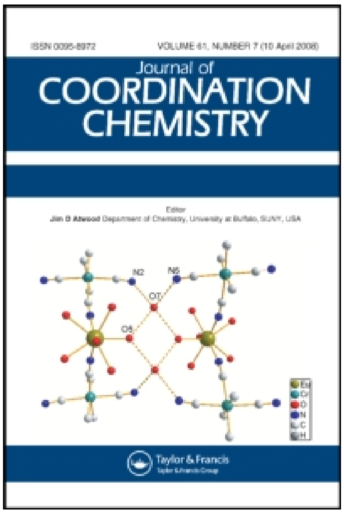

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# X-ray structure of *trans*-chloro(1-naphthyl) bis(triphenylphosphine)nickel(II) and its application for catalytic dehalogenation of aryl chlorides

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# X-ray structure of *trans*-chloro(1-naphthyl) bis(triphenylphosphine)nickel(II) and its application for catalytic dehalogenation of aryl chlorides

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X-ray structure of *trans*-chloro(1-naphthyl)bis(triphenylphosphine)nickel(II) (**4**) was determined. The complex crystallizes in the triclinic system, space group $P\bar{1}$ with $a = 12.0623(3)$, $b = 13.8844(4)$, $c = 14.5261(4)$ Å, $\alpha = 104.787(2)$, $\beta = 104.861(2)$, $\gamma = 107.602(2)^\circ$, and $Z = 2$. Dehalogenation of aryl chlorides was successfully performed in isopropyl alcohol (IPA) by using **4** as a precatalyst in the absence of reducing agent. The dehalogenation proceeded smoothly at ambient temperature to provide desired arenes in almost quantitative yields.

*Keywords*: X-ray structure; Nickel complex; Dehalogenation; Aryl chlorides

## 1. Introduction

Transition metal-catalyzed dehalogenation of aryl halides has attracted considerable attention because aromatic halides, especially polychlorinated examples, are quite difficult to degrade either by reductive or oxidative enzymatic pathways. Over the past decade, many palladium and nickel catalyst systems have been developed for the activation of the C–X bonds of aryl halides (for a review see [1]; for palladium-catalyzed dehalogenation see [2]; for supported-palladium catalyzed dehalogenation see [3]; and for nickel-catalyzed dehalogenation see [4]). Usually these systems need to combine with a reducing agent such as $Me_2NH \cdot BH_3$, HCOOM ($M = Na^+, NH_4^+$) and $N_2H_4 \cdot HCl$ to reduce aromatic halides to arenes.

During the course of our study on Ni-catalyzed coupling of aryl chlorides with arylboronic acids using tricyclohexylphosphine ($PCy_3$) as a ligand [5], instead of obtaining the expected cross-coupling product, 4-phenylacetophenone, a dehalogenated compound, acetophenone, was obtained as a sole product (scheme 1).

In this dehalogenation, $PhB(OH)_2$ acted as a reducing agent to generate the Ni(0) species through homocoupling [6], and then the Ni(0) species underwent oxidative

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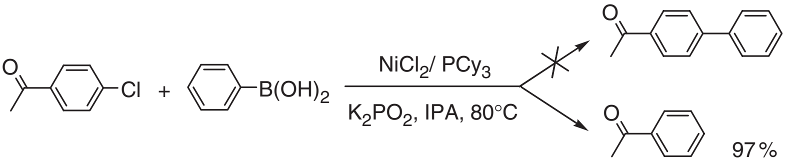
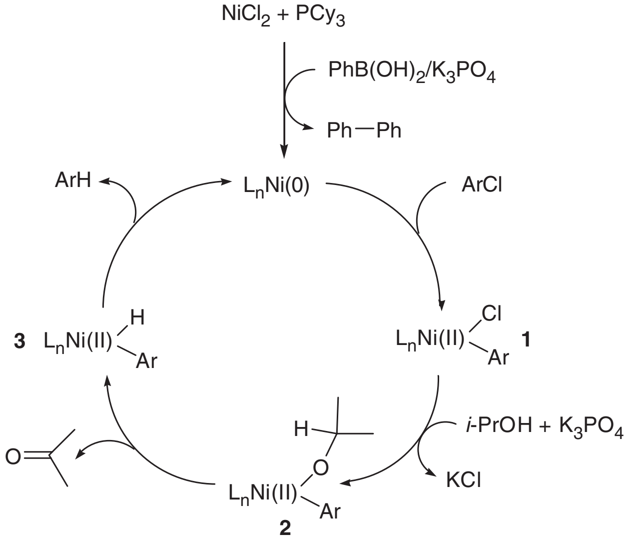


Scheme 1. Ni-catalyzed dehalogenation reaction of 4-chloroacetophenone.



