Synthesis, Structure, and Reactivity of Pincer-type Iridium Complexes Having Gallyl- and Indyl-Metalloligands Utilizing 2,5-Bis(6-phosphino-2-pyridyl)pyrrolide as a New Scaffold for Metal–Metal Bonds

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Synthesis and structural analyses of pincer-type iridium complexes having gallyl- and indyl-metalloligands were achieved utilizing 2,5-bis(6-phosphino-2-pyridyl)pyrrolide as a new scaffold for metal–metal bonds. BH_3-coordinated PInP-Ir dihydride complex was also developed as an equivalent to an iridium dihydride complex, which could be a useful catalyst for synthetic reactions.

Heavier group 13 metals have been attracting much attention as a new class of supporting ligands for transition metals in organometallic chemistry.[1] The low electronegativity and high Lewis acidity due to their vacant *p*-orbital are highly promising to realize unique electronic property and reactivity of transition metal complexes. However, in general, bonds between group 13 metals and transition metals are weak, and it is not necessarily easy to make such bonds, thus limiting synthesis and application of such metal complexes in synthetic chemistry. To solve these problems, several *N*,*P*-multidentate ligands have been developed as a scaffold for E–M bonds (E = Al, Ga, In).[2] Pre-introduction of group 13 metals into the ligand with the *N*-moiety followed by complexation with various transition metals with *P*-moiety enables facile formation of a series of E–M bonds with keeping sufficient stability to be utilized as catalysts. For examples, Lu and co-workers established efficient synthesis of nickel complexes having group 13 metalloligands utilizing group 13 metal triamide derivatives **A** ((N$^-$)$_3$-P$_3$ type) as metalloligands, which work as a Z-type ligand for nickel (Figure 1-a).[3] Nakao developed an aluminum diamide-amine complex **B** (N(N$^-$)$_2$-P$_2$ type), which coordinates as Z- or X-type ligand to metals such as palladium and rhodium (Figure 1-b).[4] Our group focused on 6,6”-bis(phosphino)terpyridine derivatives, which bind group 13 metals with three neutral *N*-moieties, and reported that the cationic group 13 metalloligands **C** (N$_3$-P$_2$ type) enable facile synthesis of a series of E–Pd complexes (Figure 1-c).[5a] Recently, we also demonstrated the first synthesis of pincer-type Ir^{III} complexes bearing an L-type, neutral Ga^{I} (gallylene) metalloligand simply by reacting **C** (E = Ga) with Ir^{I} via redox reaction between two metals.[5b] Therefore, it has been demonstrated that rationally designed *N*,*P*-multidentate ligands enable diverse modes for coordination of group 13 metalloligands to transition metals.

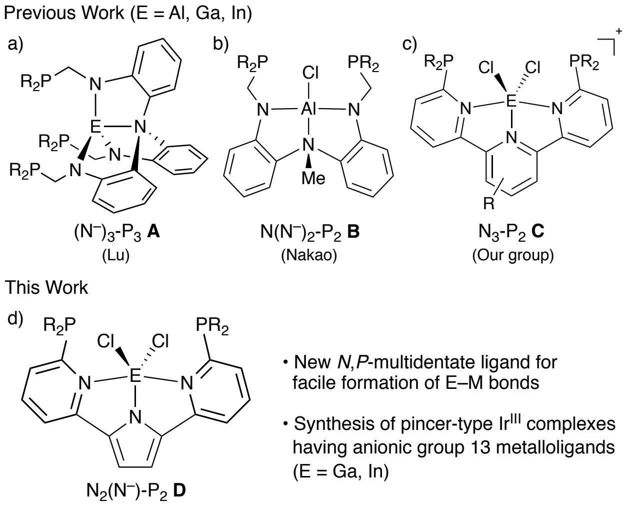

Figure 1. Selected examples of group 13 metalloligands utilizing *N*,*P*-multidentate ligands as a scaffold for E–M bonds (E = Al, Ga, In).

