Synthesis, Structure, and Reactivity of Heterobimetallic Complexes Featuring Period 4 Transition Metal–Rh bonds

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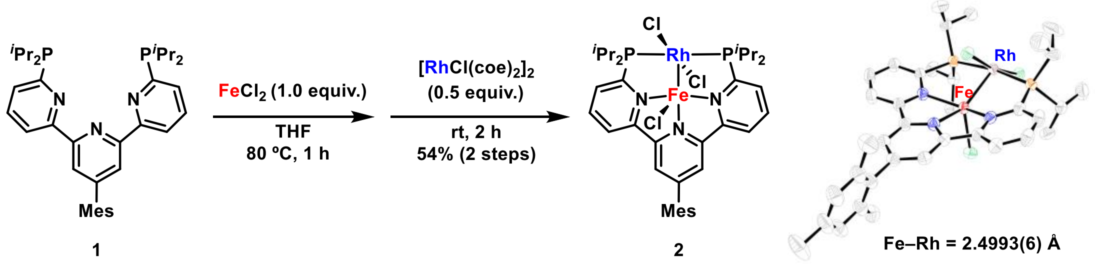
Keywords: Heterobimetallic complex; Rhodium; Period 4 transition metals; Iron; Nickel

In the last decade, metal–metal bonded complexes have been reported to exhibit specific reactivities in catalytic transformations due to their unique electronic configurations. Period 4 transition metals are usually redox active via single electron transfer processes, thus invoking their potential utility as electron reservoirs in bimetallic systems. Therefore, exploration of synthesis and catalysis of bimetallic complexes having period 4 metal–late transition metal bonds is significantly attractive.

Herein, we report systematic synthesis of heterobimetallic complexes featuring period 4 transition metal–Rh bonds utilizing a 6,6”-bis(phosphino)-2,2’:6’,2”-terpyridine derivative **1** as a scaffold for the metal–metal bond (**Scheme 1**). Sequential addition of $FeCl_2$ and $[RhCl(coe)_2]_2$ to the multidentate ligand **1** afforded an Fe–Rh complex **2** in good yield. XRD analysis disclosed that the Fe–Rh distance is shorter than the sum of the corresponding covalent radii, supporting formation of direct Fe–Rh bonding. This method was also applicable to other period 4 metals instead of Fe. Furthermore, it was found that treatment of the Fe–Rh complex with HBpin generated a Fe–Rh hydride species, which could be useful for catalytic molecular transformations.



- Structure and reactivity
- Applicable to other period 4 metals

Scheme 1. Synthesis and structure of the Fe–Rh complex **2**.