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Diiminopyridine Ligands

Reactions of BCl_3 with Diiminopyridine Ligands

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Abstract: The reactions of boron trichloride with diiminopyridine ligands featuring 2,6-diisopropylphenyl groups on the imine nitrogen atoms and varying groups on the α-carbon atoms (H, CH_3, and Ph) were investigated. *N*,*N*′-chelated cationic BCl_2 complexes with BCl_4^- counteranions were isolated with the hydrogen and phenyl-substituted ligands while a mixture was obtained for the methyl variant.

Introduction

Transition metal complexes with diiminopyridine ligands (DIMPY) have been widely studied with many compounds being implicated in catalysis,[1] including olefin polymerization,[2] borylation,[3] cycloaddition,[4] hydrogenation,[5] and hydrosilylation reactions.[5,6] The rigidity of the conjugated imine and pyridine tridentate framework typically results in meridional coordination and serves as a redox reservoir for the metal center to engender unique properties and reactivity.[7] The substituents on both nitrogen and the α-carbon atoms can be varied and serve as a method to tune the catalytic activity and subsequent reactivity.[1b]

In contrast to the chemistry of DIMPY ligands with the d-block,[8] which is well developed, for the remaining elements it is emerging. The f-block has garnered attention with uranium,[9] lanthanum,[10] neodymium,[10] and lutetium complexes having been prepared.[11] In regard to the s-block,[12] alkali metals are often used to reduce the ligand and directly react with the metal precursors in situ while Jones and co-workers recently reported the complement of alkaline earth DIMPY complexes (save beryllium).[13] Within the p-block, all row 3–5 DIMPY complexes have been isolated for group 13–16 elements with the exception of antimony and silicon.[14] Notably, unusual electronic structures have been isolated such as low oxidation state species [i.e. Ge^0, In^I, and P^I][14c,14e,14k] as well as exotic dications (P^{2+}, S^{2+}, Se^{2+}, and Te^{2+}).[14i,15]

For group 13 compounds, Jones and co-workers first demonstrated reactions of "GaI" with a diiminopyridine ligand generate the *N*,*N*′,*N*′′-chelated GaI_2 cation with a GaI_4 counteranion (**A**, Figure 1).[16] Recently, the Berben group has made significant headway on *N*,*N*′,*N*′′-chelated aluminum species accessing a variety of ligand redox states and even applying them in catalytic reduction reactions of small molecules (**B**).[7a,7c,17] Reacting $InCl_3$ with a DIMPY ligand furnished an $InCl_2$ complex analogous to **A** with an $InCl_4$ anion but with indium triflate, a In^I species was obtained that had weak interactions with the two imine nitrogens (**C**).[14c] No example of a Tl^{III} compound exists but a Tl^I species has been prepared from TlOTf akin to the In^I species but with even weaker interactions with the DIMPY framework.[14l] In all of known examples, the three nitrogens interact with the group 13 element. No boron DIMPY complexes have been prepared to date. We herein report the reactions of diiminopyridine ligands with boron trichloride.

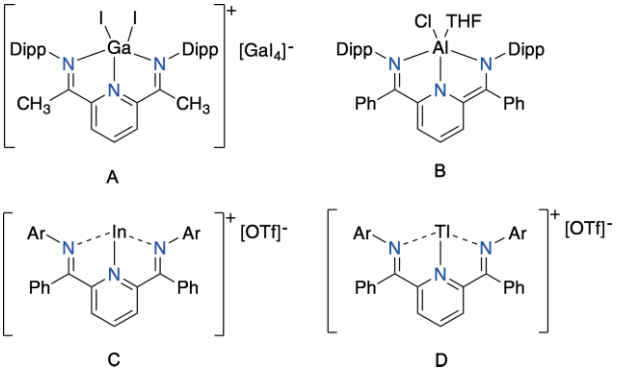

Figure 1. Selected examples of group 13 DIMPY complexes (Dipp = 2,6-$iPr_2C_6H_3$, Ar = 2,5-$tBu_2C_6H_3$).

