

Synthesis and Reactivities of Cyclopentadienone Group 5 Metal Complexes

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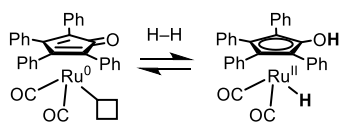
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Cyclopentadienone(=CpO)/hydroxycyclopentadienyl(=CpOH) late transition-metal complexes have been well-studied as an active metal–ligand bifunctional catalyst in hydrogenation.^{1,2} The reaction of the complex with, e.g., H₂ is driven by the electron transfer from the metal to the CpO ligand (**Scheme 1**). In this study, we applied the system to unprecedented low-valent group 5 metals that have stronger reducing characters³ than late transition metal counterparts.

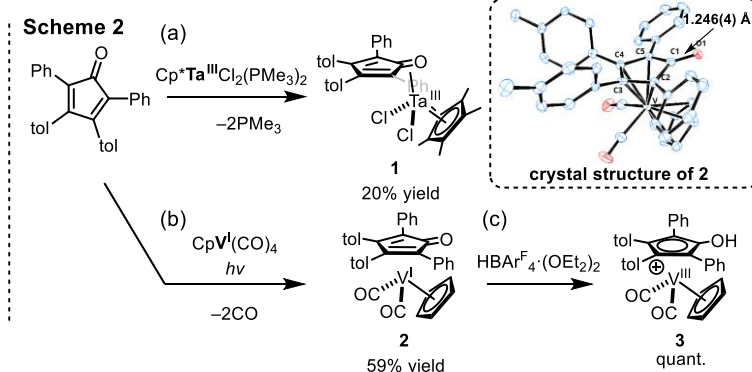
The reaction of tetraarylcyclopentadienone with Cp*Ta^{III}Cl₂(PMe₃)₂ gave CpO tantalum(III) complex **1**, in which π -orbital of the ligand C=O bond was bound to the metal center in an η^2 -fashion (**Scheme 2a**). On the other hand, the reaction with CpV^I(CO)₄ resulted in the formation of η^4 -CpO vanadium(I) complex **2**, which was fully characterized by single crystal XRD analysis (**Scheme 2b**). The structural analysis for **2** clarified that it had the longest C–O bond length of 1.246(4) Å on the ligand among the family of analogous CpO metal complexes. This observation suggests a large electron transfer from the low-valent vanadium center to the CpO ligand. The redox activity of the CpO vanadium(I) complex **2** was confirmed by the reaction with a proton source. Upon addition of HBAr^F₄·(OEt₂)₂ to the solution of **2**, the formation of CpOH vanadium complex **3** was confirmed (**Scheme 2c**). Notably, IR measurements for **3** identified the disappearance of the signal for the carbonyl of the CpO ligand and the increased $\nu(\text{CO})$ value for metal-carbonyls. These spectral changes elucidated the oxidation of the vanadium center from I to III.

Scheme 1

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Scheme 2



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