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Stabilized Gallylene in a Pincer Type Ligand: Synthesis, Structure, and Reactivity of PGa^{I}P-Ir Complexes

Narumasa Saito[a], Jun Takaya*[a,b], and Nobuharu Iwasawa*[a]

Abstract: Iridium complexes having a pincer-type gallylene ligand were successfully synthesized utilizing bis(phosphino)terpyridine as an efficient scaffold for the Ir–Ga^I bond. The stabilization of the gallylene moiety by the pincer type structure enabled various reactions at Ir with keeping the gallylene ligand intact, realizing unique structures and reactivities of PGa^{I}P-Ir complexes.

Group 13 metallylenes (:E^IR, E = Al, Ga, In, Tl), which are neutral group 13 metal compounds having the +1 formal oxidation state, have been attracting much attention as a new type of supporting ligands in organometallic chemistry. They coordinate to transition metals potentially through the σ-donation and π-back donation with lone pair electrons and a vacant p-orbital, behaving as isolobal species of PR_3, CO, and carbene. Numerous group 13 metallylene-ligated transition metal complexes have been developed utilizing various mono- or multidentate ligands on the group 13 metal such as Cp*, bulky Ar and several nitrogen-containing compounds to stabilize the metallylene (Figure 1, L = L-type ligand, X = X-type ligand).[1,2] However, investigations on the reactivity of those metal complexes are still limited despite their promising utility as new transition metal catalysts in synthetic chemistry.[3] This is partly due to the high reactivity of metallylenes and instability of the monodentate coordination of the RE^I to transition metals, thus resulting in easy loss of the metallylene moiety during reactions.[4]

One of the promising approaches to stabilize and utilize group 13 metallylenes as a spectator supporting ligand is to incorporate the group 13 metal into a component of a multidentate ligand. Pincer type ligands seem to be suitable for such a purpose because the pincer motif is advantageous for introducing a variety of elements into the central position and stabilizing the metal–element bonds while keeping sufficient reactivity of the transition metal.[5] Several pincer-type group 13 metalloligands and their transition metal complexes have been developed, in which the group 13 metal coordinates as a Z-type ligand,[6] formally accepting 2 electrons in a vacant p-orbital from the transition metal, or as an X-type ligand,[7] having two anionic ligands on the group 13 metal and formally donating 2 electrons to the transition metal. However, a group 13 metallylene-based pincer-type ligand has remained unexplored in the pincer chemistry. Although Langer recently reported synthesis and property of iron and palladium complexes having pincer-type borylene ligands,[8] there has been no report on the corresponding heavier group 13 metallylene systems.

Herein we report synthesis, structure, and reactivity of iridium complexes having a pincer-type gallylene ligand utilizing bis(phosphino)terpyridine as an efficient scaffold for the Ir–Ga^I bond. The pincer type structure enabled easy synthesis and various reactions at Ir with keeping the gallylene moiety intact as a supporting ligand, realizing unique structures and reactivities of PGa^{I}P-Ir complexes.

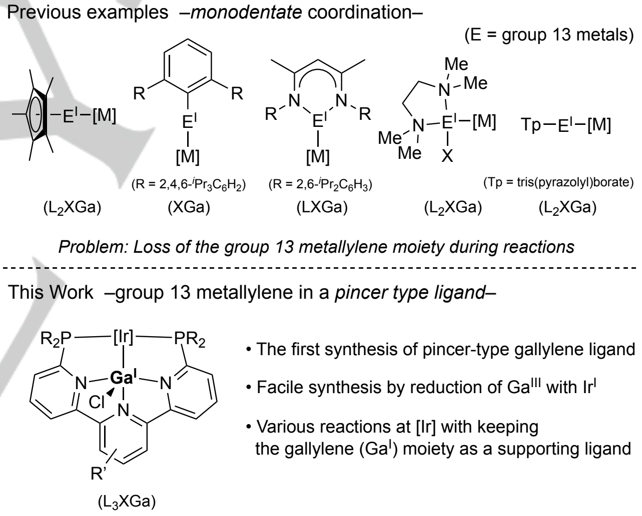

Figure 1. Group 13 metallylenes as a supporting ligand for transition metals

Recently, we have reported efficient synthesis and unique catalysis of E–Pd bimetallic complexes (E = Al, Ga, In) utilizing a 6,6”-bis(phosphino)terpyridine derivative as a scaffold for the E–Pd bonds, in which the group 13 metals coordinate as formally anionic E^I-metalloligands (Cl_2E^I).[9] We attempted to apply this system to iridium with slight modification of substituents on the phosphorus atoms and terpyridine. A newly designed 6,6”-($^iPr_2P$)$_2$-terpyridine **1** having a mesityl group at the 4’-position was synthesized in a gram scale through Pd-catalyzed cross coupling reactions (see the Supporting Information for details).[10] Treatment of **1** with 2.3 equivalent of $GaCl_3$ afforded a cationic terpyridine-$GaCl_2$ complex **2** in 77% yield (Scheme 1). The structure of **2** was identified by X-ray analysis (see the SI). Introduction of Ir was achieved by the reaction of **2** and $[IrCl(cod)]_2$ in toluene at 80 ˚C, giving a Ga–Ir bimetallic complex

