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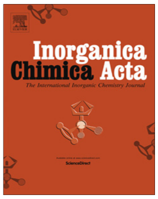

Activation of vinylic carbon–chlorine bond by nickel complexes supported with phosphine ligands

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ABSTRACT

The vinylic C–Cl bonds of *ortho*-chlorinated cycloalkenyl aldehydes (**1–4**) and *ortho*-chlorinated cycloalkenyl acetal derivatives (**5–6**) were successfully activated by nickel(0) and nickel(II) complexes supported by trimethylphosphine ligands. Except one *trans*-five-coordinate nickel(II) chloride complex *trans*-[Ni(PMe$_3$)$_2$Cl—{(C$_5$H$_6$)—CH═O}] (**7**) as a cyclometalation product with coordination of the aldehyde group, the other six four-coordinate nickel(II) chloride complexes *trans*-[Ni(PMe$_3$)$_2$Cl—{(C$_5$H$_6$)—CH═O}] (**8**), *trans*-[Ni(PMe$_3$)$_2$Cl—{(C$_6$H$_8$)—CH═O}] (**9**), *trans*-[Ni(PMe$_3$)$_2$Cl—{(C$_6$H$_7$Me*meta*)—CH═O}] (**10**), *trans*-[Ni(PMe$_3$)$_2$Cl—{(C$_6$H$_7$Bu-t*meta*)—CH═O}] (**11**), *trans*-[Ni(PMe$_3$)$_2$Cl—{(C$_6$H$_8$)—CH(OCH$_2$CH$_2$O)}] (**12**) and *trans*-[Ni(PMe$_3$)$_2$Cl—{(C$_6$H$_7$Bu-t-*meta*)—CH(OCH$_2$CH$_2$O)}] (**13**) as C–Cl bond activation products were obtained without coordination of the aldehyde groups. These complexes were characterized by IR and NMR. The crystal and molecular structures of complexes **8**, **9** and **12** were determined by single crystal X-ray diffraction.

1. Introduction

Aryl and vinyl halides are important starting materials in synthetic organic chemistry because of their ready availability and low cost. When compared with the reactive and expensive iodo- and bromo-arenes, as well as both costly and inert fluoroarenes, chloroarenes and chloroalkenes are certainly the most attractive aryl and vinylic halides for synthetic applications. Several methods have been developed to activate C–Cl bond. The C–Cl bond activation mediated by transition metal complexes is one of the most effective methods to realize C–Cl bond functionalization [1]. There have been some examples of catalytic activation of the C–Cl bond in chloroarenes by nickel [2–7], cobalt [8–22], and iron complexes [23–30], which are widely applied in cross-coupling reactions, such as the Heck reaction, Suzuki coupling, Kumada coupling, Sonogashira coupling, and Stille coupling. The C–Cl bond activation by electron-rich low-valent transition metal center is the key step in these catalytic reactions.

Our research interest is focused on the C–Cl bond activation mediated by electron-rich cobalt, nickel and iron complexes supported by trimethylphosphine ligands. In the past few years, a series of *ortho*-chelated cobalt(II) [12], nickel(II) [6] and iron(II) [30] were synthesized and characterized through C–Cl activation with imine as an anchoring group. The C–Cl bonds of *ortho*-chlorinated benzamides could be activated by tetrakis(trimethylphosphine)nickel(0) and tetrakis(trimethylphosphine)cobalt(0) [7]. Owing to the similarity between aryl chlorides and vinyl chlorides and the even more versatile chemistry of the latter, in this paper we expanded our interest to the activation of vinylic C–Cl bonds in chloroalkenes. The new nickel(II) complexes **7–13** were formed by oxidative addition of the vinylic C–Cl bonds. The crystal and molecular structures of complexes **8**, **9** and **12** were determined by single crystal X-ray diffraction.

