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   Kinetic Stabilization   Low-coordinated Species
Heteroatom            Transition Metal Complexes

Selected Publications
Sakagami, M.; Sasamori, T.; Sakai, H.; Furukawa, Y.; Tokitoh, N., 1,2-Bis(ferroceny1)-Substituted Distibene and Dibismuthene: Sb=Bi Units as μ Spacers between Two Ferrocenyl Units, Chem. Asian J., 8, 690-693 (2013).
Synthetic Equivalent of a Dialumene

Multiply bonded species involving heavier main-group elements have been extensively investigated, whereas the chemistry of analogous species involving group 13 elements is still in its infancy. Examples for isolable neutral heavier group 13 dimetallenes with the formula of R–M=M–R (M: Al, Ga, In, Tl) remain scarce for the homologues of gallium, indium, and thallium, and have been unknown for aluminum so far.

The dialumene-benzene adduct $1$ was obtained by the reduction of the 1,2-dibromodialumane in benzene. The C$_6$H$_6$ moiety of $1$ was readily exchanged with C$_6$D$_6$, naphthalene, anthracene, and bis(trimethylsilyl)acetylene at room temperature, thus affording the corresponding trapping products of dialumene $2$. It was demonstrated that $1$ shows unique reactivity as a synthetic equivalent of $2$ for applications in the development of new organoaluminum species.

Alumole and Its Dianion

Heteroles of electron-deficient group 13 elements are expected to have low-lying LUMOs owing to the orbital interactions between the empty $\pi$ orbital of group 13 elements and the $\pi^*$ orbitals. To date, only a few examples of alumole (aluminacyclopentadienes)–Lewis base complexes have been structurally characterized. The coordination of Lewis bases to the aluminum center may substantially affect the electronic structures, therefore the synthesis of Lewis base-free alumoles has been desired to provide a basis for the elucidation of the intrinsic nature of alumoles.

We have succeeded in the synthesis of a Lewis base free alumole $3$ by the introduction of bulky substituent, Mes* group. The AlC$_4$ ring of $3$ exhibits the C–C bond alternation. Reduction of $3$ with lithium afforded the lithium salt of the alumole dianion $4$. DFT calculations revealed that the 3p(Al)-$\pi^*$ conjugation effectively lowers the LUMO energy level of the alumole and that coordination of two lithium cations to the alumole dianion is a key factor to keep the planar AlC$_4$ ring structure.

1,2-Bis(ferrocenyldistibene) and Dibismuthene

The d–$\pi$ electron conjugated systems consisting of bimetallic complexes with $\pi$-electron spacers, M–($\pi$-conjugated system)–M (M=transition metals), are extensively investigated from the viewpoint of their interesting electronic, optical, and magnetic properties.

We have succeeded in the synthesis of the first stable 1,2-bis(ferrocenyldistibene) $5$ and 1,2-bis(ferrocenyldibismuthene) $6$ by taking advantage of a newly developed bulky ferrocenyl group. The assessment of their structural parameters and physical properties indicated their definite Sb=Sb and Bi=Bi double-bond character. The electrochemical measurements revealed that distibene $5$ and dibismuthene $6$ exhibit stable, four-step (one reduction, three oxidation) redox processes reflecting the unique character of Sb=Sb and Bi=Bi $\pi$ bonds, and Sb=Sb and Bi=Bi $\pi$-electron units can act as effective $\pi$ spacers to couple with the two ferrocenyl moieties.