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Aluminabenzene-Rh and -Ir Complexes: Synthesis, Structure, and Application toward Catalytic C-H Borylation

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Supporting Information Placeholder

ABSTRACT: Aluminabenzene-rhodium and -iridium complexes were synthesized, in which the aluminum atom played as a proximal Lewis acidic site. Based on their structural analysis, aluminabenzene ligand could coordinate to Rh and Ir as a η^5 -pentadienyl ligand. The Lewis acidic character of aluminum atom in aluminabenzene ligand was confirmed by a treatment with 4-dimethylaminopyridine (DMAP) to form the corresponding Lewis acid-base complexes. In addition, the α -selective C-H borylation of triethylamine with the aluminabenzene-ligated iridium catalyst was demonstrated.

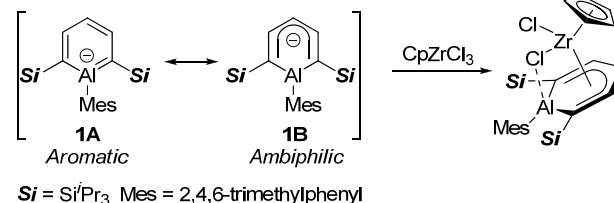
Transition metal complexes with ligands bearing a group 13 element show a variety of structure and reactivity due to its Lewis acidity inducing Z-type coordination mode.¹ Cooperative intramolecular interaction of metal center and Lewis acidic moiety can activate various small molecules.^{2,3} However, such cooperative interaction of metal and Lewis acid has rarely applied to catalytic reactions.³ The limited examples are (a) catalytic hydrogenation of alkenes and alkynes by using Ni-borane, Fe-borane, and Ru complexes bearing pendent borane group, and (b) catalytic dehydrogenation/transfer hydrogenation of aminoborane using Co-PBP pincer complex.^{3,4}

On the other hand, the regioselectivity of catalytic C-H borylation is generally controlled by the steric environments.⁵ To control the regioselectivity, directing groups on substrates,⁶ remote steric hindrance of ligand,⁷ bulky Lewis acid capturing substrate,⁸ and interaction between substrate and ligand such as hydrogen bonding, ion pairing, electrostatics, and complexation with alkali metal,⁹⁻¹³ have been reported. Thus, the interactions between substrate and catalysts are found to be useful strategy for the selective C-H borylation. In this context, Lewis acid-base interaction has also been applied to catalytic borylation. Hartwig pointed out that the boron atom of intermediate boryl complex could interact with nitrogen atom of ethylamine substrates in β -selective borylation.¹⁴ Kanai and Kuninobu reported *ortho*-selective C-H borylation of aryl sulfides by utilizing Lewis acid-base interaction between a pendent boryl group on ligand and thioether substrate.¹⁵

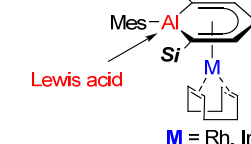
Recently, we reported an isolation of the first anionic aluminabenzene, which has aromatic and ambiphilic resonance contributions as a lithium salt (**1A** in Figure 1).^{16a} It is noteworthy that the aluminum atom in **1** shows Lewis acidic character even with a net negative charge, confirmed by the Lewis acid-base interaction

with DMAP. Since the ambiphilic structure consists of the pentadienyl anion moiety and Lewis acidic aluminum atom (**1B** in Figure 1), the aluminabenzene **1** could coordinate to the zirconium in η^5 -fashion.^{16b} Due to the η^5 -coordination mode of aluminabenzene ligand, the aluminum atom shows intramolecular coordination to the lone pair on chloride ligand on zirconium, indicating the Lewis acidic character of the aluminum atom. Herein, we report synthesis of aluminabenzene-Rh and Ir complexes as the first examples of aluminabenzene-late transition metal complex (Figure 1, bottom). The Lewis acidic character of the aluminum atom in aluminabenzene ligand was confirmed by a reaction with an external Lewis base. The resulting aluminabenzene-Ir complex was applied as catalyst for α -selective C-H borylation of NEt_3 . In this borylation reaction, the internal CH_2 could be borylated rather than the sterically favorable terminal CH_3 group.