The 2:1 stoichiometric reactions of diiminopyridine ligands bearing 2,6-diisopropylphenyl groups (Dipp) and hydrogen (**1H**), methyl (**1CH$_3$**), and phenyl (**1Ph**) substituents on the α-carbon atoms with boron trichloride were conducted at room temperature (Scheme 1). In situ monitoring by ^{11}B NMR spectroscopy indicated consumption of BCl_3 with the absence of the resonance at 46.7 ppm in 2 h for **1H** and 24 h for both **1CH$_3$** and **1Ph**. In each spectrum, two peaks were observed (**1H**: 9.0 and 7.1 ppm, **1CH$_3$**: 9.2 and 6.9 ppm, **1Ph**: 9.2 and 6.9 ppm) with the sharp peaks at ≈ 7 ppm consistent with a BCl_4^- anion[18] and the peaks at ≈ 9 ppm corresponding to four-coordinate boron species. Crystals from each of the three reactions were grown and single-crystal X-ray diffraction studies revealed the identity to be κ^2-*N*,*N*′-chelated BCl_2 cationic complexes in which the nitrogen atom of the pyridine ring and one imine

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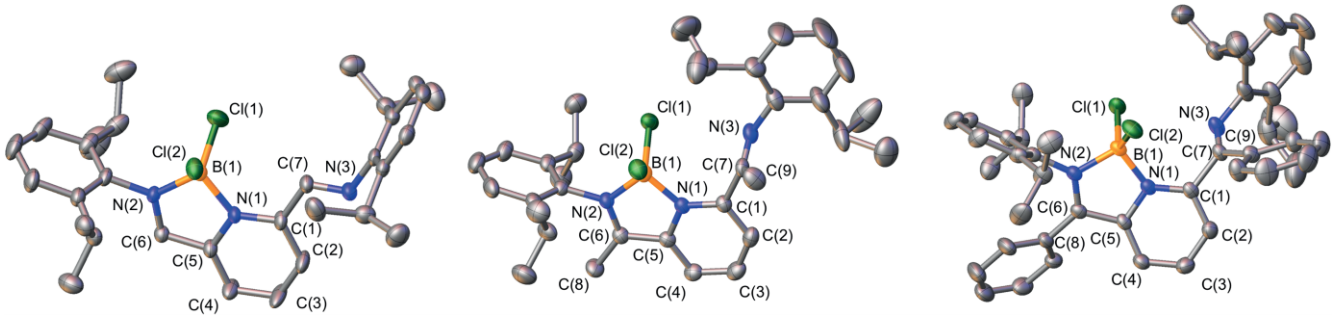
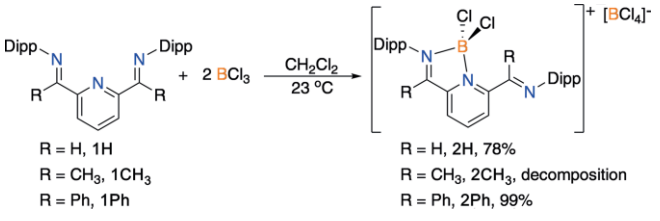


Figure 2. Solid-state structures of **2H**, **2CH$_3$**, and **2Ph** (left to right). Thermal ellipsoids are drawn at the 50 % probability level. All hydrogen atoms, solvent molecules, and counteranions are omitted for clarity. For positionally disordered atoms, only the major component is shown.

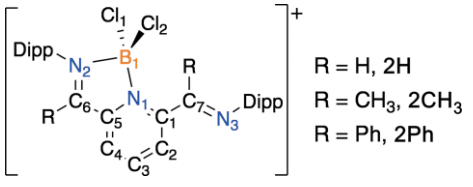
nitrogen of the ligand are coordinated to boron with a BCl_4^- counteranion (**2H**, **2CH$_3$**, and **2Ph**; Figure 2). The other imine is a spectator oriented away from boron. The peaks at ≈ 9 ppm in the ^{11}B NMR spectra are assigned to the chelated boron centers. Acquiring crude ^{1}H NMR spectra of the reactions with **1H** and **1Ph** revealed clear major products. The crude spectrum for the reaction with **1CH$_3$** indicated a complex mixture that decomposed over time. After workup, boron complexes **2Ph** and **2H** were isolated in good yields (99 % and 78 %, respectively) while we were unable to isolate clean **2CH$_3$**. The methyl-substituted ligand **1CH$_3$** differs from the other two ligands as it can tautomerize to the enamine.[19] This has been problematic in chemistry with the related 1,4-diazabutadiene ligands[20] as well as other reactions of main group reagents with **1CH$_3$** with mixtures reported for some examples[14k] and isolation of *N,N′,C*-bound species in the cases of Se[14f] and Te.[14f,14j]



