

Synthesis and characterization of hexacoordinate cobalt(III) complexes bearing three *C,O*-bidentate ligands

Hirotsuna Yamada ^a, Shiro Matsukawa ^b, Yohsuke Yamamoto ^{a,*}

^a Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan

^b Institute for Advanced Materials Research, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan

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Abstract

Hexacoordinated Co(III) complexes bearing three *C,O*-bidentate ligands (**9a** and **9b**) were prepared from 1-bromo-2-(*p*-tolylloxymethyl)benzene (**8a**) and 1-bromo-2,6-bis(*p*-tolylloxymethyl)benzene (**8b**), respectively. Both complexes were stable in air at room temperature. X-ray analyses revealed that the structures of both complexes were essentially the same. According to variable temperature ¹H NMR study, it was found that the two oxygen ligands on the same aromatic ring of **9b** interchanged with each other.

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1. Introduction

Cobalt complexes have been playing important roles in organic synthesis as typified by the Pauson–Khand reaction [1] or cyclotrimerization of alkynes [2]. In recent investigations, Oshima et al. reported many useful organocobalt-mediated coupling reactions, including the Mizoroki–Heck type reaction and allylation of tertiary alkyl halides [3]. These reactions show different properties compared with conventional coupling reactions, and are assumed to involve radical intermediates based on the reaction products.

Pincer ligands have been of great interest in the field of recent synthetic chemistry as well as in organometallic chemistry [4]. Over the past decade, a large number of investigations on the catalytic activity of metal–pincer complexes, which involves nickel, palladium, platinum, rhodium, iridium, etc., have clarified that, for example, the Pd(II)–pincer complex **1** acts as a catalyst for the Mizoroki–Heck reaction [4a], and the Ir(III)–pincer com-

plex **2** is capable of aliphatic dehydrogenation [4c]. On the other hand, although the stabilizing effect of the pincer ligand has been extensively investigated, there are only a limited number of known cobalt–pincer complexes until now [5], and compound **3** has not been fully characterized because of its air-sensitivity [5a]. Additionally, some examples of the cyclopentadienylcobalt complexes bearing a 1,3-bis(dimethylaminomethyl)benzene ligand (**4**) have been reported by Pfeffer's group, however, in those cases, one of the two amino groups did not coordinate to the cobalt atom [6] (Fig. 1).

During the course of our studies on rigid tridentate ligands for hypervalent carbon and boron chemistry [7], we reported the first full characterization of novel hypervalent carbon (10-C-5 [8]) species utilizing the 1,8-dimethoxyanthracene ligand (**5**) [7a] as well as the 10-B-5 species (**6**) [7b]. In addition, we also succeeded in the synthesis of 10-C-5 species utilizing the *C,O,O*-tridentate pincer ligand (**7**), which is more flexible than the anthracene system [7e]. In these studies, the two oxygen atoms of these ligands moderately coordinate to the central cationic carbon atom, that effectively stabilizes the novel 10-C-5 species. On the other hand, utilizing the 1,8-diaminoanthracene [7c] and

* Corresponding author. Fax: +81 82 424 0723.

E-mail address: yyama@sci.hiroshima-u.ac.jp (Y. Yamamoto).

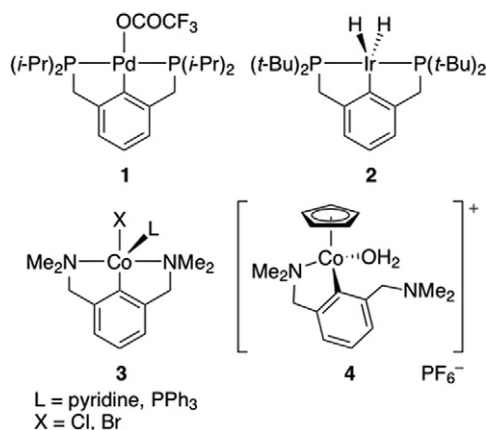


Fig. 1. Examples of organometallic species bearing a pincer ligand.