In pursuit of this chemistry, we herein report newly designed group 13 metalloligands **D** supported by an N$_2$(N$^-$)-P$_2$ type scaffold, 2,5-bis(6-phosphino-2-pyridyl)pyrrolide (Figure 1-d). We expected that replacement of the central pyridine ring of **C** by an anionic pyrrolide ring results in the formation of *neutral* five-coordinate group 13 metalloligands while the metalloligands **C** were *cationic*.[6] Such a charge difference of the group 13 metalloligands will realize a new mode of coordination

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to Ir^{I}; the *neutral* metalloligands **D** will give neutral Ir^{III} complexes having *anionic* M^{I} metalloligands via two electron redox reaction between M^{III} and Ir^{I} in terms of formal oxidation state (Figure 2-a) whereas the *cationic* **C** afforded the cationic Ir^{III} complex having a *neutral* M^{I} (M = Ga, gallylene) metalloligand (Figure 2-b).[5b] Indeed, the reaction of **D** with Ir^{I} led to the formation of pincer-type Ir^{III} complexes bearing anionic Ga^{I} and In^{I} metalloligands (gallyl- and indyl-metalloligands) for the first time, which would be promising catalysts for various synthetic reactions.

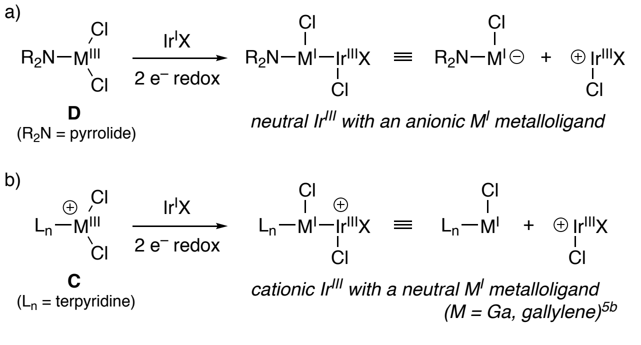
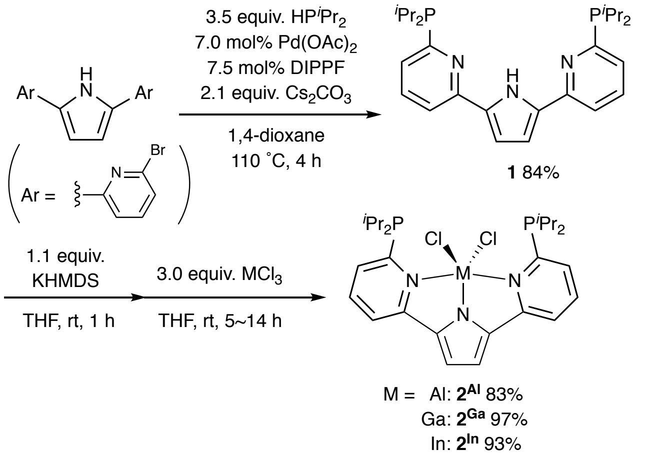


Figure 2. a) Expected complexation of **D** with Ir^{I}. b) Previously reported complexation of **C** with Ir^{I}.[5b]