Scheme 2. Proposed mechanism for the dehalogenation of 4-chloroacetophenone.

addition with aryl chloride to give an aryl nickel chloride intermediate **1**. Finally, reductive elimination of the arene from a nickel-hydride intermediate **3** obtained by $\beta$-elimination regenerates the Ni(0) catalyst (scheme 2, see [4d]). It occurred to us that the nickel-catalyzed dehalogenation could be performed utilizing an aryl nickel chloride like intermediate **1**, as precatalyst without using a reducing agent. Indeed, when a combination of *trans*-chloro(1-naphthyl)bis(triphenylphosphine)nickel(II) (**4**) and $PCy_3 \cdot HBF_4$ was employed as catalyst system, the dehalogenation of aryl chlorides proceeds smoothly in isopropyl alcohol (IPA) at room temperature. Herein we wish to report the X-ray structure of **4**, and the first instance of the utilization of an aryl nickel chloride complex as a precatalyst for dehalogenation of aryl chlorides.

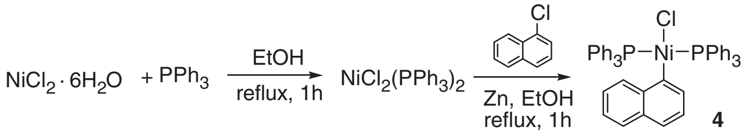
## 2. Experimental

### 2.1. *Materials and physical measurement*

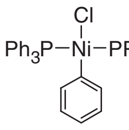
All reactions were carried out in dry $N_2$ using standard Schlenk techniques. Solvents were dried and distilled prior to use by standard methods. $^1H$ and $^{31}P$ NMR spectra were recorded on a Varian Inova-400 spectrometer. The chemical shifts are reported in $\delta$ units relative to internal tetramethylsilane for $^1$H NMR and 85% $H_3PO_4$ as external standard for $^{31}$P NMR. Elemental analysis was performed on a Vario EL III elemental analyzer. The single crystal structure was measured on a Rigaku AFC7R diffractometer.

### 2.2. *Synthesis of* trans-*chloro(1-naphthyl)bis(triphenylphosphine)nickel(II) (4)*

Complex **4** was synthesized according to the procedure provided in [7] with slight modification as follows: a 50 mL three-necked flask, equipped with a reflux condenser, was charged with $NiCl_2 \cdot 6H_2O$ (0.48 g, 2.0 mmol), $PPh_3$ (1.10 g, 4.2 mmol) and 1-chloronaphthalene (0.33 g, 2.0 mmol). The flask was evacuated and backfilled with nitrogen three times, then 20 mL of ethanol was added. After the resulting mixture was heated to reflux for 1 h, a dark-green suspension of $NiCl_2(PPh_3)_2$ formed, and then zinc powder (0.26 g, 4.0 mmol) was introduced under nitrogen atmosphere. The reaction mixture was stirred at reflux for 1 h, allowed to cool and filtered, and the crude product was washed with ethanol (10 mL × 3) and petroleum ether (50 mL). Orange crystals of **4** were obtained by recrystallization from $CH_2Cl_2$/petroleum ether. Anal. Calcd for $C_{46}H_{37}ClNiP_2 \cdot CH_2Cl_2$ (%): C, 67.9; H, 4.7. Found: C, 67.7; H, 4.6. $^{31}$P NMR ($CDCl_3$): $\delta$ 21.49.



**4**



**5**

### 2.3. *X-ray crystallography*

Intensity data of **4** ($0.45 \times 0.40 \times 0.30\,mm^3$) were measured with a Rigaku AFC7R diffractometer using a rotating anode with graphite monochromated Mo-K$\alpha$ ($\lambda = 0.71073$ Å) radiation at 273 K. Reflections (9438) were measured over the ranges $-15 \le h \le 13$, $-17 \le k \le 17$, $-18 \le l \le 17$, yielding 6341 unique reflections. The raw data were corrected with direct methods and the structure was solved using the SHELX-97 program. Non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement. The full-matrix least-squares calculations on $F^2$ were applied to the final refinement. The refinement converged at $R_1 = 0.2313$ and $wR_2 = 0.1260$ values for reflections with $I > 2\sigma(I)$. Details of the crystal structural determinations are summarized in tables 1 and 2.

### 2.4. *Dehalogenation*

General procedure for the nickel-catalyzed dehalogenation of aryl chlorides: a 20 mL Schlenk tube was charged with **4** (3 mol%, relative to aryl chloride), $PCy_3 \cdot HBF_4$ (6 mol%, relative to aryl chloride), $K_3PO_4 \cdot H_2O$ (2.0 mmol), aryl chloride (1.0 mmol), and IPA (3 mL). The reaction mixture was stirred under nitrogen at room temperature for 24 h and filtered on a short silica gel column to remove the catalyst and base. The yields were determined by GC, or the crude products were purified by silica gel column chromatography.

