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POBOP pincer complexes of nickel(II): Synthesis and B—H activation of the carborane ligand upon oxidation with iodine

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ABSTRACT

The (POBOP)NiCl pincer complex (POBOP = 1,7-OP(*i*-Pr)$_2$-*m*-carboranyl) was synthesized by the selective B—H activation of the chelating carboranyl ligand and structurally and spectroscopically characterized. The reaction of (POBOP)NiCl and 1 equiv. of I_2 at room temperature led to the selective iodination of the vicinal B—H bond in the complex. The reaction of (POBOP)NiCl and 7 equiv. of I_2 at room temperature led to further iodination of the ligand and dissociation of the metal from the complex.

1. Introduction

Nickel complexes have recently attracted significant attention due to their versatile reactivity in catalysis and relevance to “green” chemistry [1–5]. Rigid tridentate pincer ligand frameworks provide a promising balance between stability and reactivity of the complexes. Nickel pincer complexes have been utilized in various catalytic systems, including carbon-carbon and carbon-heteroatom coupling reactions, hydroamination, and other processes [6–13]. In addition to carbon-based pincer backbones, there is a growing number of heteroatom ligand architectures including nitrogen, silicon, and boron-based pincer complexes [14,15]. In particular, complexes containing metal-boron bonds have attracted attention due to the strong trans-influence of the ligand, the versatility of possible coordination modes, and cooperative metal-ligand reactivity [16–22]. For example, nickel-based boryl pincer complexes have been demonstrated to engage in cooperative dihydrogen activation [23,24].

Polyhedral boron clusters have been actively utilized in ligand design due to their unique steric hindrance and unusual electronic properties [25,26]. Carborane cages are often incorporated as a bulky auxiliary group attached to a heteroatom donor in phosphines, amines, and, recently, in heterocyclic carbene systems [27–32]. Furthermore, the carboranyl complexes containing a metal center directly connected to a cage through either C—M or B—M exohedral bonds have been demonstrated to provide even more dramatic steric hindrance and protection in the vicinity of the metal center [33–37]. The unique three-dimensional geometry of icosahedral boron cages enforces a close contact between vicinal B—H bonds of the cage and the exohedral metal center which differentiates carborane-based ligands from planar aryl- or pyridine-based systems. Recently, our group demonstrated the direct involvement of these vicinal B—H bonds in the aryl group transfer reactivity of carborane pincer complexes as well as the synthesis of the first example of the η^2-coordinated BB-carboryne complex by double B—H activation of two adjacent cluster vertices in the strained pincer framework [38,39].

Herein we report the synthesis of the first structurally characterized B-metalated nickel(II) carborane pincer complex and its unusual metal-ligand reactivity upon reaction with molecular iodine.

2. Results and discussion

For the synthesis of B-carboranyl pincer complexes, the POBOP ligand platform (POBOP = 1,7-OP(*i*-Pr)$_2$-*m*-carboranyl) featuring two diisopropylphosphinite donor arms connected to both carbon atoms of the *m*-$C_2B_{10}H_{12}$ carborane cage was employed. This ligand geometry has been shown to promote B—H activation of the cage upon coordination of both ligand arms to a metal center resulting in the formation of pincer complexes containing B—M bonds [35–39]. The reaction of (POBOP)H ligand precursor (POBOP = 1,7-OP(*i*-Pr)$_2$-

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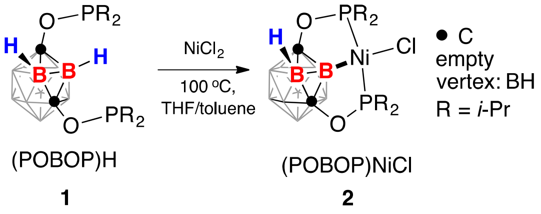
m-carboranyl) **1** and anhydrous nickel chloride in a mixture of THF and toluene at 90 °C for 18 h under nitrogen atmosphere led to the formation of one predominant product **2** with a signal in ^{31}P NMR spectrum at 206.6 ppm suggesting the coordination of both phosphinite arms to a single metal center (Scheme 1). The orange crystalline product was isolated upon recrystallization from hexanes at −30 °C in high yield (79%). The complex was found to be soluble in a majority of the commonly used organic solvents including benzene, THF, and hexanes.

Rather harsh conditions for the synthesis of **2** (reflux at 90 °C) were mainly directed by insolubility of the starting anhydrous $NiCl_2$ in organic solvents at room temperature. It is possible that the use of a molecular metal salt precursor such as $NiCl_2$(dme) (dme = dimethoxyethane) or a direct synthesis of the complex using a nickel metal powder, dialkylchlorophospine, and dihydroxycarborane would also afford **2**, similarly to the recently reported streamlined synthesis of (POCOP)NiCl complexes [40–42]. Interestingly, the use of base (triethylamine) did not change the yield of the reaction, suggesting that HCl that is formed during the synthesis did not impede formation of the complex and, possibly, partially evaporated from the reaction mixture. Initial attempts to use $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) for the metalation of the POBOP-H ligand precursor led to formation of multiple products according to ^{31}P NMR spectroscopy data and were not pursued in detail.