A 2,5-bis(6-phosphino-2-pyridyl)pyrrole derivative **1** was synthesized as a precursor for the new N$_2$(N$^-$)P$_2$ type metalloligand **D** through Pd-catalyzed cross coupling reaction of 2,5-bis(6-bromo-2-pyridyl)pyrrole[7] with a secondary phosphine, HP^{i}Pr$_2$ in 84% yield (Scheme 1). The group 13 metal pyrrolides **2** were successfully synthesized in good yields by deprotonation of **1** with potassium hexamethyldisilazide (KHMDS) followed by reactions with 3 equiv. of group 13 metal trihalides MCl$_3$ (M = Al, Ga, In). The structures of **2**$^{\mathbf{Ga}}$ and **2**$^{\mathbf{In}}$ were confirmed by X-ray analyses as shown in Figure 3.[8] The geometries around gallium and indium are trigonal bipyramidal having two pyridine moieties at apical positions. Although ^{1}H and ^{31}P NMR of these complexes supported symmetric coordination of two pyridyl moieties to metals in solution (δ_P = 3.2(s) for **2**$^{\mathbf{Al}}$, 6.4(s) for **2**$^{\mathbf{Ga}}$, 16.3(s) for **2**$^{\mathbf{In}}$), the Ga–N1 and Ga–N2 bond lengths are substantially different (Ga–N1 = 2.440(3), Ga–N2 = 2.212(3)) whereas the corresponding In–N1 and In–N2 lengths are almost the same in **2**$^{\mathbf{In}}$ (In–N1 = 2.436(4), In–N2 = 2.422(5)), indicating larger indium fits the tridentate coordination of 2,5-pyridylpyrrolide. The distances between two phosphorous side arms are 6.209(2) for **2**$^{\mathbf{Ga}}$ and 6.293(2) for **2**$^{\mathbf{In}}$. These values are larger than those in previously reported terpyridine derivatives **C** (5.21-5.34 Å),[5a] reflecting the difference of the central ring structure, pyridine or pyrrole.



Scheme 1. Synthesis of group 13 metal pyrrolide complexes **2**.

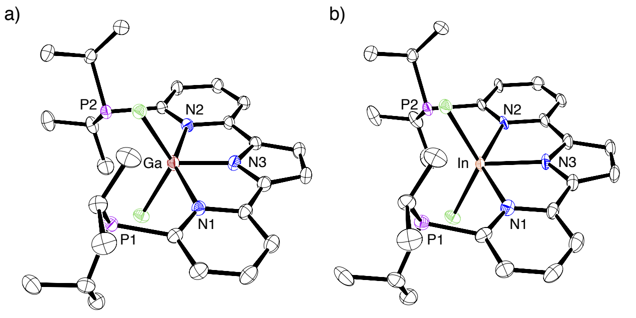
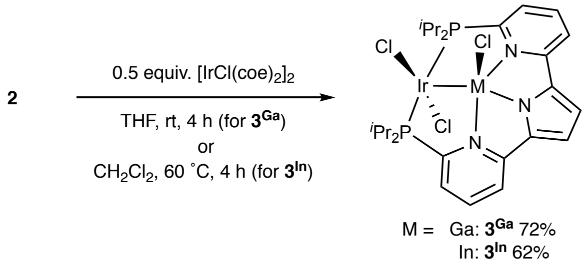


Figure 3. ORTEP drawings of a) **2**$^{\mathbf{Ga}}$ and b) **2**$^{\mathbf{In}}$ at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) **2**$^{\mathbf{Ga}}$: Ga–N1, 2.440(3); Ga–N2, 2.212(3); Ga–N3, 1.870(3), P1---P2, 6.209(2). **2**$^{\mathbf{In}}$: In–N1, 2.436(4); In–N2, 2.422(5); In–N3, 2.082(5), P1---P2, 6.293(2).

With the desired group 13 metalloligands in hand, we next investigated complexation of **2** with various Ir^{I} complexes. After screening of various Ir complexes, [IrCl(coe)$_2$]$_2$ was found to react with **2**$^{\mathbf{Ga}}$ smoothly in THF at room temperature to afford a Ga–Ir bimetallic complex **3**$^{\mathbf{Ga}}$ in good yield (Scheme 2). The reaction with **2**$^{\mathbf{In}}$ in CH$_2$Cl$_2$ at heating conditions also gave the corresponding In–Ir complex **3**$^{\mathbf{In}}$ in 62% yield. ^{1}H and ^{31}P NMR supported symmetric coordination of two phosphorous side arms to iridium (δ_P = 50.1(s) for **2**$^{\mathbf{Ga}}$, 56.2(s) for **2**$^{\mathbf{In}}$), indicating the formation of pincer-type iridium complexes.[9] Structures of these complexes were fully characterized by X-ray analyses using single crystals obtained from CH$_2$Cl$_2$/Et$_2$O for **3**$^{\mathbf{Ga}}$ and CH$_2$Cl$_2$/hexane for **3**$^{\mathbf{In}}$ (Figure 4), and selected bond lengths and angles are listed in Table 1. Although the distances between two phosphorous side arms in **2**$^{\mathbf{Ga}}$ and **2**$^{\mathbf{In}}$ seem to be too long for bidentate coordination, the ^{i}Pr^{2}P- ligands coordinate to iridium within a range of standard Ir–P lengths (Table 1). To compensate for those structural changes, the structure of the bis(pyridyl)pyrrolide-coordinated gallium and indium moieties largely bent from original planar structure as shown in Figure 4. The geometries around iridium in these complexes are distorted square pyramidal having the group 13 metals at an apical



