Journal of Organometallic Chemistry 743 (2013) 114–122

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis and characterization of novel organonickel and organocobalt complexes via carbon–chlorine bond activation

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ARTICLE INFO

Article history:
Received 24 April 2013
Received in revised form
21 June 2013
Accepted 24 June 2013

Keywords:
ortho-Metalation
C–Cl activation
Nickel
Cobalt
Diimine
Trimethyphosphine

ABSTRACT

The *ortho*-metalated nickel(II) complexes **3**, **4**, **7** and **8** were obtained by the reaction of *ortho*-halogeno aromatic bis-Schiff bases **1**, **2**, **5** and **6** with the stoichiometric amount of $Ni(PMe_3)_4$. The combination of **5** and **6** with two equivalents of $Ni(PMe_3)_4$ resulted in oxidative addition of the double C–Cl bonds to afford *ortho*-bis-chelated nickel(II) complexes **9** and **10**. The reaction of **6** with $Co(PMe_3)_4$ gave rise to dinuclear *ortho*-metalated cobalt(II) complex **12** through C–Cl bond activation while the reaction of **5** with $Co(PMe_3)_4$ delivered bis-chelated cobalt(I) complex **11** through both C–Cl and C–H bond activation. The structures of complexes **3**, **4**, **8**, **9**, **11** and **12** were determined by X-ray single crystal diffraction. The catalytic activity of bis-chelated cobalt(I) complex **11** as catalyst for C,C-coupling reaction was explored.

1. Introduction

C–Cl bond activation is one of the important methods to realize the catalytic C–Cl bond functionalization [1–10]. A few strategies have been reported for the activation of C–Cl bonds of aryl chlorides by transition metal complexes [11–25]. Recently, cyclometalation reaction with imine as an anchoring group to activate C–Cl bond has received increasing attention. Tungsten [26], nickel [27], iron [28], Platinum [29] and copper [30] complexes were reported for activation of C–Cl bonds. Our research interest is focused on 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) [31], nickel(II) [32] and iron(II) [33] complexes were synthesized and characterized through C–Cl activation with imine as an anchoring group [34]. The C–Cl bonds of *ortho*-chlorinated benzamides were activated by tetrakis(trimethylphosphine)nickel(0) and tetrakis(trimethylphosphine)cobalt(0) complexes.

As part of our continuing research work on C–Cl bond activation, organic chlorides were extended from *ortho*-chlorinated mono-imines in our early study to *ortho*-chlorinated diimine to explore the opportunity of double C–Cl bond activation through di-*ortho*-metalation in this paper. The new *ortho*-chelated nickel(II) complexes **3**, **4**, **7** and **8** were obtained by oxidative addition of aromatic C–Cl bonds. The *ortho*-bis-chelated Ni(II) complexes **9**, **10** and cobalt(II) complex **12** were also isolated via double C–Cl bond activation. Interestingly, bis-chelated Co(I) complex **11** was confirmed through both C–Cl and C–H bond activation. The C,C-coupling reaction between chlorobenzene and Grignard reagents with complex **11** as catalyst was explored. The related reaction mechanisms were proposed. The structures of complexes **3**, **4**, **8**, **9**, **11** and **12** were determined by X-ray single crystal diffraction. All this work of this paper is illustrated in Scheme 1.

2. Results and discussion

2.1. Reactions of chlorinated diimines with $Ni(PMe_3)_4$

Reactions of $Ni(PMe_3)_4$ with *ortho*-chlorinated aromatic compounds (**1** and **2**) containing *di*-imine as anchoring groups proceed by oxidative addition of the C–Cl bond to give rise to *ortho*-metalated nickel(II) chlorides **3** and **4** (Eq. (1)). The expected dinuclear nickel(II) complexes (as the analog of complexes **9** and **10**) formed via double C–Cl bond activation were not observed even if two equivalents of $Ni(PMe_3)_4$ were added in the reaction solution. It is suggested that the double C–Cl activation was excluded owing to the steric effect of the two adjacent imine groups. Only one of the two imine groups can act as anchoring group.

In the infrared spectra of complexes **3** and **4**, the characteristic $\nu(C{=}N)$ bands were recorded at 1606 (**3**) and 1605 (**4**) cm^{-1}.

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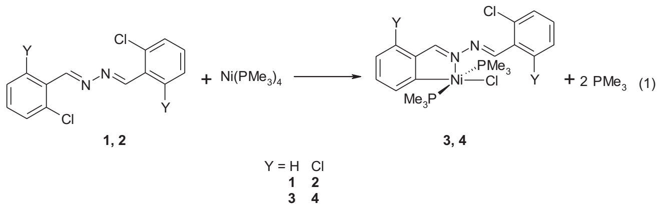
0022-328X/$ – see front matter
http://dx.doi.org/10.1016/j.jorganchem.2013.06.033

