Synthesis, Structure, and Reactivity of a Gallylene Derivative Bearing a Phenalenyl-Based Ligand

Takuya Kodama,*[a,b] Nijito Mukai [a] and Mamoru Tobisu *[a,b]

a. Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan. E-mail: kodama@chem.eng.osaka-u.ac.jp; tobisu@chem.eng.osaka-u.ac.jp
b. Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI) Suita, Osaka 565-0871, Japan. E-mail: kodama@chem.eng.osaka-u.ac.jp; tobisu@chem.eng.osaka-u.ac.jp
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Phenalenyl-based N,N-bidentate ligand-stabilized monovalent gallium(I) 1 was synthesized and characterized. Compound 1 promotes the oxidative addition of I–I, Si–Cl, C–I, and S–S bonds and oxidative cyclization with various π-components. Compound 1 can also coordinate to a tungsten complex to form a gallium–tungsten bond.

Since the first report on structurally characterized alumylene in 1991,[1] group 13 metallylenes (:ER, E = a group 13 element), monovalent group 13 compounds with an oxidation state of +1, have attracted considerable interest in the field of modern main group element chemistry because of their distinctive electronic properties and chemical reactivities.[2–4] Due to the valence electron configuration of ns^2np^1, the stable oxidation state of group 13 compounds is +3, except for thallium,[2] which has made the synthesis of group 13 metallylenes a challenge. Numerous efforts to design appropriate ligands for dealing with these highly reactive species have been made. The use of anionic N,N'-type bidentate ligands bearing bulky substituents (i. e. Dip = 2,6-diisopropylphenyl group) (Chart 1) has played a particularly important role in these efforts.[5] Among them, β-ketiminate type (NacNac) ligands (i. e. **III** in Chart 1) have been widely used because of their structural modularity,[4–7] which allows for the fine tuning of steric and electronic properties and the associated reactivity of metallylenes bearing these ligands. In fact, a number of NacNac derivatives in which hydrogen atoms are replaced with other substituents or heteroatoms are introduced into the skeleton have been reported. Curiously, however, few attempts have been made to fuse aromatic rings on NacNac ligands,[8] despite promise that they would confer distinct optical properties and improve robustness based on their extended π-system. Our group recently reported on a low-valent germanium complex bearing a phenalenyl-type ligand[11,12] having a bulky Dip group on the nitrogen (DipN-PLY), which allows for a high thermal stability to be achieved (Chart 2a).[13] Inspired by the considerable stability associated with a DipN-PLY ligand, we envisioned that the DipN-PLY ligand could also be used to stabilize group 13 metallylenes. We report herein on the synthesis, properties and reactivity of gallylene [DipN-PLY]Ga (**1**) (Chart 2a).
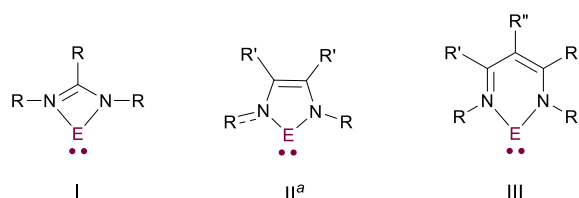

Chart 1 Representative structures of reported group 13 metallylenes bearing N,N'-Type bidentate ligands. E = group 13 element; R, R', R" = H, alkyl, aryl, NHC etc. aBoth neutral and anionic species were reported.
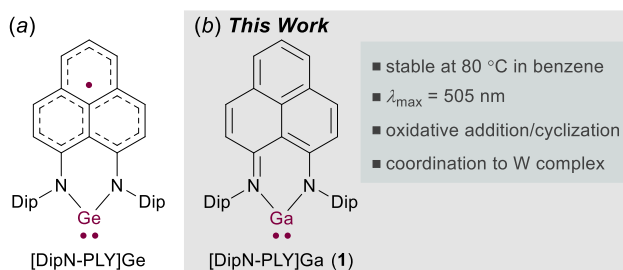

Chart 2 Molecular structures of (a) [DipN-PLY]Ge and (b) [DipN-PLY]Ga (**1**).