Scheme 1. Reactions of BCl_3 with **1H**, **1CH$_3$**, and **1Ph**. Reaction times, **2H** = 2 h, **2CH$_3$** = 24 h, **2Ph** = 24 h.

^{1}H NMR spectroscopy was particularly diagnostic for **2Ph** since **1Ph** contains broad resonances at room temperature due to the bulk of the phenyl groups restricting rotation on the NMR timescale.[14b] In contrast, the ^{1}H NMR spectrum of **2Ph** is resolved at 23 °C, rationalized by locking the conformation as a result of chelation. The ^{1}H NMR spectrum of both **2Ph** and **2H** revealed inequivalent resonances for the *meta*-protons on the pyridine ring, consistent with a break in symmetry in the ligand framework from *N,N′*-chelation with the resonances shifted downfield from the free ligands (**1Ph**: 7.87[14b,21] cf. **2Ph**: 8.25 and 8.76 ppm; **1H**: 8.40[22] cf. **2H**: 9.26 and 9.65 ppm). The compounds all share the same framework, enabling a direct comparison of their structures (Table 1). The boron–nitrogen bond lengths are all between 1.581(5)-1.597(4) Å without differentiation between the imine and pyridine B–N bond lengths. There is no interaction between the other imine nitrogen and the chelated boron in any of the three structures. The C=N bonds are marginally longer for the imine coordinated to boron than the uncoordinated imine {range 1.277(4)-1.300(4) Å cf. 1.256(4)–1.272(4) Å}.

Table 1. Salient bond lengths of the cations in **2Ph**, **2CH$_3$**, and **2H**.



	2Ph	2H	2CH$_3$
B(1)–N(1)	1.581(5)	1.592(4)	1.582(6)
B(1)–N(2)	1.597(4)	1.594(4)	1.589(6)
B(1)–Cl(1)	1.803(4)	1.796(3)	1.815(5)
B(1)–Cl(2)	1.816(4)	1.814(3)	1.810(5)
C(1)–N(1)	1.344(4)	1.343(3)	1.347(5)
C(5)–N(1)	1.365(4)	1.365(3)	1.357(5)
C(7)–N(3)	1.272(4)	1.256(4)	1.265(6)
C(6)-N(2)	1.300(4)	1.277(4)	1.290(5)
C(1)–C(7)	1.508(4)	1.482(4)	1.503(6)
C(5)–C(6)	1.467(4)	1.446(4)	1.468(6)
C(1)–C(2)	1.390(5)	1.396(4)	1.387(6)
C(2)–C(3)	1.379(5)	1.369(5)	1.373(7)
C(3)–C(4)	1.383(5)	1.393(4)	1.385(7)
C(4)–C(5)	1.369(5)	1.366(4)	1.368(6)

The reactions between DIMPY ligands bearing different substituents at the α-carbon with boron trichloride afforded κ^2-*N,N′*-chelated BCl_2 species. The phenyl and hydrogen substituted complexes were isolable, while the methyl-substituted complex was not, attributed to the susceptibility of the ligand toward imine/enamine tautomerization. The resulting complexes complete the series of group 13 DIMPY complexes and represent the first row two p-block DIMPY complexes.

Deposition Numbers 2007651 (for **2H**), 2007652 (for **2CH$_3$**), and 2007650 (for **2Ph**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Keywords: Boron · Coordination chemistry · Diiminopyridine ligands · Structure elucidation

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