The NMR spectroscopy data of the diamagnetic complex **2** were congruent with the expected pincer-type structure and square-planar geometry of the nickel center. As mentioned above, two phosphorus atoms in the complex are equivalent and give rise to a signal in $^{31}P\{^1H\}$ NMR spectrum at 206.6 ppm which is shifted significantly downfield from a typical range for the related Ni(II) POCOP complexes. For instance, the (POCOP)NiCl complex bearing analogous diisopropylphosphinite arms exhibits the signal at 185.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The apparent correlation between the electronegativity of a halide ligand in (POCOP)NiX complexes (X = F, Cl, Br, and I) and the chemical shift of the pincer phosphinite arms has been noted [43]. While this correlation is an empirical observation and may seem counterintuitive, the ^{31}P NMR chemical shift for the (POBOP)NiCl complex might be caused by the stronger σ-donating ability of the metalated boron atom of the cage in comparison with the metalated carbon atom in the aryl-based (POCOP)NiCl complex. No $^{31}P{-}^{11}B$ coupling was observed in the $^{31}P\{^1H\}$ spectrum of **2**, which is typical for boryl complexes containing *cis*-phosphine ligands [22,23,38,39]. The $^{11}B\{^1H\}$ NMR spectrum contained signals in two sets of distinct regions: one single resonance at −3.5 ppm corresponding to one boron atom and a set of partially overlapping resonances in the range from −10 to −16 ppm. These upfield resonances converted to doublets in the proton-coupled ^{11}B NMR spectrum, while the signal at −3.5 ppm remained a singlet, indicating the absence of the hydride on that boron atom. This spectral pattern is consistent with the formation of the exohedral nickel-boron bond upon coordination of the metal center to donor arms of the ligand. Interestingly, the ^{1}H NMR spectrum of the complex in C_6D_6 contained only one signal from the methine CH fragments of isopropyl groups while the expected three-dimensional boron cage pincer geometry would render these isopropyl groups inequivalent for a given phosphorous atom due to the presence of both syn- and anti- orientations of CH groups relative to the vicinal B–H bond (Fig. 1c). At the same time, the ^{1}H NMR spectrum of **2** contained four sets of signals from methyl groups of the phosphinite ligand. The change of the solvent to CD_2Cl_2 led to the appearance of two methine signals, suggesting that they are accidentally isochronous in C_6D_6.



Scheme 1. Synthesis of (POBOP)NiCl complex **2**.

The yellow needle-shaped single crystals of **2** formed upon slow evaporation of a hexane solution. The X-ray crystal structure confirmed the expected square-planar geometry of the complex and successful metalation of the boron cluster (Fig. 1). The molecular structure of **2** is consistent with NMR spectroscopy data with two equivalent phosphorous atoms and inequivalent sets of isopropyl groups on each ligand arm. The B–H activation at one of the boron atoms adjacent to two carbon atoms of the cluster led to the formation of the B–Ni bond. The boron-metal distance is 1.922(3) Å, which is comparable to that in rare examples of isolated nickel boryl complexes (1.902(3)–1.928(4) Å) [23,24,44,45]. The chloride ligand (the Ni–Cl bond length 2.201(1) Å) is located *trans*-to the carboranyl. The P1–Ni1–P2 angle is 158.5(1)° which deviates from the expected linearity indicating a rather large bite angle of the POBOP ligand in comparison to the POCOP ligand (ca. 165°).

The crystal structure of **2** revealed a strain of the metal-boron bond enforced by the chelating ligand arms. The B2–B1–Ni1 angle is 102.9(2)° which is smaller in comparison to the unstrained exohedral B–H bonds in the ligand precursor **1** (the B2–B1–H1 angle is 116.1(1)°) [38]. This metal-boron bond strain is caused by the three-dimensional geometry of the carboranyl pincer ligand where the plane, which is formed by carbon atoms of the boron cluster and oxygen atoms of the phosphinite arms, is significantly shifted from the metalated boron atom (Fig. 1, right). This geometry feature contrasts typical aryl- and pyridyl-based pincers where the metalated backbone atom, ligand arms, and the metal center are essentially co-planar. It is important to note that the complex **2** is the first example of structurally characterized *closo*-carborane cluster containing an exohedral Ni–B bond.

Ni(III) complexes stabilized by chelating ligands, including pincers, have recently attracted increased attention. The use of oxidizing agents such as elemental halogens (Br_2, I_2) or N-halosuccinimides led, in some cases, to the synthesis and isolation of stable trivalent nickel species [46–52]. We attempted to oxidize the metal center in **2** with I_2.

Interestingly, the reaction of (POBOP)NiCl and one equiv. of I_2 at room temperature in THF led to the consumption of the starting material and the appearance of one new sharp signal in the ^{31}P NMR spectrum of the reaction mixture at 216.7 ppm, indicating formation of a diamagnetic complex **3** (Scheme 2). The product of the reaction was isolated by recrystallization from hexanes at −30 °C as a yellow crystalline solid in excellent yield (95%). The crystal structure of **3** revealed the unexpected activation of the B–H bond vicinal to the metal center with the formation of a new B–I bond (Fig. 2). The nickel center is divalent and diamagnetic in the distorted square-planar environment. The B–Ni bond length is 1.919(6) Å which is comparable to that in **2**. Analogously to **2**, the metal-boron bond is distorted with the B2–B1–Ni1 angle of 105.0(3)°. The B2–I1 bond length is 2.126(6) Å which is comparable to corresponding distances in iodocarboranes. The Ni1···I1 distance is 3.443(1) Å indicating no significant vicinal interaction. The B1–Ni1–I2 angle is slightly bent at 168.0(2)°.

The proton-decoupled $^{11}B\{^1H\}$ NMR spectrum of **3** contained a signal at 2.3 ppm and the set of overlapping signals from −10 to −16 ppm. The signal at 2.3 ppm remained a singlet in the proton-coupled ^{11}B NMR spectrum, indicating the absence of directly

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