Scheme 2. Synthesis of gallyl- and indyl-pincer-type iridium complexes **3**.

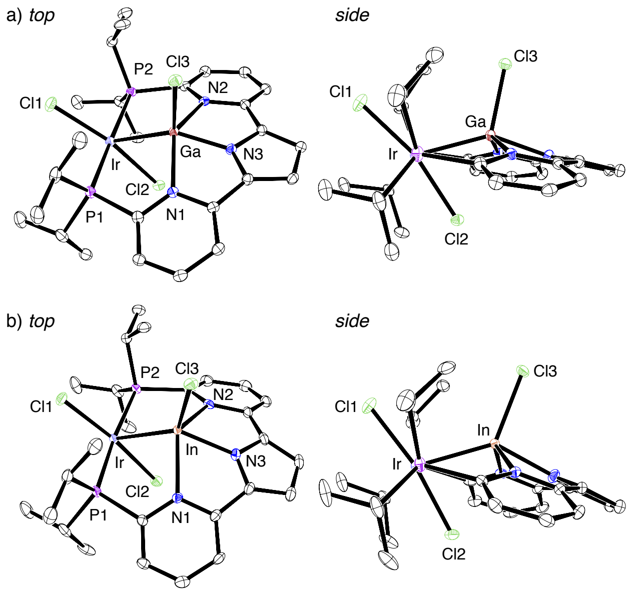


Figure 4. ORTEP drawings of a) 3^{Ga} and b) 3^{In} at 30% probability level. Hydrogen atoms are omitted for clarity.

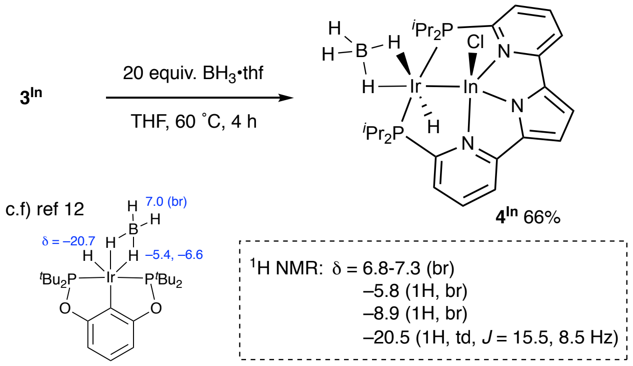
Table 1. Selected bond lengths and angles of 3^{Ga} and 3^{In}

	3^{Ga} (M = Ga)	3^{In} (M = In)
Ir–P1 / Å	2.336(1)	2.345(2)
Ir–P2 / Å	2.329(1)	2.348(2)
Ir–M / Å	2.3923(6)	2.5177(6)
Sum of Ir and M[a] / Å	2.63	2.83
Ir–Cl1 / Å	2.325(1)	2.327(2)
Ir–Cl2/ Å	2.372(1)	2.367(2)
M–Cl2 / Å	2.797(1)	3.078(2)
M–Cl3 / Å	2.240(1)	2.396(2)
Sum of M and Cl[b] / Å	2.24	2.44
d[c] / deg	343.0	327.7

[a] Sum of covalent radii of iridium and group 13 metal. [b] Sum of covalent radii of Cl and group 13 metal. [c] Sum of bond angles of Ir–In–N1, N1–In–N3, N3–In–N2, and N2–In–Ir.

