Organic chemistry has been developed as that of second-row elements such as carbon, oxygen, and nitrogen so far, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds have been one of “dreams” for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of not only fundamental chemistry but also opening the way to more extensive application of main group chemistry.

KEYWORDS
Steric Protection  Heteroatom  Transition Metal Complexes
Kinetic Stabilization  Low-coordinated Species

Selected Publications
Terminal Arylalumylene Complexes

Group 13 element (B, Al, Ga, In, and Tl) compounds have less than an octet and have tendency to form an octet by accepting an electron pair from a Lewis base. Therefore, it is difficult to construct π-electron systems (multiple bond, π-conjugated system, and so on) containing a Group 13 element with keeping the vacant p-orbital. Especially, there had been few reports on the Al-containing π-electron systems. We have already succeeded in the synthesis of a benzene-adduct of dialumene (an Al–Al double-bond compound) and revealed its synthetic equivalency to dialumene. During the course of our studies on the reactivity of dialumene-benzene adducts, we have succeeded in the synthesis of novel platinum complexes of terminal alumylene (monovalent aluminum species).

Terminal arylalumylene complexes of platinum \([\text{ArAl–Pt(PCy}_3)_2]\) \([\text{Ar} = 2,6-\{\text{CH(SiMe}_3)_2\}_2\text{C}_6\text{H}_3 \text{(Bbp)} \text{ or } 2,6-\{\text{CH(SiMe}_3)_2\}_2-4-(t\text{-Bu})\text{C}_6\text{H}_2 \text{(Tbb)}]\) have been synthesized either by the reaction of a dialumene-benzene adduct with \([\text{Pt(PCy}_3)_2]\). X-Ray crystallographic analysis (Figure 1) revealed that the Al–Pt bond lengths of these arylalumylene complexes are shorter than the shortest Al–Pt distance reported previously. DFT calculations suggest that the Al–Pt bonds in the arylalumylene complexes have a significantly high electrostatic character.

Bis-NHC Adducts of Silyliumylidene Cations

Silyliumylidene cation (RSi⁺) is highly coordinatively-unsaturated silicon species and is one of the most challenging intermediates in silicon chemistry. Although several examples of Lewis base-coordinated silyliumylide have been reported, we have found a novel method to access silyliumylide stabilized by \(N\)-heterocyclic carbenes (NHC) by using 1,2-dibromodisilenes as starting materials.

Reactions of stable 1,2-dibromodisilenes \([\text{((E)}-\text{Ar(Br)Si=Si(Br)Ar}])\) with NHC afforded NHC-arylbromosilylene \([\text{Ar(Br)Si:}]\) adducts or bromide salts of the corresponding bis-NHC adducts of the formal arylsilyliumylide cations \([\text{[ArSi:]+}]) \) (Figure 3). In some cases, an NHC was able to replace a bromide anion in the coordination sphere of the arylbromosilylene-NHC adduct. X-Ray crystallographic analysis revealed that the silicon centers of the bis-NHC adducts of the silyliumylide cations possess pyramidal geometries, indicating that the lone pair electrons are substantially localized on the silicon atoms.