

Synthesis of A Pincer-Ir(V) Complex with A Base-Free Alumanyl Ligand and Its Application toward Dehydrogenation of Alkanes

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Abstract: A pincer-iridium complex bearing a Lewis-base-free X-type alumanyl ligand was synthesized. X-ray diffraction study, NMR, IR and XANES analysis confirmed its tetrahydrido-Ir(V) structure and Lewis acidity at the Al center as supported by DFT calculations. The resulting complex was applied as a catalyst for transfer dehydrogenation of cyclooctane.

PXP pincer ligands, consisting of two phosphine-tethers and an anionic X-ligand, have widely been applied in organometallic chemistry by using the characteristic electronic features of the central X atom and high thermal stability.¹ Recently, group 13 elements have attracted attention as the anionic X-ligand of PXP pincer ligand in the viewpoint of its stronger σ -donating property due to their small electronegativity.² For example, our group reported the synthesis, various bond cleavage reactions, and catalytic application of group 8-10 transition metal complexes bearing a phosphine-tethered boryl (PBP pincer) ligand (**A** in Figure 1).³ Peters and Lin utilized the lability of boryl ligand in PBP-Co/Ni complexes for catalytic hydrogenation of olefin.⁴ Ozerov explored chemistry of PBP*-pincer complexes **B** having a carbon-based backbone, including oxidative addition of C–B bond and its reverse reaction, catalytic dehydrogenation of alkanes, and stoichiometric C–H activation of pyridine.⁵

By contrast to the rich chemistry of anionic X-type boryl ligand for transition metal complexes,⁶ chemistry of anionic X-type alumanyl ligand⁷ has been behind. In fact, only three transition metal complexes having an unsupported X-type alumanyl ligand have been reported to date.⁸⁻¹⁰ Addition of Lewis base¹¹ and bridging coordination mode to two metals¹² have also been known to synthesize alumanyl complexes. Among them, only two examples of base-stabilized alumanyl complexes have been used as a homogeneous catalyst. Nakao reported C2-selective monoalkylation of pyridine by using Rh complex **C** bearing a base-stabilized ^NPAIP-pincer ligand as a catalyst,^{11h} in which the alumanyl ligand increases electron density on the Rh center and provides a Lewis acidity leading to the high selectivity.¹³ Takaya and Iwasawa reported a highly active catalyst consisting of Pd

complex **D** bearing a terpyridine-coordinated alumanyl ligand (^{N,N,N}PAIP pincer ligand) and cesium pivalate for hydrosilylation of CO₂.^{11fj} Thus, there has been no example for a homogeneous catalyst with Lewis-base-free alumanyl ligand. Herein, we report the synthesis of a PAIP-pincer iridium complex bearing a Lewis base-free alumanyl ligand. The structure, electronic property, reactivity toward Lewis base, and catalytic activity for transfer dehydrogenation of cyclooctane were also investigated.

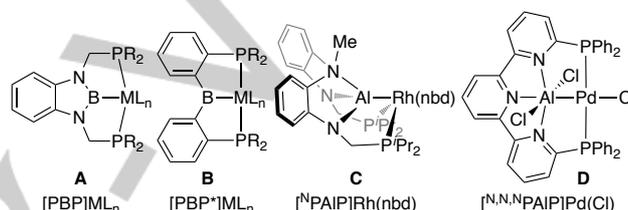
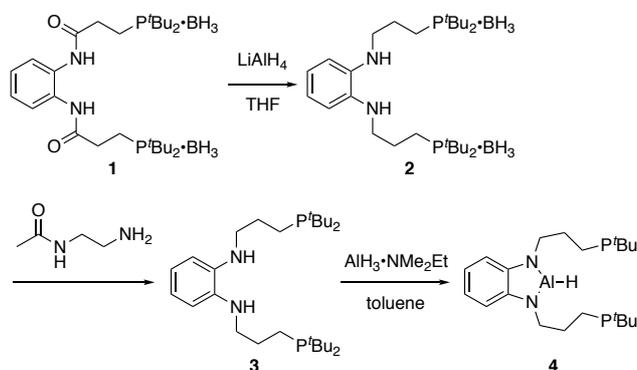


Figure 1. Selected examples of transition metal complexes bearing anionic group 13 ligands. R = alkyl, aryl; M = metal; L = ligand.

