

Synthesis and Structure of Hexaarylrhodate and -iridate Complexes

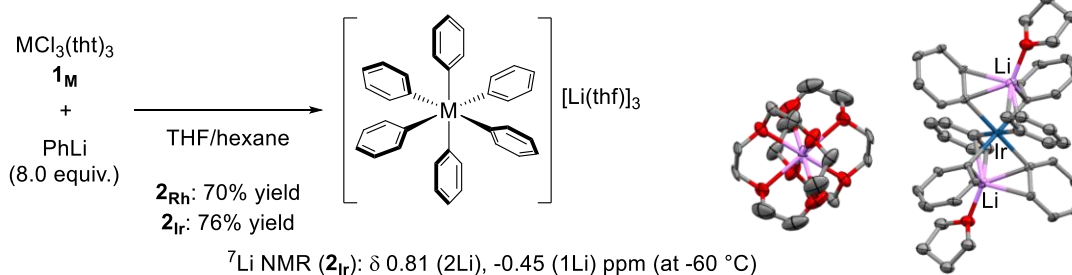
(Graduate School of Engineering, The University of Tokyo) ○ Yuko Hirooka, Takanori Iwasaki, Kyoko Nozaki

Keywords: Ate Complexes; Higher Order Anionic Complexes; Rhodate Complex; Iridate Complex; X-ray Crystallography

Anionic transition metal complexes, generated by the reaction of transition metals with organometallic reagents, have been proposed as active species in carbon-carbon bond formations, but their molecular structures are not clear in many cases.¹ Homoleptic higher order anionic complexes with six carbanions coordinated to the metal center have been synthesized with early transition metals but are rarely discussed with late transition metals. In group 9 metals, tetraalkyl- and/or tetraarylcobalates and -iridates are known. In the case of rhodium, not only tetraaryl- but also pentaarylrhodates are reported.² However, octahedral analogs of group 9 metals have not been reported with only one exception of hexaalkenylcobalate.³ During our continuous study on rhodate and iridate complexes, we found that Rh(III) and Ir(III) also form higher order hexaaryl complexes that have a formal -3 charge at the metal center.

Hexaphenylrhodate **2_{Rh}** and -iridate **2_{Ir}** were successfully synthesized by treating $\text{MCl}_3(\text{tht})_3$ (**1**: $\text{M} = \text{Rh}$ or Ir , $\text{tht} = \text{tetrahydrothiophene}$) with an excess amount of PhLi as beige and white solid in 70% and 76% yields, respectively. The X-ray crystallography revealed that the six phenyl groups bind to the metal center in an ideal octahedral geometry. The C–M bond lengths of **2_{Rh}** and **2_{Ir}** are in the range of 2.12–2.16 Å, which are *ca.* 0.1 Å longer than that of $\text{Ph}_2\text{M}(\text{cod})^-$.⁴ Two Li cations contact to the anionic part, and the other one exists as solvent-separated ion pair. ^7Li NMR analysis of **2_{Ir}** at -60°C showed two signals at 0.81 and -0.45 ppm in 2:1 ratio, which may suggest that two Li cations contact to the anionic part even in THF. This strong interaction between Ph_6Ir anion and Li cations is probably due to the delocalization of negative charge by electron-donation from C–Ir bonding orbitals to Li to stabilize the higher ordered state.

Scheme 1. Synthesis of hexaphenylrhodate and -iridate and the molecular structure of **2_{Ir}**



1) A. Gómez-Suárez, D. J. Nelson, S. P. Nolan, *Adv. Organomet. Chem.* **2018**, 69, 283. 2) M. Angeles García-Monforte, P. J. Alonso, J. Forniés, B. Menjón, *Dalton Trans.* **2007**, 3347. 3) L. A. Berben, J. R. Long, *Inorg. Chem.* **2005**, 44, 8459. 4) T. Iwasaki, T. Akaiwa, Y. Hirooka, S. Pal, K. Nozaki, N. Kambe, *Organometallics* **2020**, 39, 3077.