2. Results and discussion

2.1. Reaction of Ni(PMe$_3$)$_4$ or Ni(PMe$_3$)$_3$Me$_2$ with aliphatic vinylic chloride *1*

The reaction of Ni(PMe$_3$)$_4$ with β-chlorinated vinylic aldehyde **1** with aldehyde as an anchoring group afforded two nickel complexes by oxidative addition of the C–Cl bond, the five-coordinate chelate nickel(II) chloride **7** as a cyclometalation product with coordination of the O$_{\mathrm{aldehyde}}$ atom and the four-coordinate nickel(II) complex **8** without coordination of the O$_{\mathrm{aldehyde}}$ atom (Scheme 1).

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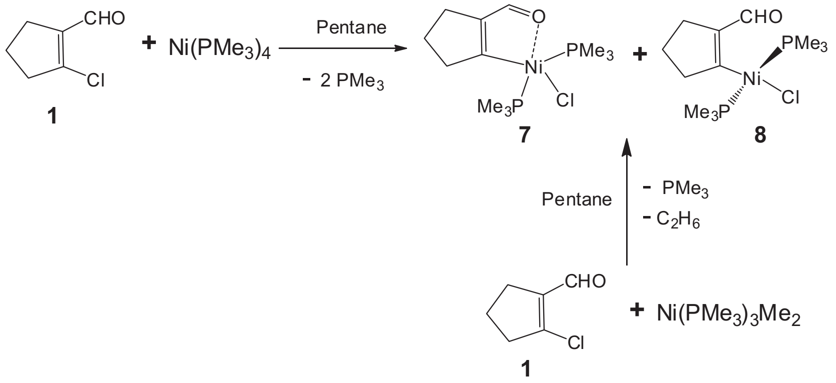

Scheme 1.

This result is different from our early reports about aromatic C–Cl bond activation at nickel(0) center [6,7]. In the case of *ortho*-chlorinated benzimine, through cyclometalation reactions involving aromatic C–Cl bond activation at nickel(0) center, only five-coordinate nickel(II) complexes were obtained. However in the case of *ortho*-chlorinated benzamides, only four-coordinate nickel(II) chloride complexes without an benzamide-O atom or -N atom as an anchoring group were isolated [7]. It is concluded that the coordination ability of these atoms can be ordered as imine-N > aldehyde-O > benzamide-O atom or -N atom. Therefore, we obtained two kinds of nickel(II) chloride complexes with different coordination modes and coordination numbers in this reaction.

Under similar reaction conditions, the reaction of $Ni(PMe_3)_3Me_2$ with aldehyde **1** gave rise to the similar results as $Ni(PMe_3)_4$. Complexes **7** and **8** were hardly separated from each other. The pure products can be obtained through re-crystallization and mechanical separation. We have found that the yields of complexes **7** and **8** depend on the reaction time. Complex **7** is the main product in a short reaction time. If the reaction time was prolonged, complex **8** is the main product. There is a dissociation–coordination equilibrium between complexes **7** and **8**. Complex **7** can be transformed into **8** in solution. This result indicates that four-coordinate complex **8** was formed through the dissociation of the $O_{aldehyde}$ atom of five-coordinate complex **7**. The cyclometalation with oxidative addition of C–Cl bond is the key step in the formation of four-coordinate complex **8**. In this process complex **7** was formed as a kinetically favorable product while **8** is the thermodynamically stable product. Complexes **7** and **8** were fully characterized through IR and NMR spectra.

In the infrared spectra of complexes **7** and **8**, the characteristic ν(C=O) bands were recorded at 1625 (**7**) and 1639 (**8**) cm^{-1}. Compared with the (C=O) band (1667 cm^{-1}) of free ligand **1**, a substantial red shift (42 cm^{-1}) upon coordination of the O-donor atom of the aldehyde group indicates a weakening of the (C=O) double bond after coordination to the nickel centre in the case of **7**. In contrast, the red shift (28 cm^{-1}) for complex **8** is relatively small.