Previous works



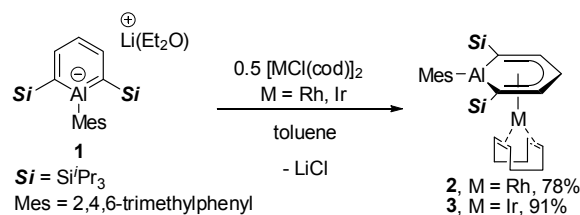
This work



Synthesis
Structural Analysis
Reaction toward Lewis Base
Catalytic α -C-H Borylation of NEt_3

Figure 1. Complexation of ambiphilic aluminabenzene with transition metal complexes

The aluminabenzene-Rh complex **2** was synthesized by the reaction of anionic aluminabenzene **1** with $[\text{RhCl}(\text{cod})]_2$ in 78% yield (Scheme 1). In the same manner, the aluminabenzene ligand could be introduced to Ir to give aluminabenzene-Ir complex **3** in 91% yield. The resulting **2** and **3** were characterized by ^1H and ^{13}C spectroscopy, HRMS, and X-ray crystallography.

Scheme 1. Synthetic scheme for **2** and **3**

The crystal structures of **2** and **3** were shown in Figure 2. These complexes have similar structures, being aluminabenzene-capped metal-diene structure. M-Al1 distances [2.8168(12) Å for **2**, 2.7901(13) Å for **3**] were quite longer compared to the corresponding coordination bond [2.4581(8) Å]¹⁷ between Rh(I) and Z-type dialkylchloroaluminum ligand. In the aluminabenzene ligand, the six-membered ring was almost planar (sum of the inner bond angles: 720°). Planarity of sp^2 hybridized aluminum atom was confirmed by the sum of the bond angles around aluminum to 360° in **2** and **3**. According to the results, the tangible interaction between the aluminum atoms and metals could not be observed. M- C_{para} distances [2.151(4) Å for **2**, 2.174(4) Å for **3**] and M- C_{meta} distances [2.316(4), 2.313(4) Å for **2**, 2.299(4), 2.307(4) Å for **3**] were similar to C-Ir bond length [2.1476(19)-2.2861(17) Å] in $\eta^5\text{-(Z,Z)}\text{-pentadienyl Ir(I)}$ complex.¹⁸ However, M- C_{ortho} distances [2.522(4), 2.572(4) Å for **2**, 2.485(4), 2.533(4) Å for **3**] were longer maybe due to steric repulsion of bulky $i\text{Pr}_3\text{Si}$ and Mes group toward cod ligand. In the aluminabenzene ligand, $C_{ortho}\text{-}C_{meta}$ lengths [1.391(5), 1.405(5) Å for **2**, 1.407(6), 1.400(6) Å for **3**] were almost same to those in the previously reported cation-free anionic aluminabenzene. In contrast, $C_{meta}\text{-}C_{para}$ lengths [1.433(5), 1.439(5) Å for **2**, 1.432(6), 1.443(6) Å for **3**] and Al- C_{ortho} lengths [1.940(4), 1.942(4) Å for **2**, 1.927(4), 1.933(5) Å for **3**] were slightly longer than those in cation-free anionic aluminabenzene.

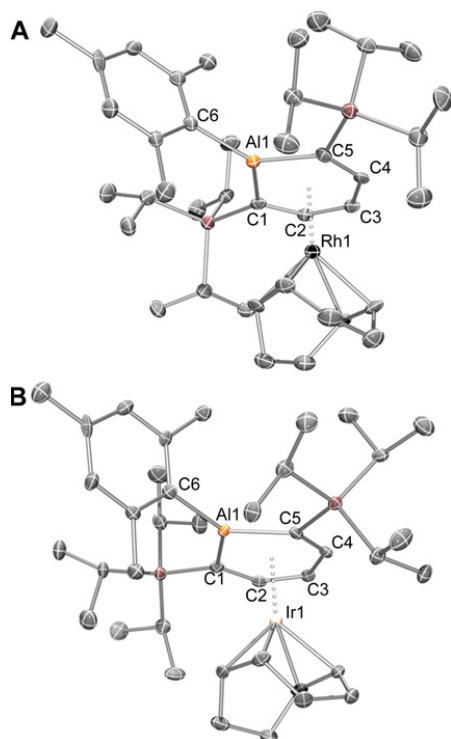
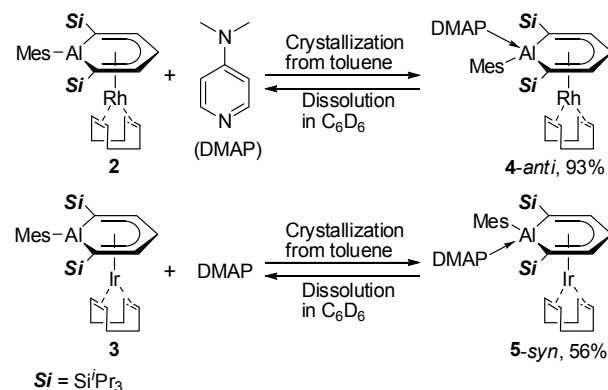