To introduce a larger Al atom than B atom, we focused on the long-tethered scaffold of previously reported PBP-pincer iridium complex.¹⁴ The PAIP pincer ligand precursor **4** was synthesized with a slightly modified procedure for the preparation of the PBP pincer ligand precursor (Scheme 1).¹⁴ Reduction of phosphinoborane-tethered phenylenediamine **1** with LiAlH₄ followed by hydrolysis afforded **2**. Deprotection of the phosphine-borane moiety of **2** with *N*-acetythylenediamine resulted in the formation of **3**. Reaction of **3** with AlH₃·NMe₂Et provided phosphine-tethered Al–H precursor **4**. The IR spectrum of **4** showed a characteristic absorption band at 1861 cm⁻¹, being assignable to an Al–H stretching vibration, which was similar to those of previously reported diaminoaluminum hydrides.¹⁵



Scheme 1. Synthesis of the PAIP Pincer Ligand Precursor **4**.

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Complexation of **4** with $[\text{Ir}(\text{cod})\text{Cl}]_2$ (cod = 1,5-cyclooctadiene) in toluene at 100 °C led to an isolation of $[\text{PAIP}]\text{Ir}(\text{H})_4$ **5** (Scheme 2).¹⁶ The ^1H NMR spectrum of **5** showed two different signals each having 2H integral ratio in the hydride region (Figure S12): a broad singlet signal at $\delta_{\text{H}} -11.40$ ppm (fwhm = 23 Hz, $T_1 = 420$ ms) and a broad triplet of triplet signal at $\delta_{\text{H}} -12.52$ ppm ($^2J_{\text{HH}} = 16$ Hz, $^2J_{\text{PH}} = 3$ Hz, $T_1 = 362$ ms), which are assignable to the four hydride ligands around the Ir center.^{17,18} The long relaxation time T_1 for both signals also supported four hydrogen atoms attached to the Ir center as hydride ligand rather than dihydrogen ligand.^{19,20} Two phosphorus atoms in **5** resonated as one singlet signal at $\delta_{\text{P}} 64.5$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The IR spectrum also confirmed the existence of four hydride ligands around the Ir center (ν_{IrH} 1802 and 2110 cm^{-1}).²¹ Complex **5** was thermally stable even in *o*-xylene solution at 150 °C as judged by the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The solid-state structure of **5** is shown in Figure 2. All four hydride ligands around the Ir center were assigned to the residual peaks in the differential Fourier map. The Al–Ir bond [2.3819(14) Å] is apparently shorter than the sum of covalent radii of Al and Ir atoms (2.51 Å),²² and is shortest hitherto reported for Ir complexes bearing an Al atom in the coordination sphere.²³ The slightly shorter N–Al bonds [1.812(4), 1.818(4) Å] in **5** than those of previously reported $^{\text{N}}\text{PAIP-Rh}$ complexes (1.822–1.884 Å)^{11h} indicated $\text{p}\pi\text{-p}\pi$ interaction between N and Al atoms in **5**.^{11h} However, a significant Lewis acidity of the Al atom in **5** was confirmed by a coordination of an external Lewis base. The reaction of **5** with DMAP immediately proceeded at room temperature to form **6** quantitatively (Scheme 2).²⁴ In the solid-state structure of **6** (Figure 3), the Al–Ir bond length elongated to 2.4779(11) in comparison with that of **5** by the coordination of DMAP, caused by re-hybridization of the Al atom from sp^2 in **5** to sp^3 in **6**. The bond length between the coordinated nitrogen atom N3 and Al atom [2.037(3) Å] was comparable to those observed in $[\text{N}^{\text{PAIP}}]\text{Rh}(\text{CO})_2$ (2.071(3), 2.094(3) Å).⁹

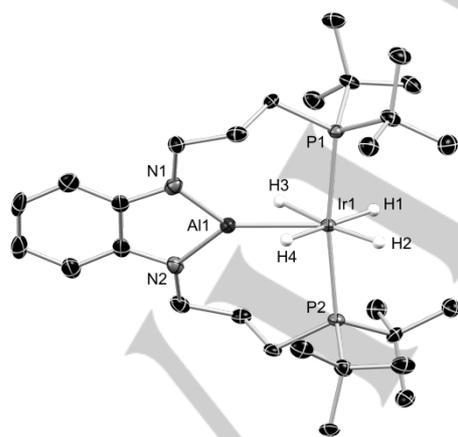
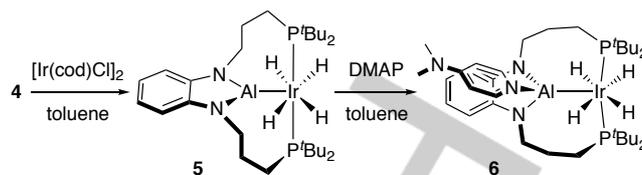


