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Synthesis and structure of cobalt(II) iodide bearing a bulky *N*-heterocyclic carbene ligand, and catalytic activation of bromoalkanes

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ABSTRACT

A divalent cobalt iodine complex bearing 1,3-bis(mesityl)imidazol-2-ylidene and pyridine ligands was synthesized and its structure was determined. The cobalt center has a typical d^7-tetrahedral geometry, as expected. Catalytic application of this cobalt complex with bromoalkanes and Grignard reagents demonstrated high-yield formation of alkenes as a result of β-hydrogen elimination; in sharp contrast, the activation of alkyl halides was not successful using the larger *N*-heterocyclic carbene ligand, 1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene. In the presence of styrene, Heck reaction proceeded with *trans* selectivity. The reaction of a substrate containing a bromobenzyl moiety yielded a homocoupling product.

1. Introduction

The first-row late transition metals such as iron, cobalt, nickel and copper are now the most important transition metals used as catalysts in the development of organic reactions [1], rather than the catalytically active noble metals, such as ruthenium, rhodium, and palladium [2]. The development of alternative processes for cross-coupling reactions mediated by these first-row metal catalysts has also attracted much attention [3]. Because of the difficulty of identification as a result of their paramagnetic properties, structurally defined cobalt complexes have rarely been used as catalysts [4], in comparison with their nickel and iron counterparts. Using well-defined complexes is essential to obtain information on the reaction mechanism and/or discover novel reactions. Fruitful results have been obtained in studies of cross-coupling reactions of alkyl halides catalyzed by in situ-generated cobalt species [5]. It is therefore important to develop active and useful cobalt complexes for cross-coupling reactions of alkyl halides.

Recently, *N*-heterocyclic carbenes (NHCs) have become one of the most valuable candidates designing active and stable metal catalysts [6]. Several cobalt NHC complexes have been synthesized and structurally determined [7]. However, only a few examples of catalysts for organic reactions, particularly for cross-coupling reactions, have been reported [4]. In addition, cobalt catalysts bearing bulky NHC ligands are unknown, although Oshima and Yorimitsu et al. have reported efficient cobalt-mediated activation of alkyl halides in the presence of bulky NHC ligands as cocatalysts [8]. Our previous report showed that the bulky NHC ligand, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) coordinates to divalent cobalt halides to form unstable dinuclear cobalt(II)–IPr complexes, which were stabilized by addition of pyridine to yield monomeric cobalt(II) complexes, namely Co(IPr)X_2(Py) (**1a**: $X = \mathrm{I}$, **1b**: $X = \mathrm{Br}$, **1c**: $X = \mathrm{Cl}$) (Scheme 1) [9]. These compounds successfully catalyzed Kumada–Tamao–Corriu cross-coupling reaction of aryl halides, but were not suitable for catalytic activation of alkyl halides. We hypothesized that cobalt complex bearing less bulky NHC ligand such as 1,3-bis(mesityl)imidazol-2-ylidene (IMes) instead of IPr could perform catalytic activation of alkyl halides. Here we report the synthesis, structure, and reactivity of a new IMes–cobalt(II) diiodide, which mediates catalytic activation of alkyl halides. Interestingly, the products obtained depended on the conditions: 1-alkene or homocoupling products in the presence of a Grignard reagent, and Heck reaction products in the presence of styrene and a Grignard reagent.

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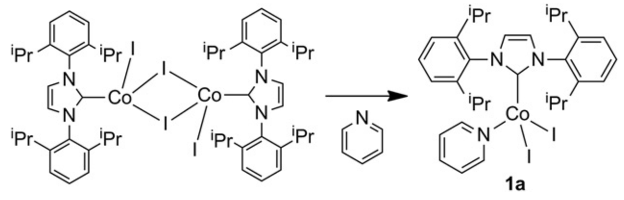


Scheme 1. Synthesis of **1a** in the previous report [9].

2. Results and discussion

2.1. Synthesis and structure of cobalt(II) (IMes) diiodide (**2**)

In our previous study, IPr was added to THF solutions of cobalt(II) iodide, bromide, and chloride to form dicobalt IPr complexes $[Co(IPr)X]_2(\mu{-}X)_2$ (X = I, Br, Cl) [9]. However, the complexes sometimes decomposed to a monomeric cobalt anion $[Co(IPr)X_3]^-[IPrH]^+$, probably because of the presence of a small amount of water. Addition of pyridine to these dimers effectively stabilized them and gave monomeric neutral complexes, $Co(IPr)X_2(Py)$ (**1a**: $X = I$, **1b**: $X = Br$, **1c**: $X = Cl$), in good yields. Among the complexes, the iodide **1a** was the most active catalyst in the Kumada coupling of aryl halides. Based on the above experimental results, the monomeric cobalt iodide analog bearing the IMes ligand, Co(IMes) I_2(Py) (**2**), was similarly synthesized by the reaction of CoI_2 with IMes in THF, followed by addition of pyridine (Scheme 2). The reaction proceeded smoothly in THF at room temperature. Direct addition of IMes and CoI_2 to pyridine also gave **2** efficiently. Dimeric species are probably generated in situ, as the corresponding IPr complexes were formed previously [9].