Figure 2. Crystal structures of **2** (A) and **3** (B) (50% thermal ellipsoid probability). Hydrogen atoms are omitted for clarity.

Z-type coordination mode has been known to have electron donation from an occupied d-orbital on the metal center to an unoccupied orbital on Lewis acidic atom.¹ To consider the existence of Z-type Al-M ($\text{M} = \text{Rh, Ir}$) interaction, we performed DFT calculations.^{19,20} The optimized structures of **2** and **3** reproduced the experimentally observed structures. The HOMO in **2** and **3** consisted of π orbital of $C_{ortho}\text{-Al-C}_{ortho}$ unit on the aluminabenzene ring, d-orbital of Rh or Ir, and π orbital of cyclooctadiene ligand (Figure S23 and S24). Although the orbital overlapping between aluminum and metal was observed in both cases, the second-order perturbation energy by electron donation from d-orbital on metal to the vacant orbital of the aluminum atom was calculated to be only 2.0 kcal/mol for **2** and 2.4 kcal/mol for **3**, reflecting long Al-M distances in crystal structures.

Despite of the weak interaction between metal and aluminum atoms, the aluminum atom in **2** and **3** would have Lewis acidic character. Thus, we investigated the formation of Lewis acid-base complex. Although the reaction of **2** and **3** with DMAP showed no evidence for the formation of the Lewis base adducts in solution as judged by NMR spectroscopy, recrystallization of the reaction mixture gave crystals of DMAP adducts **4-anti** and **5-syn** (Scheme 2), indicating the Lewis acidic character of the aluminum atom. The structures of **4-anti** and **5-syn** were confirmed by X-ray crystallographic analysis (Figure 3).

Scheme 2. Reactions of **2** and **3** with DMAP

In **4-anti**, DMAP coordinated to the aluminum atom from an opposite side of Rh. However, DMAP coordinated to iridium from the same side to Ir in **5-syn**. The Al atoms in both complexes were bent away from the metals [M-Al distances: 3.1576(9) Å for **4-anti**, 3.154(2) Å for **5-syn**]. The Al-N1 bond lengths [2.020(2) Å for **4-anti**, 1.991(5) Å for **5-syn**] were shorter compared to the coordination of DMAP to aluminum atom [2.030(3) Å] in the anionic aluminabenzene.^{16a} In **4-anti**, the Rh- C_{ortho} distances between rhodium and carbon atoms [2.728(3), 2.534(2) Å] were elongated relative to those of **2**, probably due to the steric repulsion between Rh(cod) and mesityl moieties, while the Ir- C_{ortho} distances of **5-syn** [2.224(5)-2.544(7) Å] were comparable to those of **3**. To understand the reason why the coordination mode was different in **4-anti** and **5-syn**, the relative energies between two isomeric pairs were calculated (Figure S25). In both of Rh and Ir cases, the energy differences between *anti*- and *syn*-isomers were estimated to be small (< 2 kcal/mol, See SI). Thus, these DMAP adducts and DMAP-free complexes would exist as an equilibrating mixture. By taking advantages of the crystal packing force, the experimentally observed isomers **4-anti** and **5-syn** might be crystallized. In fact, the coordinated DMAP dissociated by the dissolution of **4-anti** and **5-syn** into C_6D_6 , as judged by ^1H NMR spectra.²¹ These results indicate that the aluminum atom in **2** and **3** can act as an weak Lewis acid.