Figure 2. Molecular structure of **5** obtained by single-crystal X-ray diffraction analysis. Thermal ellipsoids are displayed at 50 % probability. All hydrogen atoms except for hydride ligand are omitted for clarity. Selected bond distances (Å) and angles (°): Al1–Ir1 2.3819(14), P1–Ir1 2.3232(11), P2–Ir1 2.3275(11), N1–Al1 1.812(4), N2–Al1 1.818(4), P1–Ir1–P2 170.50(4), N1–Al1–N2 90.75(19).



Scheme 2. Synthesis of ^tBu -Substituted $[\text{PAIP}]\text{Ir}(\text{H})_4$ **5** and its DMAP adduct.

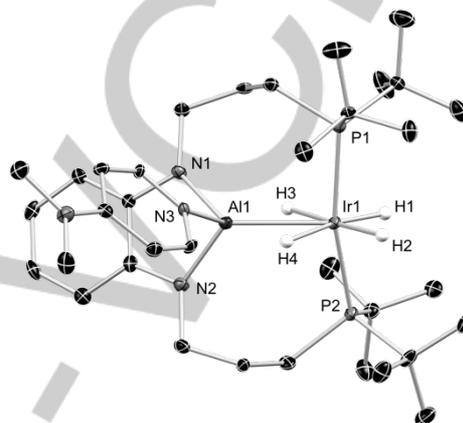


Figure 3. Molecular structure of **6** obtained by single-crystal X-ray diffraction analysis. Thermal ellipsoids are displayed at 50 % probability. All hydrogen atoms except for hydride ligand are omitted for clarity. Selected bond distances (Å) and angles (°): Al1–Ir1 2.4779(11), P1–Ir1 2.3119(10), P2–Ir1 2.3179(10), N1–Al1 1.863(3), N2–Al1 1.857(3), N3–Al1 2.037(3), P1–Ir1–P2 165.54(4), N1–Al1–N2 88.86(14), N1–Al1–N3 95.66(13), N2–Al1–N3 98.88(14)

The ^1H NMR spectroscopic studies and DFT calculations on **5** suggested that the Ir center of **5** has an oxidation number of five. The oxidation state of **5** was experimentally confirmed by X-ray absorption near-edge structure (XANES). The Ir L_{III} -edge XANES spectrum for **5** is presented in Figure 4 with those for Ir powder, $\text{Cp}^*\text{Ir}(\text{H})_4$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$),²⁵ and $\text{Ir}(\text{acac})_3$ as reference compounds of Ir(0), Ir(V), and Ir(III), respectively. The edge energies of the Ir L_{III} -edge XANES spectra were sensitive to the oxidation state of Ir, and differences in the edge energies of Ir(V)-, Ir(0)-, and Ir(III)-reference compounds were obvious. The XANES spectrum of **5** was similar to that of $\text{Cp}^*\text{Ir}(\text{H})_4$, indicating that **5** has Ir(V) center. Considering the corresponding boron-containing PBP-pincer ligand possessing the same *o*-phenylenediamine backbone led to a formation of Ir(III) dihydride rather than Ir(V) tetrahydride,²⁶ it is reasonable to attribute that the reason why **5** was isolable in higher oxidation state is due to the stronger σ -donicity of the alumanyl ligand than that of boryl ligand.

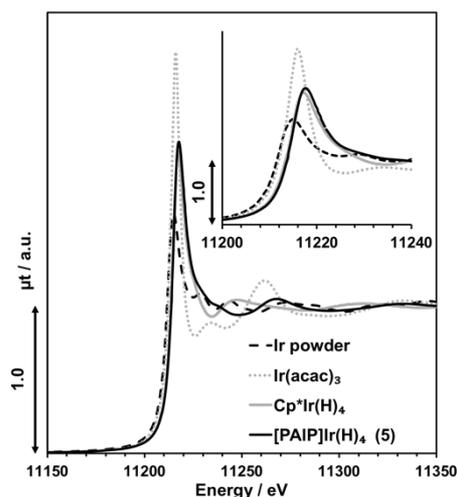


Figure 4. Normalized Ir L_{III} -edge XANES spectra for **5** (black solid line), $Cp^*Ir(H)_4$ (gray solid line), $Ir(acac)_3$ (gray dotted line) and Ir powder (black dashed line).