position. The Ir–M distances are shorter than the sum of the corresponding covalent radii,[10] supporting bonding between Ir and group 13 metals. It should be noted that the Cl2–Ir bond lengths are 2.372(1) Å for 3^{Ga} and 2.367(2) Å for 3^{In}, which are almost the same with those of Ir–Cl1 bonds (2.325(1) for 3^{Ga}, 2.327(2) for 3^{In}). On the other hand, distances between group 13 metals and Cl2 are substantially larger than those of M–Cl3 bonds (Ga–Cl2 = 2.797(1) Å and Ga–Cl3 = 2.240(1) Å for 3^{Ga}, In–Cl2 = 3.078(2) Å and In–Cl3 = 2.396(2) Å for 3^{In}) and the sum of covalent radii.[10] These results indicate that the chloride ligand Cl2 bonds to Ir, not to group 13 metals. This was further supported by a quantum theory of atoms in molecules (QTAIM) analysis, which showed the bond critical point (bcp) for the Ir–Cl2 bond, but not between group 13 metals and Cl2 (see the SI). Therefore, these bimetallic complexes can be regarded as pincer-type Ir^{III} dichloride complexes bearing gallyl- and indyl-metalloligands (anionic Ga^{I} and In^{I}) in terms of formal oxidation state. As we expected in Figure 2, these are in sharp contrast to previous results using the terpyridine derivative **C**, which resulted in the formation of a cationic Ir^{III} dichloride complex with a gallylene metalloligand (neutral Ga^{I}).[5b]

Reactivity of these bimetallic complexes as trivalent iridium was demonstrated by the reaction with BH_3. Treatment of 3^{In} with 20 equiv. of BH_3•thf in THF at 60 ˚C afforded a BH_3-coordinated iridium dihydride complex 4^{In} in 66% yield (Scheme 3).[11] The structure was disclosed by X-ray analysis using a single crystal obtained from THF/Et_2O although four hydrogen atoms around the boron atom were not located (Figure 5-a). In ^1H NMR, a hydride resonance was observed at δ = –20.5 (1H, td, J = 15.5, 8.5 Hz) as triplets of doublets in CD_2Cl_2 at room temperature, which is attributed to an Ir–H close to the In-metalloligand. Two bridging hydrogen atoms between Ir and B appeared at δ = –5.8 (1H) and –8.9 (1H) as broadening peaks separately. Non-bridging B–H resonances were observed at δ = 6.8-7.3 as a broadening peak. These values are very similar to those of the BH_3-coordinated PCP-$Ir^{III}H_2$ complex reported by Goldberg.[12] Additionally, the structural data were almost identical to those of the optimized structure by theoretical calculation (Figure 5-b). These results strongly support the structure of 4^{In} as a BH_3-coordinated Ir^{III} dihydride complex bearing a pincer-type indyl-metalloligand.



Scheme 3. Synthesis of the BH_3-coordinated In–Ir dihydride complex 4^{In}.

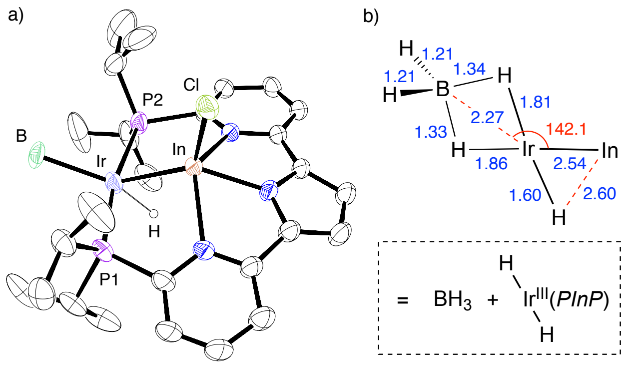
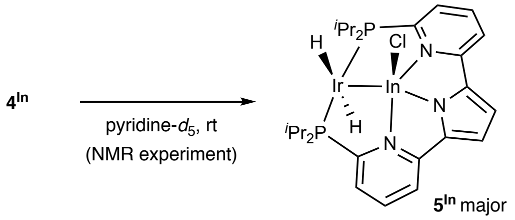