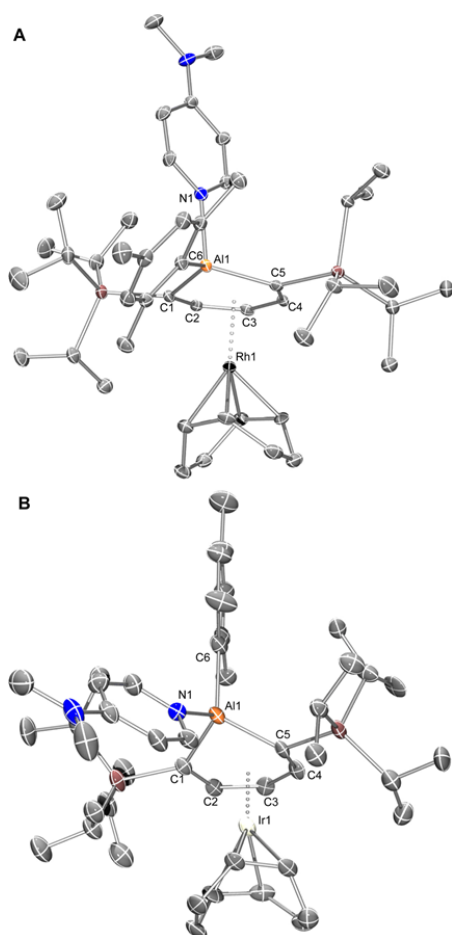
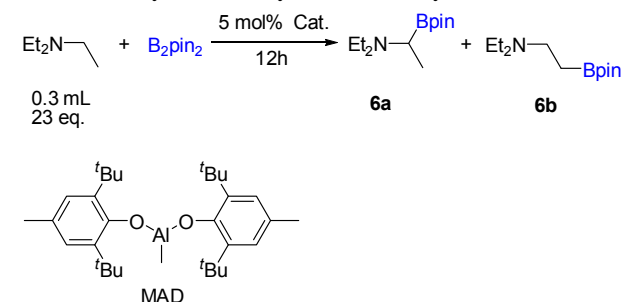


Figure 3. Crystal structures of **4-anti** (A) and **5-syn** (B) (50% thermal ellipsoid probability). Hydrogen atoms are omitted for clarity.

Next, we applied **3** as a catalyst for C-H borylation of the substrate with Lewis basic moiety. After the screening of the various substrates bearing Lewis basic moiety, we found that NEt_3 could be selectively borylated at the α -C-H position by using the aluminabenzene-Ir complex **3** as a catalyst (Table 1). In the presence of **3** (5 mol%), α -C-H of NEt_3 could be borylated to give **6a** in 83% yield with terminal borylated byproduct **6b** in neat NEt_3 (Table 1, Entry 1). Generally, the C-H borylation proceeds at sterically less-hindered terminal CH_3 as Hartwig reported that the borylation of NEt_3 by $(\eta^6\text{-mes})\text{Ir}(\text{Bpin})_3$ catalyst gave the β -borylated product selectively (Table 1, Entry 2).^{14a} In addition, using the well-known C-H borylation catalysts, such as $\text{Cp}^*\text{Rh}(\text{C}_6\text{Me}_6)$ and $[\text{IrOMe}(\text{cod})]_2$, the exclusive formation of the terminal C-H borylated product **6b** was observed (Table 1, Entry 3,4). Thus, complex **3** could proceed α -C-H borylation of NEt_3 , being the first example of the internal C-H selective borylation of acyclic trialkylamine without strong directing group. To gain insight into the effect of the Lewis acidic aluminum, the borylation using DMAP adduct **5-syn** was investigated. However, the activity of **5-syn** was low and required higher temperature to form the borylated product with low selectivity (Table 1, Entry 5,6). Although **5-syn** should dissociate to form catalytic amount of **3** and DMAP as mentioned above, the catalytic activity and selectivity was significantly decreased. This result suggests that the catalytically active species, such as boryliridium complex bearing aluminabenzene ligand, might be deactivated by the coordination of DMAP to the aluminum atom. Dissociation of DMAP from the deactivated species at higher temperature would provide the cata-

