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### SALT-FREE REDUCTION OF TRANSITION METAL COMPLEXES FOR GENERATING CATALYTICALLY ACTIVE LOW-VALENT SPECIES

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Salle D2

#### Biographie

Hayato Tsurugi is an associate professor of the Graduate School of Engineering Science, Osaka University. He received his Ph.D. degree in 2006 from Osaka University under the supervision of Prof. K. Mashima. From 2006 to 2008, he worked with Prof. M. Miura as an assistant professor at the Graduate School of Engineering, Osaka University. In 2008, he joined Prof.

K. Mashima's group at the Graduate School of Engineering Science, Osaka University as an assistant professor, and then promoted to an associate professor in 2010. His research interests are in the areas of organometallic chemistry, including catalytic applications for direct C-H transformation, radical coupling reactions,  $\alpha$ -olefin oligomerization/polymerization, as well as coordination chemistry with transition metals for synthesizing homo/heterometal clusters, and the development of new reduction methods using main-group element compounds.

#### Abstract

Low-valent transition metal species have attracted special attention due to their important role in the activation of small molecules. Reduction of high-valent transition metal complexes is the general strategy for preparing highly reactive low-valent transition metal species without any  $\pi$ -acidic ligands, and strong reductants, such as amalgams of alkaline and alkaline-earth metals, zinc dust, and alkylmetal reagents, are conventionally used as the reductants. Generation of the low-valent metal species using the reductants, however, is always accompanied by reductant-derived metal wastes as well as over-reduced impurities. Thus, such the reducing method sometimes not only hampers isolation of the desired low-valent metal complexes but also retards their reactivity or catalytic performance due to coordination of the reductant-derived metal salt to the reactive metal center.

We first reported that 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene acted as a unique reducing reagent for early transition metal halides: when  $TaCl_5$  was reduced under ethylene atmosphere, we found the selective linear trimerization of ethylene with excellent catalytic activity. The high reducing ability of the silicon compound led us to prepare low-valent tantalum, niobium, and tungsten species with easy removal byproducts, toluene and chlorotrimethylsilane. The generated low-valent species was isolated and characterized through trapping by coordinating solvents such as THF or redox-active molecules such as  $\alpha$ -diimine and  $\alpha$ -diketone ligands.

During our screening of the metal complexes and organosilicon compounds for the generation of low-valent metal species, we found that 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine derivatives reduced halides, carboxylates, and acetylacetonates of late transition metals to produce the corresponding metallic particles. Noteworthy was that  $Ni(acac)_2$  became an effective catalyst for reductive biaryl formation of haloarenes in the presence of 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine derivatives. In this reaction, metallic particles were precipitated from the reaction mixture. By monitoring the in-situ generated Ni nanoparticles (NPs) by TEM, we found that the Ni NPs was amorphous nature. Effect of organic ligands on the catalytic performance of the Ni amorphous NPs suggested the generation of reactive Ni(0) species in the reaction mixture.

#### References

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