Table 1. Crystal data and structure refinement.

| | |
|---|---|
| Empirical formula | $C_{46.5}H_{38}Cl_2NiP_2$ |
| Formula weight | 788.31 |
| Temperature (K) | 273(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit-cell dimensions (Å, °) | |
| $a$ | 12.0623(3) |
| $b$ | 13.8844(4) |
| $c$ | 14.5261(4) |
| $\alpha$ | 104.787(2) |
| $\beta$ | 104.861(2) |
| $\gamma$ | 107.602(2) |
| $V$ (Å$^3$) | 2090.00(10) |
| $Z$ | 2 |
| $D_c$ (mg m$^{-3}$) | 1.251 |
| $\mu$ (mm$^{-1}$) | 0.699 |
| Reflections collected/unique [$R_{int}$] | 9438/6341 [0.0231] |
| $F$(000) | 816 |
| Crystal size (mm$^3$) | 0.45 × 0.40 × 0.30 |
| $\theta$ range for data collection (°) | 2.57–27.4 |
| Data/restraints/parameters | 9438/0/3497 |
| $R_1$ [$I > 2\sigma(I)$] | 0.2313 |
| $wR_2$ [$I > 2\sigma(I)$] | 0.1260 |
| Goodness-of-fit on $F^2$ | 1.062 |

Table 2. Selected bond distances (Å) and angles (°).

| | |
|---|---|
| Ni(1)–C(1) | 1.885(4) |
| Ni(1)–P(3) | 2.2257(9) |
| Ni(1)–P(1) | 2.2283(9) |
| Ni(1)–Cl(1) | 2.2499(10) |
| C(1)–Ni(1)–P(3) | 88.54(12) |
| C(1)–Ni(1)–P(1) | 87.57(12) |
| P(3)–Ni(1)–P(1) | 176.11(4) |
| C(1)–Ni(1)–Cl(1) | 168.13(13) |
| P(3)–Ni(1)–Cl(1) | 90.43(4) |
| P(1)–Ni(1)–Cl(1) | 93.43(4) |

## 3. Results and discussion

### 3.1. *Description of the crystal structure of 4*

To the best of our knowledge, the X-ray structure of **4** has not been reported, even though the X-ray structure of the phenyl analogue, *trans*-chloro(phenyl) bis(triphenylphosphine)nickel(II) (**5**), was reported in 2003 [8]. The crystal cell parameters and selected bond distances and angles of **4** are given in tables 1 and 2, and the structure of **4** is shown in figure 1. The bond angles around the Ni reveal that **4** exists in a slightly distorted square-planar geometry, where the two triphenylphosphine ligands, the 1-naphthyl group and chloride bind to nickel *trans*, [P(1)–Ni(1)–P(3), 176.11(4)°; Cl(1)–Ni(1)–C(1), 168.13(13)°], similar to complex **5**. The Ni–Cl distance of 2.2499(10) Å in **4** is longer than the Ni–Cl distance of 2.2201(6) Å in **5**.

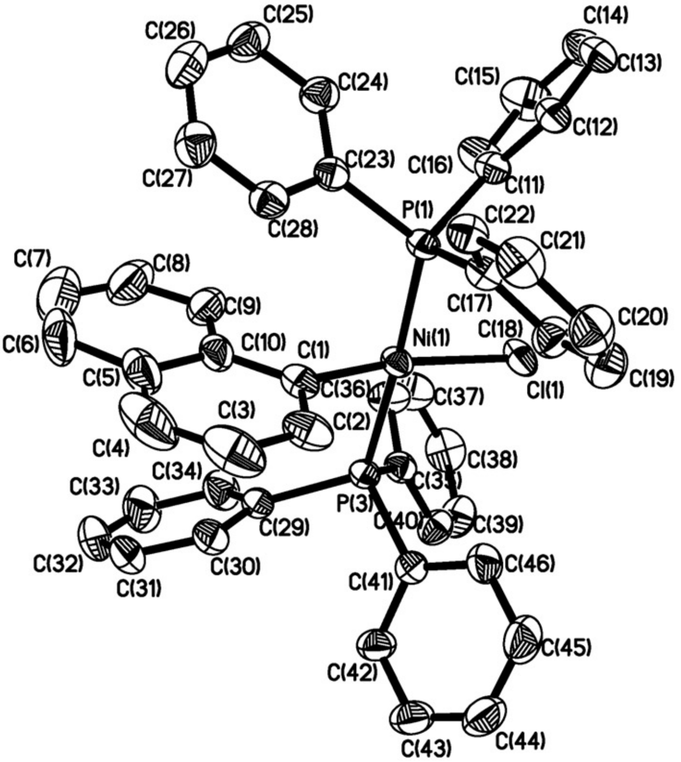
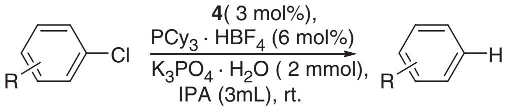