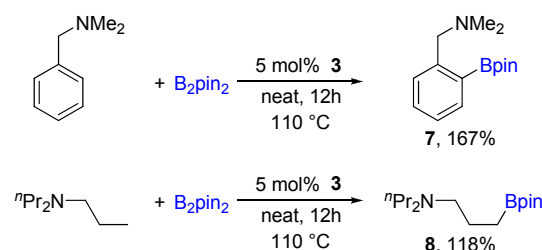
lytic activity. Thus, this result suggests the presence of the Lewis acidic aluminum site would be required for the selective α -C-H borylation of NEt_3 . As a control experiment, the borylation with $[\text{IrOMe}(\text{cod})]$ in the presence of an external Lewis acid, MAD [methylaluminum bis(2,6-di-*tert*-butyl-5-methylphenoxy)], which has been known as an additive for borylation of heteroarenes^{8,22}, was carried out (entry 7). However, in this borylation, the α -C-H borylated product **6a** was not obtained, suggesting the presence of Lewis acidic aluminum at proximal position to Ir would be effective for the α -C-H selectivity. Other substrates were also examined under the same condition to entry 1 of Table 1 (Scheme 3). Borylation of *N,N*-dimethylbenzylamine using **3** selectively proceeded at *ortho*-position of benzene ring without detectable amount of α -borylated product.²³ Bulkier amine, N^tPr_3 , than NEt_3 was borylated by catalyst **3** at the terminal CH_3 group exclusively, suggesting that the α -C-H selective borylation using **3** is sensitive to the steric bulkiness of amine. In the case of Bu_2O , the borylation gave only trace amount of the terminal C-H borylated product (< 2%) even at higher temperature (140 °C). The weaker donor such as MeSPh did not undergo catalytic borylation with **3** probably catalyst decomposed faster than the substrate reacted. It should be noted that the borylation of *n*-octane did not proceed at all (See SI for detail), suggesting the Lewis basic character of the substrate would be effective. Although the mechanism is unclear at the present stage, we assume that the regioselective C-H borylation might be achieved through the formation of Lewis acid-base complex of **3** and NEt_3 followed by the C-H activation by Ir at the proximal α -C-H position.

Table 1. Catalytic C-H borylation of triethylamine^a



Entry	Cat.	Temp. / °C	Yield ^{b,c} / %	
			6a	6b
1	3	110	83	21
2 ^d	$(\eta^6\text{-mes})\text{Ir}(\text{Bpin})_3$	120	– ^d	103
3	$[\text{IrOMe}(\text{cod})]_2$	90	0	19
4	$\text{Cp}^*\text{Rh}(\text{C}_6\text{Me}_6)$	90	0	114
5	5-syn	110	0	0
6	5-syn	140	22	29
7	$[\text{IrOMe}(\text{cod})]_2$ + MAD	110	0	11

^aReaction conditions: Cat. (5 mol%), NEt_3 (0.3 mL), B_2pin_2 (0.100 mmol), neat, 90–140 °C, 12h. ^bYields were determined based on B_2pin_2 by ^1H NMR spectroscopy. ^cDue to the borylation with HBpin formed by the borylation with B_2pin_2 , the yields were estimated to be higher than 100%. ^dref. 14a. ^enot reported.

Scheme 3. Control experiments with other substrates (See SI for details)

In summary, the aluminabenzene-Rh and Ir complexes were synthesized as the first example of aluminabenzene late transition metal complex. Based on the structural analysis and reactivity, aluminabenzene ligand could coordinate to Rh and Ir as η^5 -pentadienyl ligand having Lewis acidic aluminum atom. Aluminabenzene-Ir complex **3** could be used as C-H borylation catalyst. We demonstrate the selective α -C-H borylation of NEt_3 using **3** as the catalyst. While the role of the Lewis acidic aluminum atom in aluminabenzene ligand was not clear in the present stage, the Lewis acidic aluminum atom in aluminabenzene ligand would be required for the regioselectivity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publication Website at DOI: 10.1021/jacs. Experimental Procedures, X-ray crystallographic analysis, DFT calculations, and full citation of reference 19.

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Notes

The authors declare no competing financial interests.

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