Figure 5. a) ORTEP drawing of $\mathbf{4^{In}}$ at 30% probability level. Hydrogen atoms except for Ir–*H* are omitted for clarity. The hydrogen atom on Ir was located in the final difference map and refined isotropically. Selected bond lengths (Å) and angles (deg): In–Ir, 2.5474(6); Ir–B, 2.27(1); Ir–H, 1.54(7), H---In = 2.53(7), In–Ir–B, 131.7(3). b) Selected bond lengths and angle of the optimized structure of $\mathbf{4^{In}}$ by DFT calculation at B3PW91/6-31G(d,p)/LANL2DZ level. Description of bonding situations of $\mathbf{4^{In}}$ in terms of formal oxidation state is depicted in the dotted box.

Furthermore, we also found that $\mathbf{4^{In}}$ in pyridine-d_5 liberates an iridium dihydride complex $\mathbf{5^{In}}$ by dissociating the BH_3. Although isolation and structural characterization by X-ray were unfruitful, ^{1}H NMR of $\mathbf{4^{In}}$ in pyridine-d_5 exhibited two major hydride resonances at $\delta = -10.4$ (1H, td, J = 13.5, 3.5 Hz) and -26.8 (1H, td, J = 16.5, 3.5 Hz) as triplets of doublets, thus suggesting the formation of iridium dihydride complex $\mathbf{5^{In}}$ as a major product (Scheme 4, see the SI for details).[13] Theoretical calculation supported that the distorted square pyramidal Ir^{III} complex having two *trans* dihydride ligands is the most stable among possible isomers (see the SI). These results demonstrate that the BH_3-coordinated iridium dihydride $\mathbf{4^{In}}$ is an isolable precursor to the Ir^{III} dihydride complex, which could be useful catalysts for various synthetic reactions. For examples, iridium complexes bearing PCP-pincer ligands have been widely utilized as efficient catalysts for dehydrogenation of alkanes, and the Ir^{III} dihydride complex is one of the most important intermediates and precursors for those reactions.[14] Recently, several research groups focused on group 13 element, in particular boron, instead of carbon as a central anionic supporting ligand in the pincer structure, and the synthesis and reaction of PBP-pincer type iridium complexes have been extensively studied.[15] However, corresponding heavier analogues such as gallium and indium have not been reported yet. This is the first example of synthesis and structural analyses of pincer-type iridium complexes having gallyl- and indyl-metalloligands, and successful transformation to the iridium dihydride complex was also demonstrated. These results will open up new chemistry of pincer-type iridium complexes in organometallic chemistry and synthetic chemistry, and further investigations on catalytic reactivity of these complexes are in progress in our group.



Scheme 4. Formation of the iridium dihydride complex $\mathbf{5^{In}}$.

In conclusion, we have achieved synthesis and structural analyses of pincer-type iridium complexes having gallyl- and indyl-metalloligands utilizing the newly designed 2,5-bis(6-phosphino-2-pyridyl)pyrrolide as an $N_2(N^-)$-P_2 type scaffold for metal–metal bonds. The BH_3-coordinated PInP-Ir dihydride complex was also synthesized and demonstrated to work as an equivalent to an iridium dihydride complex. This method will enable synthesis of various pincer-type transition metal complexes having anionic group 13 metalloligands, which would be a promising catalyst for various synthetic reactions.

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Conflicts of interest

There are no conflicts to declare.

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9 The reaction of $\mathbf{2}^{\mathbf{Al}}$ with $[IrCl(coe)_2]_2$ under similar conditions also afforded an Ir complex, which could be the corresponding Al–Ir complex $\mathbf{3}^{\mathbf{Al}}$. However, the X-ray analysis was unsuccessful, and the structure was deduced by similarities of ^{1}H NMR spectra to those of $\mathbf{3}^{\mathbf{Ga}}$ and $\mathbf{3}^{\mathbf{In}}$. See the SI.

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