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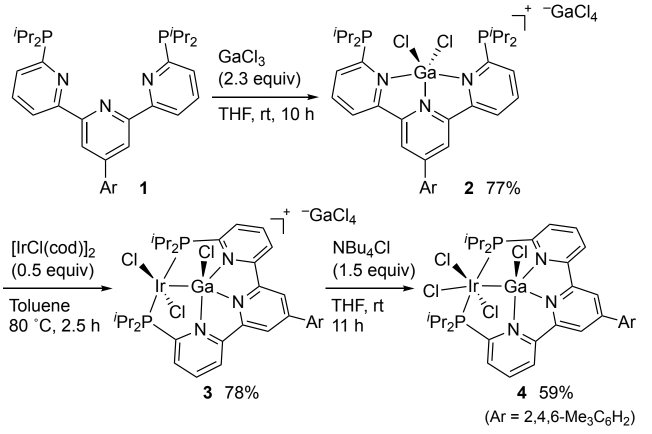
3, which can be regarded as a PGaP–pincer type Ir complex, as a red solid in 78% yield.



Scheme 1. Synthesis of Ir complexes having a pincer-type gallylene ligand.

The structure of **3** was fully determined by NMR and X-ray analyses (Figure 2-a). The Ga–Ir complex **3** is cationic having $[GaCl_4]^-$ as a counter anion, and the geometry around iridium is distorted square pyramidal with the PGaP-pincer type ligand. The Ga–Ir bond length is 2.3895(6) Å, which is in a range of previously reported values of Ga–Ir bonds (2.381(1) ~ 2.4689(5) Å).[11] Importantly, the chloride ligand Cl(2) is seemingly bridging between Ir and Ga, however, the distances to each metal are substantially different. The Ir–Cl(2) distance of 2.370(1) Å is similar to that of the Ir–Cl(1) (2.310(1) Å), whereas the Ga–Cl(2) is 2.725(1) Å, which is much longer than the sum of covalent radii (2.24 Å).[12] A quantum theory of atoms in molecules (QTAIM) analysis showed the bond critical point (bcp) for the Ir–Cl(2) bond, but not between Ga and Cl(2). These results clearly indicate that the chloride ligand Cl(2) bonds to Ir, not to Ga. Moreover, the cationic complex **3** was converted to a neutral complex **4** by treatment with NBu_4Cl (Scheme 1). The X-ray structural analysis demonstrated the added chloride bonds to Ir, not to Ga, to form the octahedral iridium trichloride complex bearing a GaCl as a supporting ligand (Figure 2-b). The coordination geometry of ligands on Ir except for the GaCl in **4** is square pyramidal judged by the τ parameter (τ = 0.11), indicating that the GaCl is a donor ligand to the Ir.[8c,13] Therefore, in these complexes, the Ir can be described as an Ir^{III}, and Ga as a neutral Ga^{I}, gallylene, generated through two electron reduction of **2** by the added Ir^{I} in terms of the formal oxidation state.[14] Notably, the Ir–Cl(2) bond of **4** is elongated (2.5459(9) Å) compared with that in the related pincer type $Ir^{III}Cl$ complexes, suggesting the strong trans influence of the Ga^{I}-metalloligand.[15] Such a complexation-induced reduction of trivalent group 13 metals to metallylenes with neutral, late transition metals are rather rare[16] whereas reactions with highly reactive, dianionic carbonyl metalates such as $K_2[Fe(CO)_4]$ with the group 13 chlorides were well developed to give $XL_nGa^{I}–Fe(CO)_4$ complexes via double salt exchange.[17] This is the first example of synthesis and structural analysis of gallylene-based pincer complexes and could be a useful method to access a variety of metallylene-coordinated late transition metal complexes.