A [DipN-PLY]H ligand was synthesized by a previously reported method.[13] The lithiated ligand ([DipN-PLY]Li) was then treated with GaI₃, which was generated in situ from elemental gallium and I₂, to give the diiodo precursor **2** in 99% yield. Complex **2** was

reduced by treatment with 2.3 equiv of potassium in toluene at room temperature, which afforded the gallylene **1** as red crystals after recrystallization from hexane (81% yield). Complex **1** was stable in benzene under a N_2 atmosphere even after heating at 80 °C for at least for 1 week.
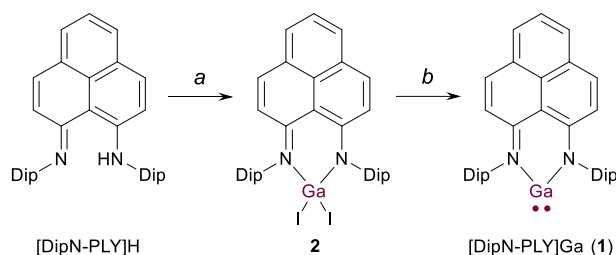
Scheme 1 Synthesis of 1. Reaction conditions: (*a*) *n*BuLi (1.2 equiv), ether, −35 °C to RT, 18 h, then GaI₃ (1.2 equiv), toluene, 65 °C, 24 h, 99%. (*b*) K (2.3 equiv), toluene, RT, 45 h, 81%.
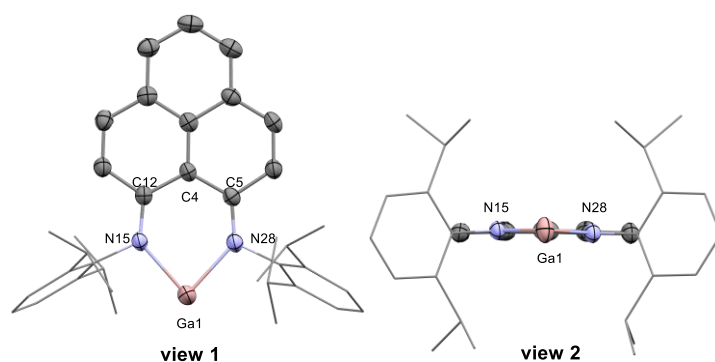

Fig. 1 ORTEP drawings of **1** depicted at the 50% probability levels. Hydrogen atoms were omitted for clarity. Dip groups were depicted as wireframe forms. Selected bond distances (Å), bond angles (deg): Ga1–N15, 2.061(2); Ga1–N28, 2.059(3); N15–C12, 1.336(4); N28–C5, 1.327(4); C4–C5, 1.448(4); C4–C12, 1.449(4); N15–Ga1–N28, 83.7(1); Ga1–N15–C12, 133.7(2); Ga1–N28–C5, 133.6(2).

X-ray crystallographic analysis revealed that **1** contains a V-shaped two-coordinate gallium center with the planar geometry of a six-membered gallacycle (Fig. 1). The average bond lengths are 2.060 Å for Ga–N and 1.332 Å for C–N bonds, and the N–Ga–N angle is 83.7(1)°. These values are comparable to those reported for ᴰⁱᵖNacNacGa.[14] The nearest Ga–Ga distance in the crystal was 5.381 Å (Fig. S2c in ESI†), suggesting that there are no bonding interactions between Ga atoms. ^{1}H and ^{13}C NMR spectra at 20 °C indicated that gallylene **1** possesses a C_{2v}-symmetry (Fig S12 and S13 in ESI†), which is consistent with the molecular structure of **1** obtained by X-ray crystallography (Fig. 1). An electronic absorption spectrum of **1** in toluene displayed an absorption maximum at 505 nm with a bathochromic shift of 165 nm (Fig. 2) compared to that of ᴰⁱᵖNacNacGa (340 nm).[14] Density functional theory (DFT) calculations at the PBE0-D3(BJ)/def2-SVP level[15] suggested that the HOMOs of both **1** and ᴰⁱᵖNacNacGa are located on the lone pair of electrons on gallium, whereas the LUMOs are distributed among the π-orbitals of the corresponding ligands (Fig. 3 and S9# in ESI†). The energy level of the HOMO (−5.60 eV) for **1** was comparable to that of ᴰⁱᵖNacNacGa (−5.43 eV), whereas the LUMO level of **1** (−2.37 eV) was ca. 1.4 eV lower than that for ᴰⁱᵖNacNacGa (−0.98 eV). The DipN-PLY ligand can be regarded as a phenalenyl fused π-extended analogue of ᴰⁱᵖNacNac, resulting in the lowering of the energy level of the LUMO of **1** compared to that of ᴰⁱᵖNacNacGa. In contrast, the corresponding HOMO is not subject to significant resonance effects induced by π-extension because the HOMO orbital is perpendicular to the π orbital of the ligand. This effective lowering of the LUMO energy of **1** explains the large bathochromic shift of the absorption spectra of **1** compared to that for ᴰⁱᵖNacNacGa.
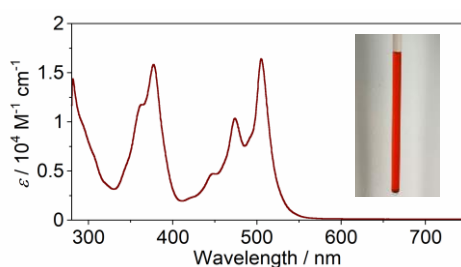