The product **2** was air-unstable and recrystallized under an inert-gas atmosphere from THF and *n*-hexane at −30 °C (26% yield by recrystallization). In elemental analysis of **2**, the obtained carbon, hydrogen and nitrogen contents of 44.68, 4.57 and 6.06%, respectively, agreed with the theoretical values of 44.85, 4.20 and 6.40%, respectively. The structure of **2** in solution was similar to that of **1a**, indicated by the UV–visible absorption spectroscopy. The absorption bands from 600 to 800 nm, 636, 675 and 713 nm, in Fig. 1 were assigned as the $d{-}d^*$ transition, whereas those of **1a** appeared at 644, 681 and 711 nm. The three separate bands are probably the result of spin–orbit coupling and the unsymmetric structure. The spectra suggest that **2** has the same tetrahedral d^7-geometry in solution as **1a** [9]. Moreover, these bands did not broaden at room temperature, suggesting that any equilibrium reactions, such as formation of the dimer with liberation of pyridine, could be ruled out. Compound **2** was paramagnetic and the spin-quantum number was 3/2, the same as in the case of the corresponding IPr analogs [9].

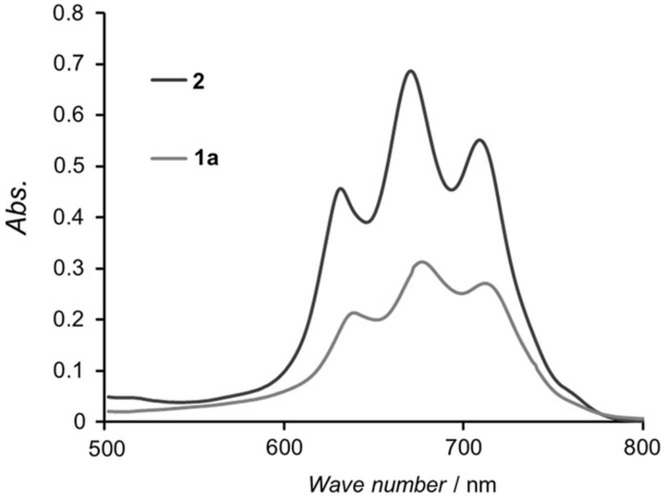
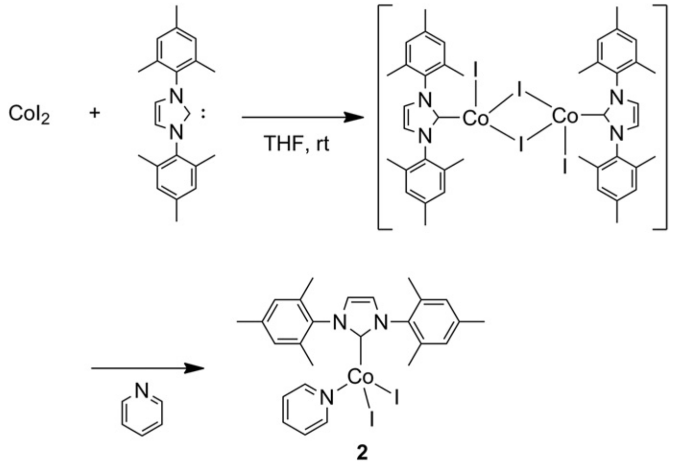


Fig. 1. UV–visible spectra for compounds **1a** and **2** in toluene (0.50 mM) in the area from 500 to 800 nm.

The structure of compound **2** was confirmed by X-ray crystallography, as shown in Fig. 2. The cobalt–carbon (C1), cobalt–nitrogen (N1), and cobalt–iodine (I1 and I2) bond distances are 2.058(8), 2.050(6), and 2.595(1) and 2.591(1) Å, respectively, which are almost the same as those of the IPr analog **1a**, 2.043(6), 2.066(3), 2.5869(7) and 2.6012(6) Å. These bond lengths are in the range of general single bond interactions. However, the C(1)–Co(1)–N(3) bond angle in the tetrahedral geometry was 111.8(3)°, that was smaller than the corresponding angle in **1a** (115.4(1)°). The other angle, C(1)–Co(1)–I(av.) was 112.0(2)°, which is also smaller than that of **1a** (115.9(1)°). The decrease of the angles in the tetrahedral geometry of **2** could be caused by the smaller methyl groups in IMes of **2** in comparison with the bulky isopropyl groups in IPr of **1a**, which could crowd the surroundings of the cobalt center. A π–π stacking interaction was found in **2** between the pyridine ring and one of the two mesityl rings; the average distance between them was 3.5 Å. This stacking interaction of the pyridine ring was not observed in **1a** because of steric hindrance caused by the two isopropyl groups in IPr. These differences are easily seen in the space-filling models of **1a** and **2** shown in Fig. 3.



Scheme 2. In situ preparation of the monomeric complex **2**.

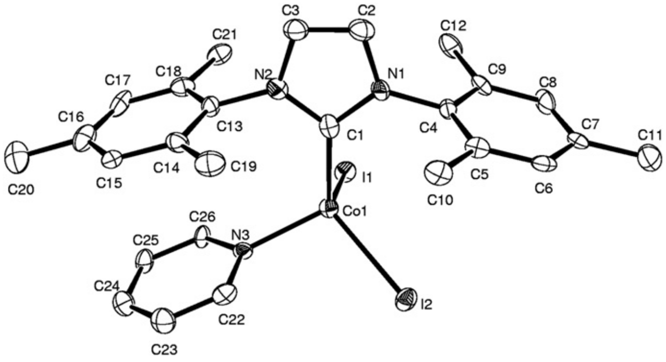


Fig. 2. ORTEP drawing of **2** (50% Probability of thermal ellipsoids). Representative bond lengths and angles are as follows: Co(1)–C(1), 2.058(8); Co(1)–N(3), 2.050(6); Co(1)–I(1), 2.595(1); Co(1)–I(2), 2.591(1) Å; C(1)–Co(1)–I(1), 105.5(2); C(1)–Co(1)–I(2), 118.5(2); C(1)–Co(1)–N(3), 111.8(3), N(3)–Co(1)–I(1), 105.9(2); N(3)–Co(1)–I(2), 103.2(2)°.