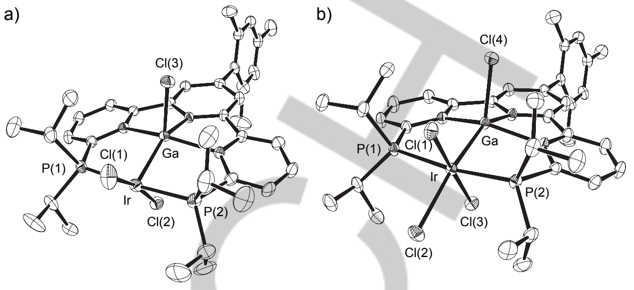
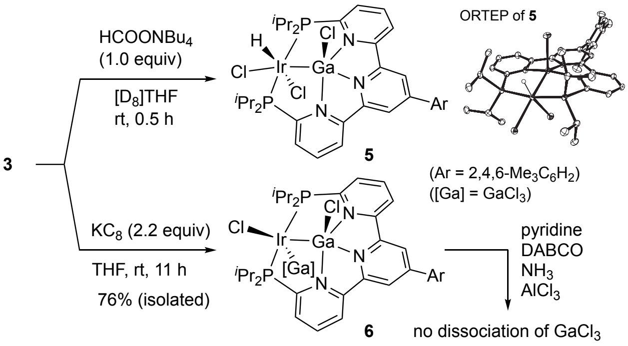


Figure 2. ORTEP drawings of a) **3** and b) **4** at 50% probability level. $[GaCl_4]^-$ and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]; **3**: Ir–Cl(1), 2.310(1); Ir–Cl(2), 2.370(1); Ga–Cl(2), 2.725(1); Ir–Ga, 2.3895(6); Ga–Cl(3), 2.226(1); Ir–P(1), 2.320(1); Ir–P(2), 2.327(1); P(1)–Ir–P(2), 176.04(4); Cl(1)–Ir–Cl(2), 170.13(4).; **4**: Ir–Cl(1), 2.3690(9); Ir–Cl(2), 2.5459(9); Ir–Cl(3), 2.3924(9); Ga–Cl(3), 2.8906(8); Ga–Cl(4), 2.2628(9); Ir–Ga, 2.3970(7); Ir–P(1), 2.3426(9); Ir–P(2), 2.3350(9); P(1)–Ir–P(2), 172.13(3); Cl(1)–Ir–Ga, 105.14(3); Cl(2)–Ir–Ga, 166.02(3); Cl(3)–Ir–Ga, 74.25(2).

The pincer-type structure enabled various reactions of the Ga–Ir complex **3** at Ir without losing the gallylene ligand. The reaction of **3** with 1.0 equivalent of tetrabutylammonium formate afforded an $Ir^{III}HCl_2$ complex **5** via ligand exchange and decarboxylation, which was characterized by NMR and X-ray analyses as described in the SI (Scheme 2). Moreover, treatment of **3** with 2.3 equivalent of KC_8 afforded a neutral Ir^{I} monochloride complex **6** having the pincer-type gallylene ligand in good yield through two electron reduction of Ir^{III} (Scheme 2).[18] The structure of **6** was clarified by X-ray analysis of a single crystal obtained from THF/Et_2O (Figure 3). Interestingly, the Ir possesses another Ga–metalloligand, a trivalent $GaCl_3$, on Ir as a Z-type ligand, which came from the counter anion $[GaCl_4]^-$ of **3**. This is a rare example of having both L- and Z-type Ga-metalloligands at a single metal center.[19] The Ir–Ga(1) bond length is almost comparable to that of **3** (2.377(1) Å for **6**, 2.3895(6) Å for **3**). The Ga1–Ga2 distance of 3.010(1) Å is longer than the sum of covalent radii (2.44 Å),[12] suggesting no bonding interaction between these two gallium atoms. This was also supported by the QTAIM analysis, in which no bond path between Ga^1 and Ga^2 was observed. Several trials to dissociate the $GaCl_3$ from Ir by adding Lewis bases such as pyridine, 1,4-diazabicyclo[2.2.2]octane (DABCO), and NH_3 were unfruitful, suggesting the dative interaction from Ir to $GaCl_3$ is very strong. Moreover, no exchange of the $GaCl_3$ with the added $AlCl_3$ was also observed. This is in sharp contrast to the case of a pincer-type carbene ligand, in which four-coordinate, 16e PCP-IrCl complexes were stably formed and isolated.[20] This could be attributed to the strong electron donating ability of the Ga^{I}-metalloligand surrounded by three nitrogen atoms of terpyridine, demonstrating unique electronic property of the pincer type gallylene ligand.