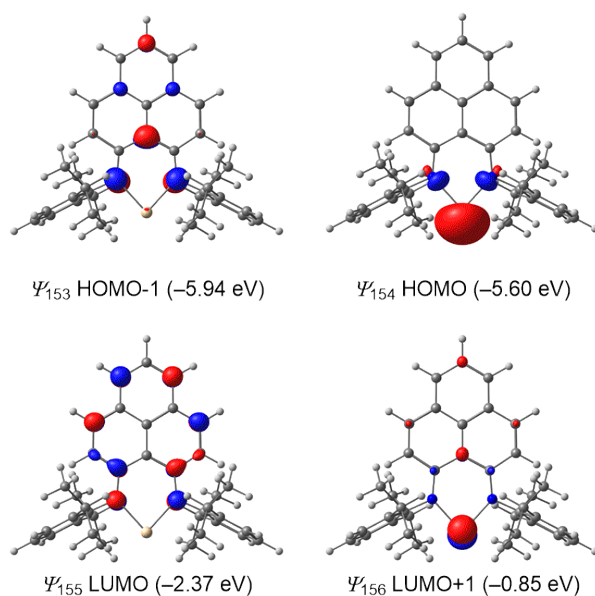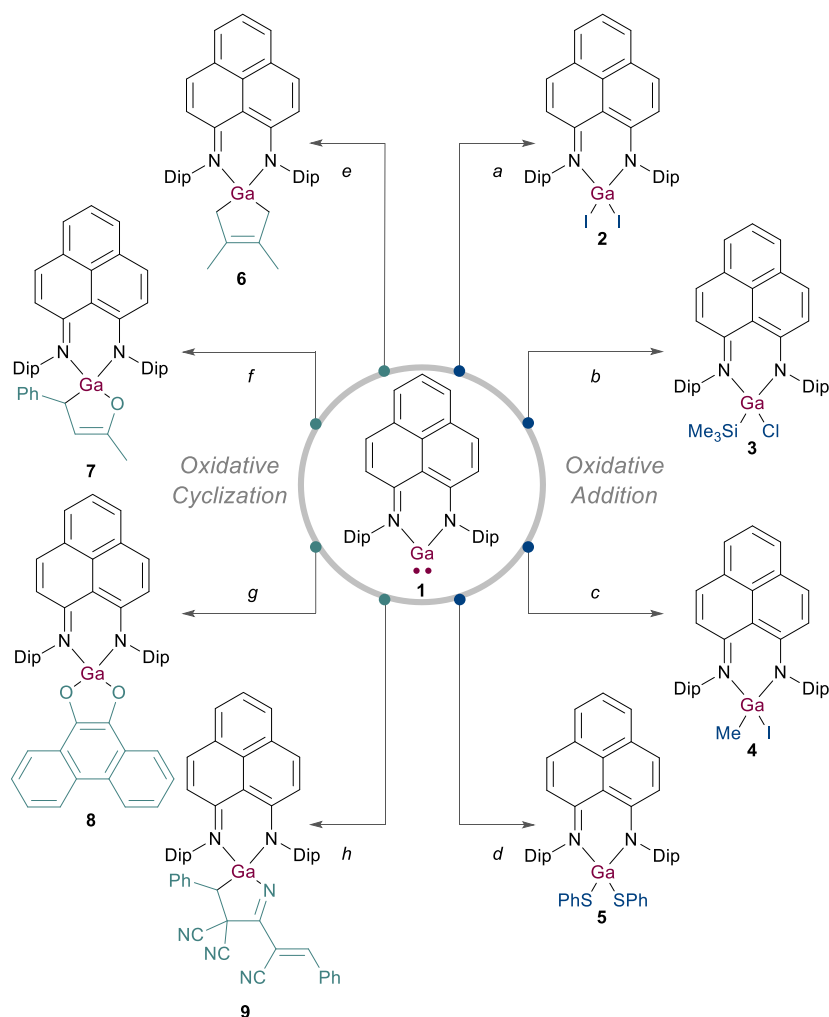**Fig. 2** Electronic absorption spectrum of **1** in toluene (5.5×10⁻⁵ M in toluene, RT).