In the ^1H NMR spectra of complex **7**, two resonances of PMe_3 were recorded as two doublet at 1.16 and 1.53 ppm with $^2J(PH) = 6.9$ Hz and $^2J(PH) = 13.5$ Hz, respectively. The ^{31}P NMR spectra of **7** indicate two doublets at −14.8 and 13.6 ppm with $^2J(PP) = 10.0$ Hz. This suggests that the two phosphine ligands have different chemical environment. Owing to the coordination of the C=O group, the resonance of CH-hydrogen of the aldehyde in complex **7** changed from 10.90 for complex **8** to 9.61 ppm.

In the ^1H NMR spectra of complex **8**, we found that the PMe_3 groups gave rise to a virtual triplet signal at 0.91 ppm with the coupling constant $|^2J(PH) + {}^4J(PH)| = 7.5$ Hz. Only one ^{31}P NMR signal was observed at −13.6 ppm as a singlet. This suggests that the two phosphorus atoms have the same chemical environment and are located in the *trans*-positions. The crystal and molecular structure of complex **8** was confirmed by X-ray diffraction analysis.

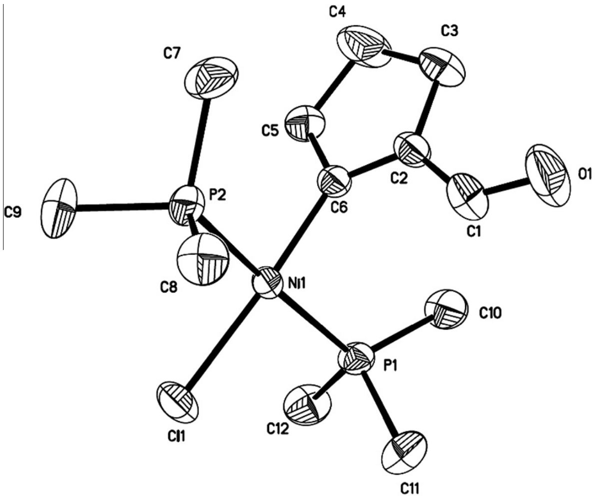

Fig. 1. Molecular structure of **8**, selected distances (Å) and angels (°): Ni1–Cl1 2.193(1), Ni1–P1 2.171(1), Ni1–P2 2.174(1), Ni1–C6 1.835(3), P1–C10 1.788(3), O1–C1 1.193(4), C2–C6 1.323(4); P1–Ni1–Cl1 90.07(5), P2–Ni1–Cl1 90.93(5), C6–Ni1–P1 90.51(8), C6–Ni1–P2 89.51(8), P1–Ni1–P2 168.94(3).

The molecular structure of complex **8** is shown in Fig. 1. The selected bond distances and angles are listed under the figure. Complex **8** shows a distorted square planar structure with two *trans*-phosphine ligands. This is consistent with the observation from the NMR spectroscopy. The nickel atom is centered in a square planar geometry with the *trans*-orientated Cl and cyclopentene vinylic-C atom due to the *trans*-influence. Ni1–Cl1 (2.193(1) (Å)) is close to that in the related complexes (2.2096(7)–2.2570(1) Å) [7]. C1–O1 distance (1.193(4) Å) is within the region of a C=O double bond. This also indicates that there is no bonding interaction between the O atom and the central nickel atom. Additionally, the coordination of the O atom to the nickel atom does not exist because the distance between both atoms is much larger than those of the normal coordination bonds of Ni–O (1.935–2.472 Å) [31–32].

2.2. Reaction of $Ni(PMe_3)_4$ or $Ni(PMe_3)_3Me_2$ with aliphatic vinylic chlorides **2**–**4**

Under the similar reaction conditions as Scheme 1, the reactions of $Ni(PMe_3)_4$ or $Ni(PMe_3)_3Me_2$ with aldehydes **2**–**4** afforded only four-coordinate Ni(II) complexes **9**–**11** (Scheme 2). This means that the four-coordinate Ni(II) complex with cyclohexene ring is more stable than the related five-coordinated nickel(II) complex.