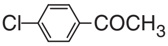
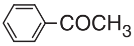
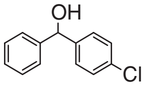
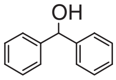
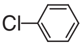
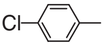
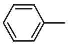
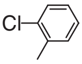
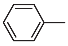
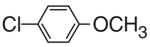
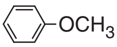
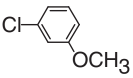
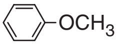
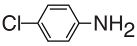
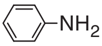
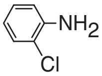
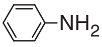
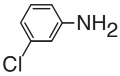
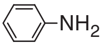
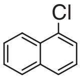
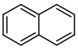
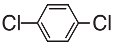
Figure 1. Structure of **4** at 30% probability level. Hydrogen atoms are omitted for clarity.

## 3.2. *The catalytic activity of 4 in dehalogenation of aryl chlorides*

Complex **4** is more stable than its analogues and can be easily handled in air (The preparation of **4** is easier than **5**. See [8] and [9]. We failed to prepare the Ni(1-naph)$(PCy_3)_2Cl$, an unknown complex). Therefore, **4** was synthesized and employed for dehalogenation of aryl chlorides; the results are summarized in table 3. Dehalogenation of 4-chloroacetophenone was performed in the presence of **4** (3 mol%) and $PCy_3 \cdot HBF_4$ (6 mol%) in IPA at room temperature for 24 h, and the dehalogenated product, acetophenone, was obtained in 99% yield (entry 1). Surprisingly, the (4-chlorophenyl)phenyl methanol also underwent dehalogenation smoothly to furnish diphenyl methanol in 86% isolated yield (entry 2). Simple substrate, the chlorobenzene, and its methyl substituted forms gave dehalogenated products in nearly quantitative yields (entries 3–5). *meta*- or *para*-methoxy on the aromatic ring had no effect on the yields of arenes (entries 6 and 7). Similar results were obtained from the dehalogenation reactions of *ortho*- and *meta*- as well as *para*-chlorobenzenamines (entries 8–10). The dehalogenation of 1-chloronaphthalene gives naphthalene in 93% isolated yield (entry 11). As expected, the dehalogenation of *para*-dichlorobenzene continued smoothly under the same reaction conditions as mentioned earlier to give benzene in 98% yield (entry 12). The results obtained indicated that hydroxyl and amino groups are tolerated by the

Table 3. Ni-catalyzed dehalogenation of aryl chlorides in IPA without using a reducing reagent.[a]



| Entry | Aryl chloride | Arene | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  | 99 |
| 2 |  |  | 86[c] |
| 3 |  |  | 99 |
| 4 |  |  | 99 |
| 5 |  |  | 95 |
| 6 |  |  | 99 |
| 7 |  |  | 99 |
| 8 |  |  | 99 |
| 9 |  |  | 96 |
| 10 |  |  | 97 |
| 11 |  |  | 93[c] |
| 12[d] |  |  | 99 |

Notes: [a]Reaction conditions:aryl chloride (1.0 mmol), $K_3PO_4 \cdot H_2O$(2.0 mmol), complex **4** (3 mol%), $PCy_3 \cdot HBF_4$ (6 mol%), IPA (5 mL), room temperature, 24 h.
[b] GC yields based on aryl chlorides.
[c] Isolated yields based on aryl chlorides.
[d] 3.0 mmol of $K_3PO_4 \cdot H_2O$ was used.

combination of reagents: $Ni(PPh_3)_2(1\text{-naph})Cl/PCy_3/K_3PO_4$ in IPA. In this dehalogenation reaction, the IPA acts as both solvent and hydrogen source to reduce aryl chlorides into arenes.

In this article, we developed a mild and operationally simple method for dehalogenation of aryl chlorides by using **4**, an aryl nickel chloride, as a precatalyst without using a reducing agent, and further extended **4** as a catalyst in organic synthesis. Complex **4** was successfully employed as a catalyst in Suzuki coupling and carbon–nitrogen coupling reaction [9].

## Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 691351 for **4**. Copies of these information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk or at http://www.ccdc.cam.ac.uk).

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