

## Organorhodate and -Iridate —Structure and Reactivity—

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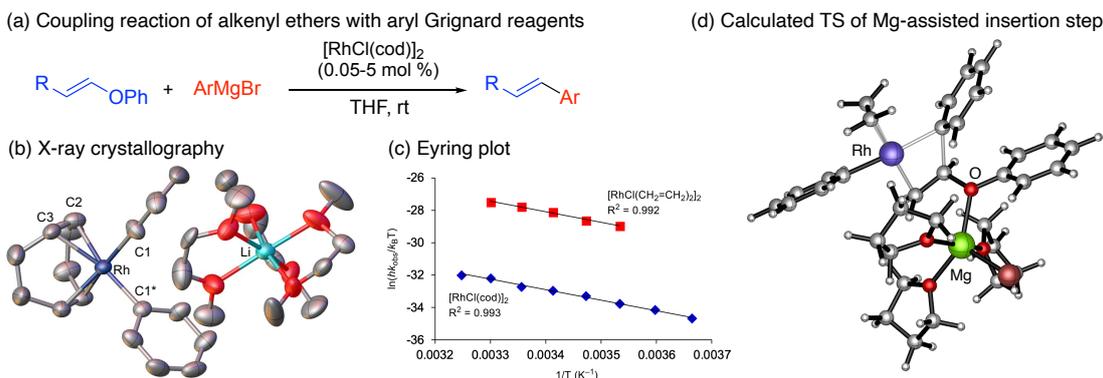
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Anionic organo transition metal complexes, so-called “ate” complexes, show unique structural feature as well as reactivity. In addition to the classical alkylating reagents such as Gilman reagents, ate complexes have recently been attracting attention as key catalytic active species as useful synthetic tools. In this context, we have developed organo metalates of various late transition metals and employed them to C–C bond formations. In this lecture, I will present our achievements on organo metalates of the group 9 metals, Rh and Ir.

In 2014, we reported that the coupling reaction of alkenyl aryl ethers with aryl Grignard reagents via the vinylic C–O bond cleavage proceeded smoothly in the presence of catalytic amount of  $[\text{RhCl}(\text{cod})]_2$  (Scheme 1a).<sup>1</sup> This catalyst showed unique chemoselectivities including selective cleavage of vinylic C–O bond even in the presence of aromatic C–O, C–S, and C–Br bonds.

Mechanistic studies revealed that the treatment of  $[\text{RhCl}(\text{cod})]_2$  with an excess  $\text{ArMgBr}$  yielded  $[\text{RhAr}_2(\text{cod})]^-$ , which reacted with a vinyl ether to give the coupling product. The corresponding  $[\text{Li}(\text{dme})_3][\text{RhPh}_2(\text{cod})]$  (**1<sub>Rh</sub>**) was successfully isolated and determined its structure by X-ray crystallography (Scheme 1b). Indeed, the isolated **1<sub>Rh</sub>** catalyzed the coupling reaction, suggesting the intermediacy of the diarylrhodate.

Recently, we conducted further mechanistic studies to gain the insight into the reaction mechanism.<sup>2</sup> A kinetic study using a flow microreactor revealed that the reaction of diarylrhodate with phenyl vinyl ether is the rate-determining step in the catalytic cycle. In addition, olefinic ligands in the Rh pre-catalysts largely affected catalytic performance, and  $[\text{RhCl}(\text{CH}_2=\text{CH}_2)_2]_2$  showed ca. 20 times higher catalytic activity in comparison with  $[\text{RhCl}(\text{cod})]_2$  (Scheme 1c). DFT calculations suggest that the reaction between diarylrhodate



Scheme 1. (a) Rh-catalyzed cross-coupling of alkenyl ethers with  $\text{ArMgBr}$ . (b) ORTEP drawing of **1<sub>Rh</sub>**. (c) Eyring plot of the reaction using  $[\text{RhCl}(\text{cod})]_2$  and  $[\text{RhCl}(\text{CH}_2=\text{CH}_2)_2]_2$ . (d) Transition state of insertion of vinyl ether.