To obtain details about electronic structure of **5**, we conducted computational studies on the optimized structure **opt-5**. The significantly long atomic distances among hydride ligands (>2.24 Å) in **opt-5** supported that **5** should be hydride complex rather than dihydrogen complex, as judged by long T_1 experimentally. The molecular orbital of **opt-5** corresponding to two-center two-electron Al–Ir σ -bond appears as HOMO–8 (Figure 5a). LUMO shows the contribution of empty 3p orbital on the Al atom (Figure 5b). These shapes of molecular orbitals indicated that **opt-5** is viewed as alumanyl–Ir(V) tetrahydride, $[PAIP]Ir(H)_4$, rather than the structure with bridging hydride, $[PAIP](\mu-H)_2Ir(H)_2$. This structural model $[PAIP]Ir(H)_4$ was also confirmed by AIM analysis²⁷ for **opt-5** using AIMALL software package²⁸ (Figure S27). A bond path was found between Al and Ir atoms to indicate the existence of Al–Ir σ -bond, in addition, no bond path was found between internal hydride ligands and the Al atom.

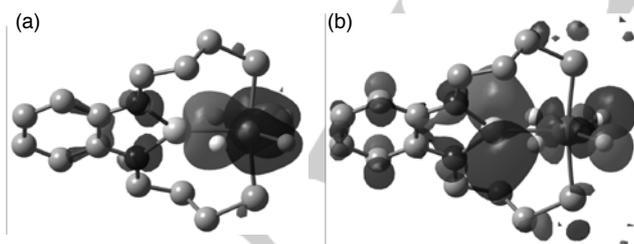
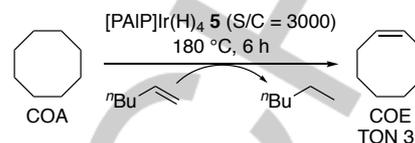


Figure 5. Molecular orbitals of **opt-5** with a contour value of 0.03 atomic unit ((a) HOMO–8, (b) LUMO). All hydrogen atoms except for hydride ligands and four t Bu groups are omitted for clarity.

Considering the application of transition metal complexes having X-type boron-based multidentate ligand in catalysis,²⁹ one can expect that the present complex **5** could also be applied as a catalyst. The thermal stability of alumanyl-pincer Ir complex **5** in hand, the catalytic activity of **5** for the transfer dehydrogenation of

cyclooctane (COA)³⁰ was also explored (Scheme 3). The highest TON of **31** was obtained at 180 °C using 1-hexene as a hydrogen acceptor (Table S1). This result demonstrated the first example of dehydrogenation of an alkane using a homogeneous catalyst with alumanyl ligand.³¹



Scheme 3. Catalytic transfer dehydrogenation of COA using the Lewis-base-free PAIP pincer iridium complex **5**.

In conclusion, we synthesized and characterized the Lewis-base-free X-type PAIP pincer–Ir complex **5**. The intrinsic strong σ -donation and Lewis acidity of the X-type Al ligand were experimentally and theoretically elucidated. The thermal stability of pincer–Ir complex **5** was applied to the catalytic transfer dehydrogenation of cyclooctane with a moderate activity.

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Keywords: alumanyl ligand • pincer complex • iridium • catalysis • XANES

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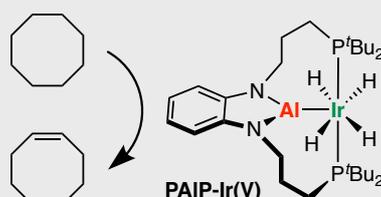
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PAIP pincer ligand: A pincer-iridium complex bearing a Lewis-base-free X-type alumanyl ligand was synthesized. X-ray diffraction study, NMR, IR, and XANES analysis confirmed its tetrahydrido-Ir(V) structure and Lewis acidity at the Al center as supported by DFT calculations. The resulting complex was applied as a catalyst for transfer dehydrogenation of cyclooctane.



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**Synthesis of Pincer-Ir(V) Complex
Having A Base-Free Alumanyl Ligand
and Its Application toward
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