

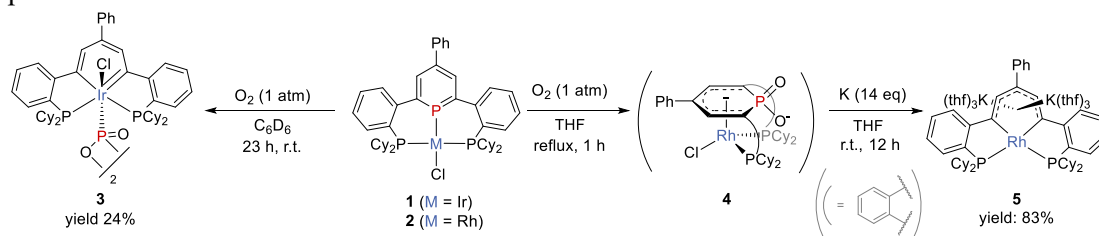
Conversion from Phosphinine Pincer Metal Complexes to Metallabenzenes Triggered by O₂ Oxidation

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Since Kekulé proposed the correct structure of benzene in 1865, tremendous progress has been made in the chemistry of aromatic compounds. In this context, transition-metal-based metallabenzenes, where a CH group on a benzene ring is replaced by a transition metal fragment, have attracted great interest¹ for the participation of metal d orbital in π conjugation of an aromatic system. After Thorn and Hoffman predicted the aromatic character of mangano- and rhoda-benzenes,² metallabenzenes have been synthesized with some late transition metals, such as Mo, Re, Fe, Ru, Os, Ir, Ni, and Pt.¹ Although various methods for the synthesis of metallabenzene have been developed, the scope of each methodology is confined by the character of transition metal centers, and thus, metallabenzenes lack of general synthetic methodology.³ Herein, we report the new route to metallabenzenes from phosphinine (phosphabenzene), directly swapping the phosphorous atom for a transition metal fragment.

Novel phosphine-phosphinine-phosphine pincer iridium (I) complex **1** and rhodium (I) complex **2** were first synthesized. The reaction of complex **1** with an atmospheric pressure of oxygen gas resulted in a spontaneous crystallization of iridabenzene **3** in 24% yield. This method, the transformation of phosphinine to metallabenzene was further applied to the synthesis of rhodabenzene, which has never been addressed in any method.⁴ Complex **2** was treated with an atmospheric pressure of oxygen gas to afford pentadienyl rhodium (III) complex **4**. Notably, further reduction of complex **4** by an excess amount of potassium metal afforded rhodabenzene **5**. The structure of rhodabenzene **5** was unambiguously determined by single-crystal X-ray diffraction analysis. The mechanism of the formation of metallabenzenes and the aromaticity of them will be discussed in this presentation as well.



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