Fig. 3 Selected molecular orbitals of **1** calculated at the PBE0-D3(BJ)/def2-SVP level.

Ψ_{153} HOMO-1 (−5.94 eV)

Ψ_{154} HOMO (−5.60 eV)

Ψ_{155} LUMO (−2.37 eV)

Ψ_{156} LUMO+1 (−0.85 eV)

Scheme. 2 Reactivity of **1**. Reaction conditions: (*a*) I$_2$ (1.4 equiv), toluene, RT, 2 h, 99%. (*b*) TMSCl (12 equiv), toluene, RT, 42 h, 70%. (*c*) iodomethane (1.5 equiv), toluene, RT, 24 h, 87%. (*d*) diphenyldisulfide (1.0 equiv), toluene, RT, 20 h, 55%. (*e*) 2,3-dimethyl-1,3-butadiene (10 equiv), toluene, RT, 16 h, 96%. (*f*) 4-phenylbut-3-en-2-one (1.0 equiv), toluene, RT, 18 h, 37%. (*g*) 9,10-phenanthrenequinone (0.9 equiv), toluene, RT, 16 h, 54%. (*g*) 4-phenylbut-3-en-2-one (1.0 equiv), toluene, RT, 18 h, 37%. (*h*) 2-benzylidenemalononitrile (2.2 equiv), toluene, RT, 20 h, 66%.

