

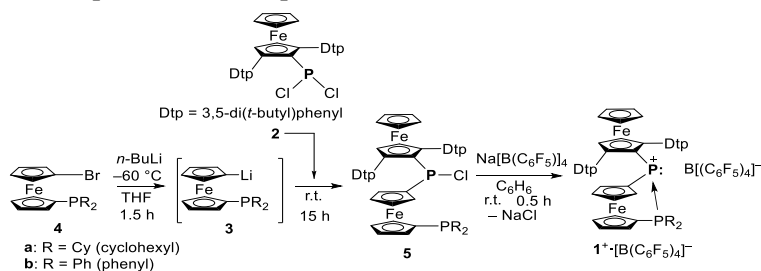
## Synthesis and Isolation of the Phosphine-Stabilized Phosphenium Complexes with a [2]Ferrocenophane Framework Compounds

(<sup>1</sup>Graduate School of Science, Nagoya City University, <sup>2</sup>Faculty of Pure and Applied Sciences, University of Tsukuba)

○Tianqing Zhang,<sup>1</sup> Vladimir Ya. Lee,<sup>2</sup> Shinobu Aoyagi,<sup>1</sup> Takahiro Sasamori,<sup>2</sup>

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Recent studies on the low-coordinate species of the heavier main group elements, such as silylenes and germylenes, have shown that they can behave similarly to the transition metal complexes.<sup>1</sup> Phosphenium ions, derivatives of divalent phosphorus  $R_2P^+$  that are isoelectronic to silylenes, are intrinsically highly reactive. In the most isolable phosphenium ions, the phosphorus center is thermodynamically stabilized by electron-donating substituents, which results in its electronic perturbation and decrease in the reactivity.<sup>2</sup> Moreover, phosphenium ion species can be stabilized kinetically by steric protection with bulky substituents.<sup>3</sup> Therefore, we used a bulky ferrocenyl group which can kinetically stabilize phosphenium ion towards self-oligomerization due to its high redox activity. As the second substituent at the phosphenium center, another ferrocenyl group containing stabilizing intramolecular-donor  $PR_2$  substituent ( $R$  = cyclohexyl or phenyl) was applied to ensure the reversible thermodynamic stabilization. The bis(ferrocenyl)chlorophosphine precursor **5** was synthesized by the reaction of (ferrocenyl)dichlorophosphine **2**<sup>4</sup> and ferrocenyllithium derivative **3** (formed by the lithiation of the bromide precursor **4**<sup>5</sup>). Oxidative dechlorination of **5** with  $Na[B(C_6F_5)_4]$  produced the target  $1^+[B(C_6F_5)_4]^-$ ,<sup>6</sup> in which phosphenium center is stabilized by the intramolecular coordination of the  $PR_2$  ligand. Particular structure and reactivity of phosphenium complexes  $1^+[B(C_6F_5)_4]^-$  are discussed on the basis of their spectral and computational data.



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