Scheme 2. Various reactions of **3**

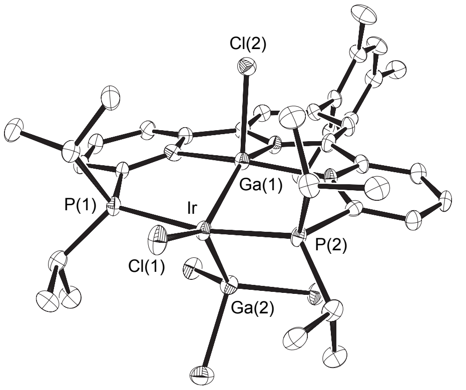


Figure 3. ORTEP drawing of **6** at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ir–Cl(1), 2.390(2); Ir–Ga(1), 2.377(1); Ir–Ga(2), 2.456(1); Ga(1)–Ga(2), 3.010(1); Ga(1)–Cl(2), 2.258(2); Ir–P(1), 2.310(2); Ir–P(2), 2.316(2); P(1)–Ir–P(2), 168.50(8); Cl(1)–Ir–Ga(1), 140.26(6); Cl(1)–Ir–Ga(2), 142.71(6); Ga(1)–Ir–Ga(2), 77.02(3).

To gain further insights into the bonding situation, theoretical calculations were performed on model complexes omitting the mesityl group (Figure 4). The bonding character between Ir and the gallylene ligand is mainly composed of a σ-bond between Ir and Ga^1 as seen in the HOMO–5. Additionally, a partial π-bond is also found in the HOMO although this contribution is relatively small. The Wiberg bond index (WBI) of 0.5553 for the Ir–Ga^1 bond also supports these descriptions that there is almost no double bond character. The HOMO–2 of $\mathbf{6}_{\mathbf{model}}$ shows a σ-bond between Ir and Ga^2, in which the $GaCl_3$ is accepting two electrons as a Z-type ligand. The stabilization energy by the coordination of $GaCl_3$ in $\mathbf{6}_{\mathbf{model}}$ is calculated to be 35.5 kcal/mol, which supports the robustness of $GaCl_3$ on Ir. Further information on these theoretical calculations are described in the supporting information.

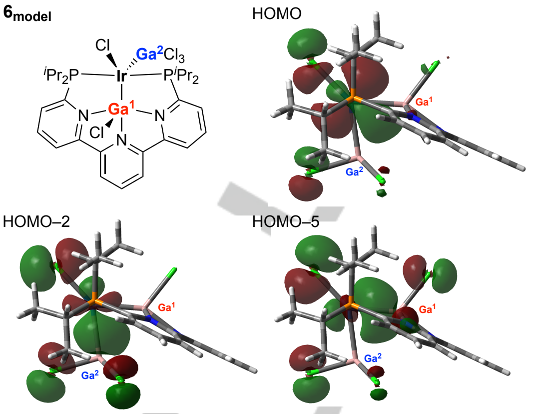
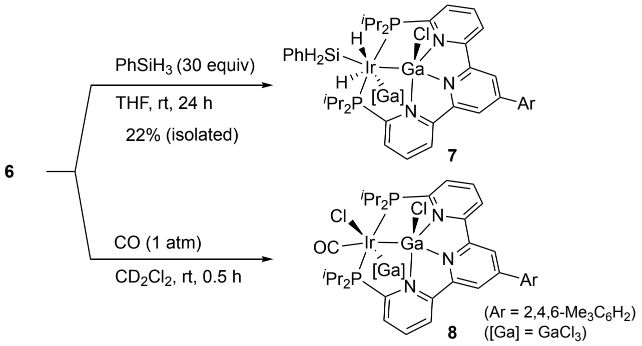


Figure 4. Molecular orbitals of $\mathbf{6}_{\mathbf{model}}$ at contour value = ±0.03 (B3PW91/6-31G(d,p)/LANL2DZ).