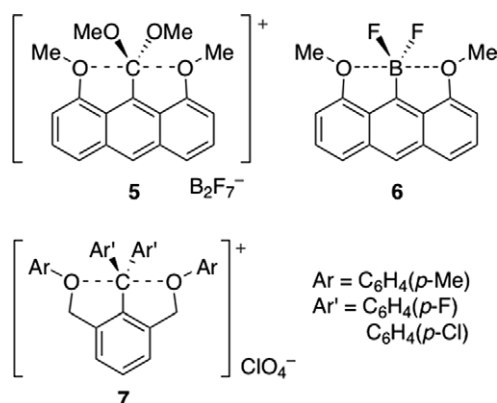


Fig. 2. Isolated hypervalent carbon (10-C-5) and boron (10-B-5) species.

C,S,S-pincer ligand systems [7e], such hypervalent carbon species, has not been observed probably due to the stronger coordinating ability of nitrogen and sulfur atoms compared to oxygen that made the tetracoordinated carbon (8-C-4) much more preferable than the pentacoordinated state (10-C-5) (Fig. 2).

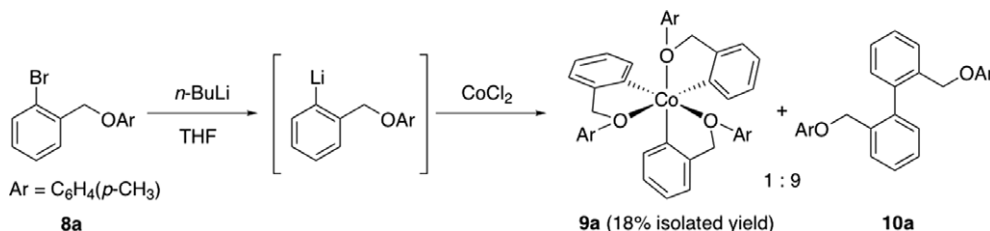
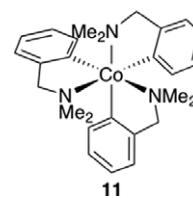
Such an oxygen-ligating multidentate ligand could be a promising solution for organocobalt catalysts because moderate coordination might make it easy to generate active species without reducing its stability during the reaction. In this study, we report the application of the *C,O,O*-pincer ligand for the synthesis of hexacoordinated organocobalt(III) complexes [9]. Structural characterization and

the dynamic process of the intramolecular ligand exchange are also described.

2. Results and discussion

2.1. Synthesis

1-Lithio-2-(*p*-tolylloxymethyl)benzene, which was generated from 1-bromo-2-(*p*-tolylloxymethyl)benzene (**8a**) [10] with *n*-BuLi in THF, was treated with anhydrous cobalt(II) chloride to afford a novel Co(III) complex **9a** along with a considerable amount of the dimer of the ligand **10a** (**9a**:**10a** = ca. 1:9 in the crude mixture) (Scheme 1). The complex **9a** was isolated in 19% yield (based on **8a**). In the case of the pincer ligand **8b** [7e], on the other hand, compound **9b** was isolated in 58% yield, and a trace amount of the corresponding dimer of the ligand was detected in the crude mixture (Scheme 2). Neither the 1:1 nor the 1:2 adduct was obtained. In each case, the cobalt(III) complex was exclusively obtained as a *fac*-isomer, which was identified by X-ray analysis (vide infra). The reaction process is the same as the reported *N,C*-bidentate system consisting of the *o*-dimethylaminomethylbenzene ligand (**11**) [9a]. For the synthesis of **9**, we could not observe any meridional isomers in both cases, which might mean that the *mer*-isomer, if it exists, decomposes during the reaction or purification process. Though the reaction mechanism is not clear, the *ortho*-disubstituted ligand **8b** is obviously effective to suppress the dimerization, which would reduce the yield of **9**, during the synthesis. Both compounds were found to be stable in air at room temperature, however, they decomposed upon heating at the melting point (159–161 °C for **9a**, and 144–146 °C for **9b**) in the solid state. These complexes are quite soluble in dichloromethane, chloroform, 1,2-dichloroethane, toluene, benzene and THF, slightly soluble in ether and acetone, and almost insoluble in hexane.



Scheme 1. Synthesis of **9a**.

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