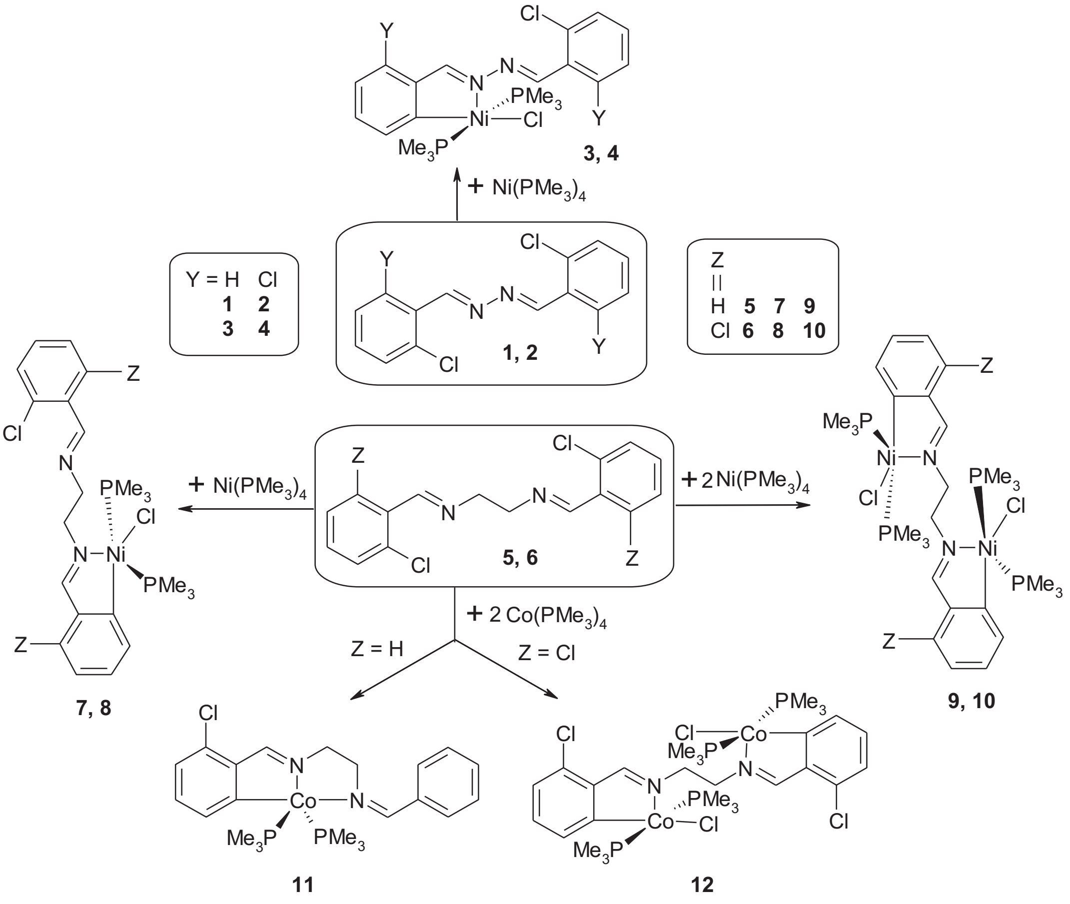


Compared with the (C=N) bands (1628 and 1655 cm^{-1}) of the free ligands **1** and **2**, a substantial red shift upon coordination of the N-donor atom of the imine group indicates a weakening of the C=N double bond after coordination to the nickel centre.

In the ^{1}H NMR spectra, the resonances of the CH-hydrogen of the coordinated imine groups were recorded at 10.63 (**3**) and 10.41 (**4**) ppm as singlet because part of the electronic cloud around of the imine double bond was transferred to the nickel centre via coordination and the imine hydrogen became acidic. Therefore, the chemical shifts of these hydrogen atoms moved to the downfield. In the ^{31}P NMR spectra, one signal at −5.5 (**3**) or −19.1 (**4**) ppm suggests that the two phosphorus atoms have the same chemical environment and are located in *trans*-positions.

Complexes **3** and **4** were isolated by crystallization from pentane at 4 °C. Both of them are stable under ambient condition and can be handled in the air for at least 3 h. The molecular structures of complexes **3** and **4** (Figs. 1 and 2) confirm a square-pyramidal coordination of a nickel (II) centre with an imine-N atom at the apical position. The conjugated diimine plane including two phenyl and two imine groups is perpendicular to the underside of the square pyramid. In other words, this is a symmetry plane of this molecule. Therefore, two phosphine ligands have the same chemical environment. This is consistent with the NMR information. The distances of Ni—Cl are 2.2531(5) (**3**) and 2.2417(4) (Å) in the normal region. There is no significant difference between the coordinated C=N bonds (N1—C13 = 1.284(2) (**3**) and C7—N1 = 1.295(3) (**4**) Å) and the uncoordinated C=N bonds (N2—C14 = 1.281(2) (**3**) and C8—N2 = 1.289(3) (**4**) Å). This is in agreement with the results from the infrared spectra. In the infrared spectra only one characteristic ν(C=N) bands were found. This indicates significant bond weakening of the second uncoordinated C=N bond upon the coordination of the nitrogen atom of the first C=N group. Furthermore, the N-donor of the uncoordinated C=N group becomes weaker. Therefore, in this reaction no expected dinuclear nickel(II) complexes were observed via double C—Cl bond activation.

The reactions of diimines **5** and **6** with the stoichiometric amount of Ni(PMe$_3$)$_4$ in THF afforded mono-chelated nickel(II) complexes **7** and **8** via C—Cl bond activation (Scheme 2). However, the reactions of diimines **5** and **6** with 2 equivalents of Ni(PMe$_3$)$_4$ in THF gave rise to dinuclear nickel(II) complexes **9** and **10** with two chelate rings via double C—Cl bond activation (Scheme 2). Complexes **9** and **10** could be also obtained through the reactions of mono-nuclear nickel(II) complexes **7** and **8** with another equivalent of Ni(PMe$_3$)$_4$. The selected IR and NMR data of complexes **7**—**10** are collected in Table 1. Compared with the (C=N) bands of the free ligand **5** and **6** (1635 and 1649 cm^{-1}) in the IR spectra, a substantial red shift upon coordination of the N-donor atom of the imine group was also observed owing to a weakening of the coordinated C=N group.



Scheme 1. Summarization of the reactions and products.