Finally, the Ga–Ir complex **6** was also found to react as a PGa^IP-Ir^I complex with keeping the Z-type ligand, $GaCl_3$, intact. The reaction of **6** with 30 equivalents of $PhSiH_3$ in THF afforded a dihydrido(silyl)Ir^{III} complex **7** bearing both the PGa^IP-pincer ligand and $GaCl_3$ Z-type ligand, which was characterized by X-ray and ^1H NMR analyses (Scheme 3, Figure 5). The Ir–Si bond length (2.422(1) Å) is comparable to those of previously reported silyliridium complexes.[21] The Ir–Ga(1) distance of 2.4616(6) Å is clearly longer than those of **3** and **4** due to the strong trans influence of the silyl ligand on **7**. In ^1H NMR, hydrogen atoms on Ir and Si appeared at δ = –11.6 (1H, Ir*H*), –8.9 (1H, Ir*H*), and 5.0 (2H, Si*H*$_2$) separately in [D_2]dichloromethane, and no exchange behavior among them was observed by ^1H EXSY NMR, supporting the $Ir(silyl)H_2$ structure is maintained in the solution without formation of a σ-(Si–H) complex. The stretching vibrations of the Si–H and Ir–H bonds were observed at 2085 and 2006 cm^{-1}, respectively.[22] Furthermore, **6** immediately reacted with 1 atm of CO to give a six-coordinate Ir^I monocarbonyl complex **8** having both PGa^IP- and $GaCl_3$ ligands. The CO ligand vibrates at 2026 cm^{-1}, which is close to the values of standard Ir^{III} complexes rather than Ir^I due to the strong electron accepting nature of the $GaCl_3$ ligand.[23] The high stability of the $GaCl_3$ on Ir during these transformations is surprising and will be highly useful toward development of cooperative molecular transformation with Ir, Ga^{III} and Ga^I. Further studies on the application of these complexes to synthetic reactions are ongoing.



Scheme 3. Reaction of the Ga^{I}–Ir^{I}–Ga^{III} complex **6**.

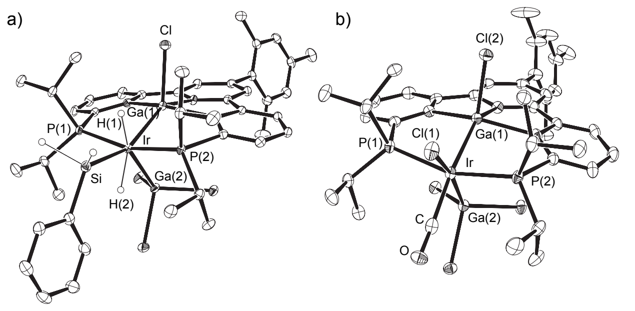


Figure 5. ORTEP drawings of a) **7** and b) **8** at 50% probability level. Hydrogen atoms except SiH_2 and IrH_2 are omitted for clarity. H(1) and H(2) on Ir were located in the final difference map and refined isotropically. Selected bond lengths [Å] and angles [deg]; **7**: Ir–Si, 2.422(1); Ir–Ga(1), 2.4616(6); Ir–Ga(2), 2.5497(5); Ga(1)–Ga(2), 3.1440(6); Ir–P(1), 2.3247(9); Ir–P(2), 2.3334(9); Ir–H(1), 1.46(3); Ir–H(2), 1.54(4); P(1)–Ir–P(2), 163.70(3); Ga(1)–Ir–Ga(2), 77.69(1); Si–Ir–Ga(1), 154.06(3); **8**: Ir–Cl(1), 2.503(2); Ir–C, 1.932(8); Ir–Ga(1), 2.484(1); Ir–Ga(2), 2.496(1); Ga(1)–Ga(2), 3.192(1); Ga(1)–Cl(2), 2.253(2); C–O, 1.137(9); Ir–P(1), 2.353(2); Ir–P(2), 2.347(2); P(1)–Ir–P(2), 160.01(6), Cl(1)–Ir–Ga(1), 111.68(5); Ga(1)–Ir–Ga(2), 79.72(3); Cl(1)–Ir–C, 84.1(2).

In conclusion, we have achieved the first synthesis of Ir complexes having a pincer-type gallylene ligand through the complexation-induced reduction of Ga^{III} by Ir^{I}. The stabilization by the pincer type structure enabled various reactions at Ir with keeping the gallylene ligand intact, which exerts high electron donating nature and enables unique structures and reactivity. This method is useful for preparation of analogous transition metal complexes having a pincer-type metallylene ligand, which would be promising catalysts in organometallic and synthetic chemistry.

Acknowledgements

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Keywords: Gallylene • Gallium • Iridium • Pincer Ligand

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Layout 1:

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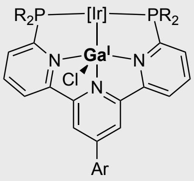
Iridium complexes having a pincer-type gallylene ligand were successfully synthesized utilizing bis(phosphino)terpyridine as an efficient scaffold for the Ir–Ga^I bond. The stabilization of the gallylene moiety by the pincer type structure enabled various reactions at Ir with keeping the gallylene ligand intact, realizing unique structures and reactivities of PGa^{I}P-Ir complexes.



***gallylene** in a pincer type ligand*

- Facile synthesis
- Unique structures
- Various reactions at Ir

Narumasa Saito, Jun Takaya, and Nobuharu Iwasawa**

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Stabilized Gallylene in a Pincer Type Ligand: Synthesis, Structure, and Reactivity of PGa^{I}P-Ir Complexes

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