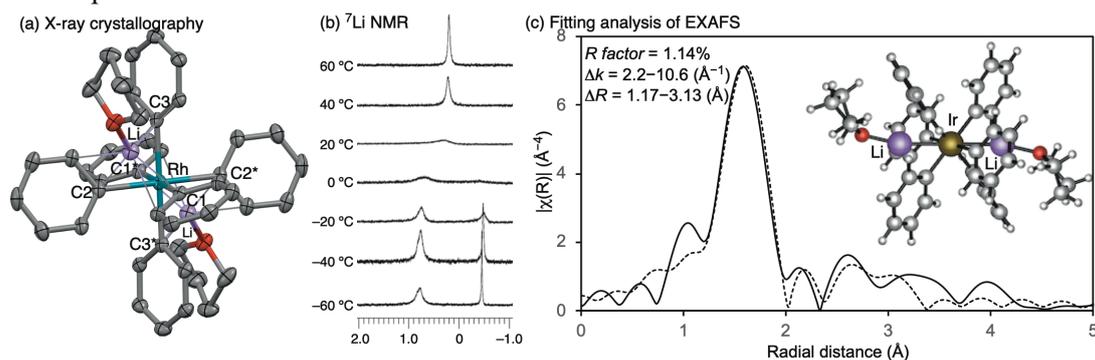
and vinylic ethers proceeds through Mg cation-assisted insertion/*anti*- $\beta$ -oxygen elimination sequence (Scheme 1d). Based on these mechanistic understanding, we successfully applied the Rh catalyst to the cross-coupling reaction of benzofurans with aryl Grignard reagents.<sup>2</sup>

Analogous lithium diphenyliridate **1<sub>Ir</sub>** was synthesized by a similar way to **1<sub>Rh</sub>**.<sup>3</sup> X-ray crystallographic analysis of the complexes showed both contact ion pair (CIP) and solvent-separated ion pair (SSIP) structures depending on the coordination environment around the Li cation.

During the course of the investigation on Rh(I) and Ir(I) organo metalates, we found that Rh(III) and Ir(III) also form ate complexes upon treating aryllithium reagents.<sup>4</sup> In 1989, Wilkinson and co-workers reported [Li(tmeda)]<sub>3</sub>[MMe<sub>6</sub>] (M = Rh and Ir) and determined their structure to be a CIP structure.<sup>5</sup> However, attempts to synthesized homoleptic hexaarylmatalate of Rh and Ir using electron-deficient pentahalophenyllithiums resulted in the formation of pentaarylmatalates, and hexaarylmatalates had not been synthesized for *d*<sup>6</sup> transition metals.

When MCl<sub>3</sub>(tht)<sub>3</sub> (M = Rh and Ir) was treated with 8 equivalents of PhLi, the corresponding [Li(thf)<sub>n</sub>]<sub>3</sub>[MPh<sub>6</sub>] **2** was obtained in 70-76% yields. Crystals suitable for X-ray crystallography were obtained by recrystallization in the presence of 12-crown-4. X-ray crystallography revealed that the crystal structure of **2<sub>Rh</sub>** contains one Rh bearing six Ph moieties in an ideal octahedral geometry and three Li cations. Two Li cations with one THF molecule contact the Ph moieties on Rh, and the other in the outer sphere is surrounded by two 12-crown-4 molecules (Scheme 2a).

<sup>7</sup>Li NMR and solution-phase EXAFS analyses of **2<sub>Ir</sub>** indicated that the partially solvent-separated ion pair structure was maintained even in a coordinating solvent, THF (Scheme 2b and c). This may suggested that the coordination of Li cations to the anionic counterpart stabilizes the trianionic iridate.



Scheme 2. (a) ORTEP drawing of anionic part of **2<sub>Rh</sub>**. (b) VT <sup>7</sup>Li NMR of **2<sub>Ir</sub>**. (c) EXAFS spectrum of **2<sub>Ir</sub>** and 10 equiv. of 12-crown-4 in THF (solid line) and fitting curve of calculated structure (dashed line).

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