Reactivity, bonding and structural elucidation of pendant methyl-pyridinato β-diketiminate ligand moiety

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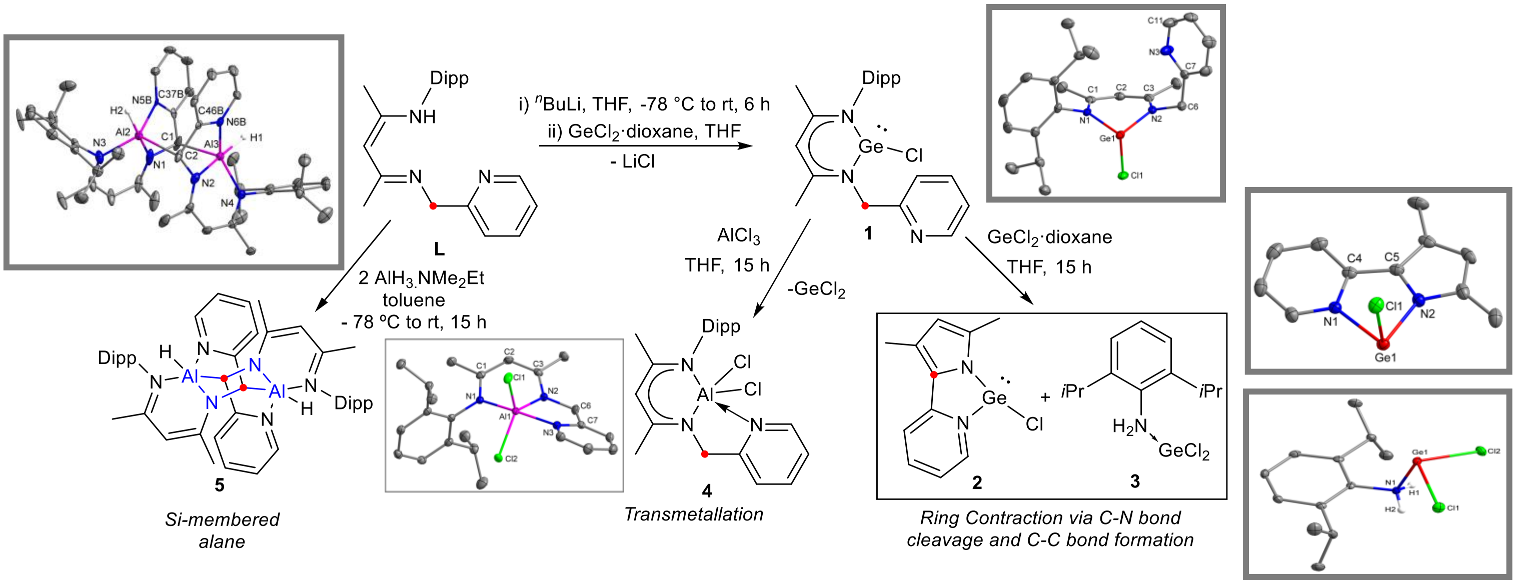
The development of sterically encumbered ligands that contain anionic nitrogen donor sites (NR^{2-}) has played a pivotal role in advancing our overall knowledge of fundamental chemical reactivity throughout the Periodic Table. Recently, we are introducing a methyl-pyridine side arm in the *β*-diketiminato framework leads to a ligand that is tridentate in its nacnac imino-pyridine state (2,6-*i*Pr_2-$C_6H_3NC(Me)CHC(Me)NH(CH_2py)$)[1]. Such ligands have not been used for compounds with low valent *p*-block elements. We presumed that additional donation from the nitrogen atom of the pyridine moiety may provide sufficient electronic stabilization that would compensate for the decrease in the sterics. Here we have successfully synthesized and characterized methylpyridinato *β*diketiminate ligand stabilized chlorogermylene **1** which undergoes unusual smooth ring contraction in presence of Lewis acid ($GeCl_2$.dioxane) via C–N bond cleavage (**2**), facile dehydrocoupling and six membered Al-heterocycle formation (**5**), which are not observed for the nacnac based systems (Scheme 1). But, in presence of another Lewis acid containing group 13 element like $AlCl_3$, leads to the formation of dicholoaluminim complex **4** via the transmetallation process (Scheme 1). Single crystal X-ray study reveals that the pyridine moiety coordinates to the aluminum center in **4**, possibly due to the radius of the aluminum atom is apparently too small compared to the ligand's bite angle, which leads to the asymmetric coordination. The work is another testimony to the fact that small variations can yield unprecedented outcomes.[2]



Scheme 1: Schematic representation of diverse reactivity and bonding attitude of ligand L

[1] X. Xu, Y. Chen, G. Zou, J. Single. Sun, *Dalton Trans*. **2010**, *39*, 3952−3958.

[2] S. Pahar, V. S. V. S. N. Swamy, T. Das, R. G. Gonnade, K. Vanka, S. S. Sen, *Chem. Commun*. **2020**, *56*, 11871−11874.

Keywords: Structural diversity, Flexibility of *β*-diketiminate ligand, Transmetallation among two p-block elements, six-membered dialane heterocycle: an analogue of cyclohexane

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