

# Division of Synthetic Chemistry – Organoelement Chemistry –

[http://oec.kuicr.kyoto-u.ac.jp/~tokitohlab/index\\_e.html](http://oec.kuicr.kyoto-u.ac.jp/~tokitohlab/index_e.html)



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## Scope of Research

Organic chemistry has mainly developed with the use of second-row elements such as carbon, oxygen, and nitrogen, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds has been a dream 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 fundamental chemistry, and open the way to the more extensive application of main group chemistry.

### KEYWORDS

Steric Protection

Kinetic Stabilization

Low-Coordinated Species

Heteroatom

Transition Metal Complexes



## Recent Selected Publications

Yanagisawa, T.; Mizuhata, Y.; Tokitoh, N., A Novel Reactivity of Phosphanylaluminum (>P–Al<): Reversible Addition of a Saturated Interelement Bond to Olefins, *Chem. Eur. J.*, **27**, 11273–11278 (2021).

Iwai, K.; Mizuhata, Y.; Tokitoh, N., Alkali-Metal-Ion-Centered Sandwich Structures of 4-Bromophenyl[Tris(Pentafluorophenyl)]Borates and Their Synthetic Utility, *Organometallics*, **40**, 570–577 (2021).

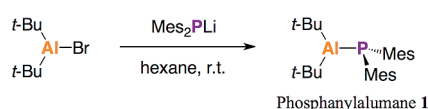
Yanagisawa, T.; Mizuhata, Y.; Tokitoh, N., Additive-Free Conversion of Internal Alkynes by Phosphanylaluminas: Production of Phosphorus/Aluminum Frustrated Lewis Pairs, *ChemPlusChem*, **85**, 933–942 (2020).

Fujimori, S.; Mizuhata, Y.; Tokitoh, N., Stannabenzylpotassium: The First Isolable Tin-Containing Benzene Derivative, *Chem. Eur. J.*, **24**, 17039–17045 (2018).

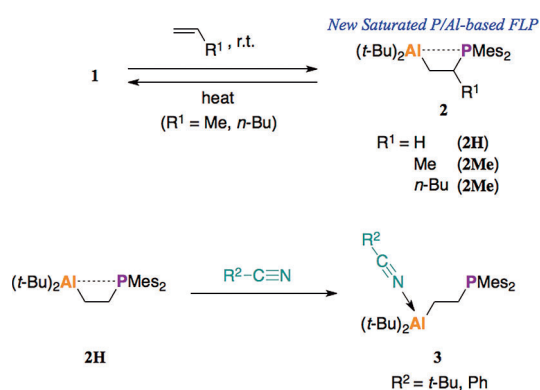
Mizuhata, Y.; Fujimori, S.; Sasamori, T.; Tokitoh, N., Germanbenzylpotassium: A Germanium Analogue of a Phenyl Anion, *Angew. Chem. Int. Ed.*, **56**, 4588–4592 (2017).

## A Novel Reactivity of Phosphanylalumane

The bonding between group 13 (E) and group 15 (Pn) elements formulated as  $R_2E-PnR_2$  have attracted much attention due to their relationship, including the vacant p orbital on E and the lone-pair electrons on Pn. In this study, we have reported synthesis and reaction of novel  $\lambda^3, \lambda^3$ -phosphanylalumane **1**, Al–P single-bond species, by the reactions of aluminum monohalides  $[(t-Bu)_2AlBr]$  with  $Mes_2PLi$ .



We found the reversible addition of olefins to phosphanylalumane **1** to be the first case for single-bond compounds of main group elements. Although the substrate scopes of alkenes are limited to terminal alkenes ( $R^1-CH=CH_2$ ) with relatively small substituents ( $R^1 = H, Me,$  and  $n-Bu$ ), corresponding alkene adducts **2** were obtained. In the case of  $R^1 = Me$  and  $n-Bu$ , the P–Al bond of the alkene adducts (**2Me** and **2Bu**) was recombined accompanied by the liberation of the corresponding alkene on heating. On the other hand, ethylene was not liberated from **2H** even on heating. We demonstrated the reactivity of **2H** as a new C2 *vicinal* P/Al-based FLP. In the reaction of **2H** with nitriles, nitriles were coordinated to Al as linear LBs with retention of the ethylene bridge, like the case of the P/B system.

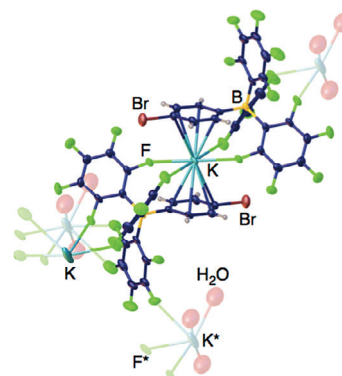
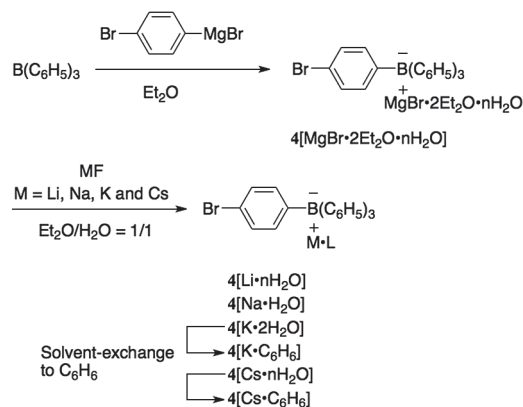


## Alkali-metal-ion-centered Sandwich Structures of 4-Bromophenyl[tris(pentafluorophenyl)]borates

Fluorinated tetraarylborates (FTABs) are known as one of the best partners of reactive cations and radical cations. In addition, fascinating effects of ionic substituents have

recently gathered much attention from organic chemists. We newly designed alkali-metal 4-bromophenyl[tris(pentafluorophenyl)]borates  $4[M \cdot L]$  ( $M = Li, Na, K, Cs,$   $MgBr$ ;  $L =$  coordinating solvents;  $H_2O, C_6H_6$ ) as synthetic units to explore reactive cations as zwitterionic compounds.

The single-crystal X-ray diffraction analysis revealed their unique sandwich structures: that is, the bimolecular-associated sandwich structures for  $4[Na \cdot H_2O]$  and  $4[K \cdot 2H_2O]$ , the sandwich structure with  $C_6H_6$  for  $4[K \cdot C_6H_6]$ , and the benzene-caged structure for  $4[Cs \cdot 2C_6H_6]$ . The key factor in constructing their sandwich structures was found to be the presence of coordinative *o*-fluoro groups and a  $\pi$ -electron-donating *p*-phenylene moiety, which form a cation-capturing pocket. Moreover, the ion radius of the counteranion was found to be a crucial factor. Remarkably, a larger cesium ion could be captured in the pocket to form a benzene-caged structure, while smaller counteranion salts  $4[MgBr \cdot 2Et_2O \cdot nH_2O]$  and  $4[Li \cdot nH_2O]$  could not form specific aggregates. The results of variable-temperature  $^{19}F$  NMR and DART-MS measurements suggested the retainment of the sandwich structures even in nonpolar solvents. The cation-capturing ability of the FTAB unit investigated in this work could be applied to the chemistry of supramolecular systems and organocatalyses.



Structure of  $4[K \cdot 2H_2O]$