32

yield [%] 30 20

In summary, we have set up a protocol for the nickel-catalyzed dehalogenation of organic halides with isopropyl zinc bromide or *tert*-butylmagenesium chloride under mild reaction conditions. With the well-defined nickel complex **6** a variety of aryl and alkyl halides were converted. Future investigations will be dedicated to a deeper understanding of the reaction mechanism.

## 4. Experimental section

## 4.1. General

All compounds were used as received without further purification. THF and toluene were dried applying standard procedures. <sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra were recorded on a Bruker AFM 200 spectrometer (<sup>1</sup>H: 200.13 MHz; <sup>13</sup>C: 50.32 MHz; <sup>19</sup>F: 188.31 MHz) using the proton signals of the deuterated solvents as reference. Single crystal X-Ray diffraction measurements were recorded on an Oxford Diffraction Xcalibur S Sapphire spectrometer. GC–MS measurements were carried out on a Shimadzu GC-2010 gas chromatograph (30 m Rxi-5ms column) linked with a Shimadzu GCMA-QP 2010 Plus mass spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR.

<sup>t</sup>BuMgCI [equiv.]



Scheme 2. Investigation of the product composition of the nickel-catalyzed dehydrohalogenation of the radical probe 36 (yield determined by GC-MS methods).

## 4.2. Synthesis of 5

A mixture of **3** (33.6 mmol) and **4** (33.6 mmol) in ethanol (50 mL) was stirred for 24 h under refluxing conditions. Afterwards the reaction mixture was filtered and the ethanol was removed in vacuum. A yellow solid was obtained by recrystallization from *n*-hexane. Yield = 2.97 g (28%, colorless crystals). Mp: 185–187 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 7.75–7.78 (m, 2H, Ar–H), 7.36–7.56 (m, 3H, Ar–H), 3.02–3.37 (m, 2H, CH<sub>2</sub>), 3.73 (s, 1H, OH), 1.06 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 172.8, 133.4, 132.1, 129.9, 127.9, 125.8, 103.7, 41.9, 41.5, 27.0, 25.8 ppm. <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = -68.0 ppm. IR (KBr):  $\nu$  = 3165 (m), 3016 (m), 2979 (m), 1716 (s), 1665 (s), 1603 (w), 1581 (w), 1556 (m), 1478 (w), 1447 (w), 1425 (w), 1368 (m), 1303 (m), 1280 (m), 1209 (m), 1184 (m), 1143 (s), 1118 (s), 1076 (w), 1057 (m), 1037 (m), 1002 (m), 949 (m), 735 (w), 698 (m) cm<sup>-1</sup>. HRMS calc. for C<sub>15</sub>H<sub>17</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub> + H: 315.13149, found: 315.13116.

#### 4.3. Synthesis of 6

To a methanol solution (10 mL) of  $Ni(OAc)_2 \cdot 4H_2O$  (3.18 mmol) was added the methanol solution (10 mL) of **5** (3.18 mmol) and triphenylphosphane (6.36 mmol). The solution was stirred over night. After removing all volatiles in vacuum a brown solid was obtained.

The residue was crystallized from ethanol. Crystals suitable for X–ray diffraction analysis were obtained from ethanol solution at room temperature. Yield = 1.52 g (75%, brown crystals). Mp: 154–156 °C. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$  = 8.07–8.12 (m, 2H, Ar–H), 7.69–7.79 (m, 6H, Ar–H), 6.98–7.11 (m, 1H, Ar–H), 6.10 (s, 1H, C–H), 0.69 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>) ppm. <sup>19</sup>F NMR (188 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$  = -64.2 ppm. <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 18.1 ppm. IR (KBr):  $\nu$  = 3436 (br), 3057 (w), 2959 (w), 1589 (m), 1558 (m), 1531 (s), 1515 (s), 1494 (m), 1481 (m), 1437 (m), 1413 (s), 1363 (m), 1325 (m), 1252 (m), 1223 (m), 1197 (m), 1174 (s), 1162 (s), 1144 (m), 1100 (m), 1068 (m), 1027 (m), 783 (m), 745 (m), 693 (s), 530 (m), 511 (m), 492 (m) cm<sup>-1</sup>. HRMS calc. for C<sub>30</sub>H<sub>21</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>NiP + H: 633.14232, found 633.14202.

## 4.4. Single-crystal X-ray structure determination [20]

Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N<sub>2</sub> flow. The data were collected using an Oxford Diffraction Xcalibur S Sapphire at 150(2) K (Mo<sub>Kα</sub> radiation,  $\lambda = 0.71073$  Å). The structures were solved by direct methods and refined on  $F^2$  with the SHELX-97 software package. The positions of the hydrogen atoms were calculated and considered isotropically according to a riding model.



Scheme 3. Proposed catalytic cycle for the nickel-catalyzed dehydrohalogenation.

#### 4.5. General procedure for the catalytic dehalogenation

A Schlenk flask was charged with an appropriate amount of complex 6 (0.05 mmol, 5.0 mol%) and the corresponding bromo, chloro, fluoro or iodo arene (1.0 mmol). The flask was cycled with nitrogen and vacuum. Afterwards THF (2.0 mL) and a diethylether solution of *tert*-butyl-magnesiumchloride (0.75 mL, 1.5 mmol, 2.0 M in diethylether) were added. The flask was sealed and heated at 70 °C for 24 h or stirred at room temperature. After that time, the mixture was cooled and a NH<sub>4</sub>Cl solution was added. The mixture was extracted with dichloromethane and the organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>. n-Dodecane was added and an aliquot was taken for GC-MS analysis. The coupling products were confirmed by GC-MS and NMR analysis using *n*-dodecane as internal standard. The analytical properties of the products are in agreement with literature data.

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## Appendix A. Supplementary material

CCDC-896701 (for 6) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data\_request/cif.

### Appendix B. Supplementary data

Supplementary data related to this article can be found at doi: 10.1016/j.jorganchem.2013.01.014.

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