We next investigated the reactivities of **1**. Oxidative addition and oxidative cyclization in which the oxidation state of the central element increases by 2 are typical reactions of metallylenes.[16] The oxidative addition of I_2 and TMSCl to gallylene **1** proceeded to afford the corresponding products **2** and **3**, respectively, in good yields, as was previously reported for other gallylenes.[17,18] Interestingly, gallylene **1** can also promote the oxidative addition of a C–I bond in iodomethane to provide the Ga(III) complex **4**. Compound **1** also activates a S–S bond of PhSSPh to form the oxidative addition product **5**. The oxidative addition of C–I and S–S bonds to Ga(I) species have never been reported. When **1** was reacted with 2,3-dimethyl-1,3-butadiene, [4+1] cycloaddition occurred with the formation of the gallacycle **6**. Although oxidative cyclization involving two molecules of gallylene and two molecules of 1,3-diene have been reported,[19] this is the first demonstration of the [4+1] cyclization of 1,3-diene at the gallium centre. Similarly, the [4+1] cycloaddition of **1** also took place when α,β-unsaturated ketones or 1,2-diketones were used, affording the corresponding gallacycle **7** and **8**, respectively. The structures of **2**, **4** and **8** were unambiguously determined by X-ray crystallographic analysis (Fig. S3–S5 in ESI†). Interestingly, when **1** was reacted with 2 equiv of 2-benzylidenemalononitrile, a three component [2+2+1] cycloaddition occurred to form **9** in 66% yield.[20] The X-ray analysis unambiguously confirmed the molecular structure of **9**, in which the C–C double bonds of 2-benzylidenemalononitrile and the C–N triple bond of another 2-benzylidenemalononitrile are incorporated to form the skeleton of the gallacycle (Fig. 4). This is the first demonstration, to the best of our knowledge, of the [2+2+1] cycloaddition of a gallylene involving a C–C double bond.[21] In addition, the reaction of **1** with W(CO)₅(MeCN) in toluene provided the tungsten-gallium complex **10**, demonstrating the coordinating ability of the lone pair of electrons in **1** (Scheme 3).[22] Single crystals of **10** were obtained by slow evaporation from a hexane solution under a nitrogen atmosphere. The Ga–W bond length was found to be 2.584(7) Å, which was comparable to that for a related gallylene–tungsten complex [2.592(1) Å for ^{Dip}NacNacGaW(CO)₅[23] and 2.566(1) Å for Cp*GaW(CO)₅].[24] Compared to the average length of the Ga–N bonds in **1** (2.060 Å, *cf*. Fig. 1), the corresponding bond lengths for **10** (1.941 Å) were shortened by coordination, while the N–Ga–N angle [91.9(2)°] was increased compared to that of **1** [83.7(1)°]. These structural changes are presumably induced by the decrease in electron density on the Ga centre by coordination with the electron deficient W(CO)₅.
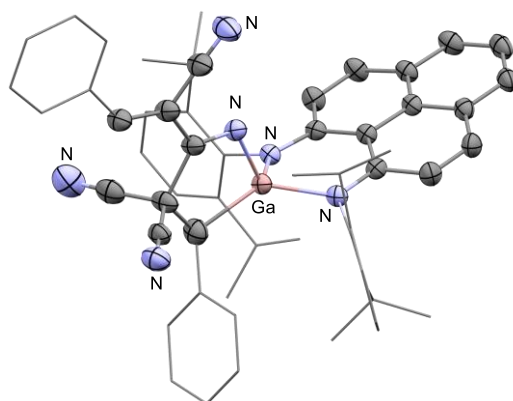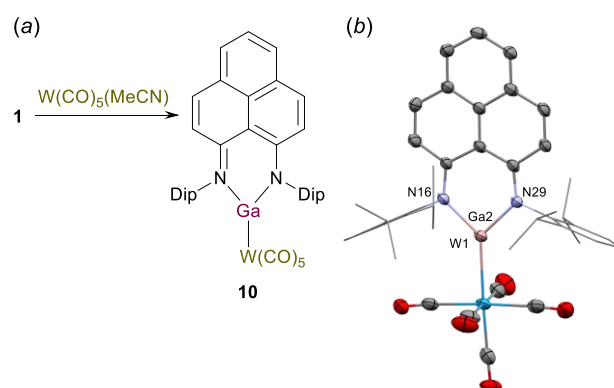

Fig. 4 ORTEP drawing of **9** depicted at the 50% probability levels. Hydrogen atoms were omitted for clarity. Aryl groups were depicted as wireframe form.

Scheme. 3 (*a*) Formation of tungsten complex **10** bearing [DipN-PLY]Ga ligand. Reaction condition: W(CO)₅(MeCN) (1.5 equiv), toluene, 80 °C, 27 h, 37%. (*b*) ORTEP drawing depicted at the 50% probability level. Hydrogen atoms were omitted for clarity. Dip groups were depicted as wireframe form. Selected bond distances (Å), bond angles (deg): Ga2–N16, 1.938(4); Ga2–N29, 1.943(4); Ga2–W1, 2.584(7); N16–Ga2–N29, 91.9(2).

In summary, we report on the design and synthesis of gallylene **1** bearing a phenalenyl ligand. In solution, **1** had a high thermal stability and **1** was isolated in crystalline form. Compound **1** displayed an absorption band in the visible region due to the narrow energy gap. Compound **1** also underwent oxidative addition and oxidative cyclization with various reagents, confirming the electron-rich nature of the gallium(I) centre. The formation of a gallium–tungsten complex was also demonstrated. Further investigations into the reactivity of **1** are now underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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