VII-H Preparation and Properties of the Homo- and Heterometallic Clusters

This project focuses on the development of a systematic synthetic route to a series of the homo- and heterometallic clusters as templates or catalysts for new types of activation and transformation of organic, inorganic, and organometallic molecules at the well-defined multimetallic reaction sites.

VII-H-1 Synthesis and Reactivities of Amido-Bridged Dinuclear Ruthenium Complexes

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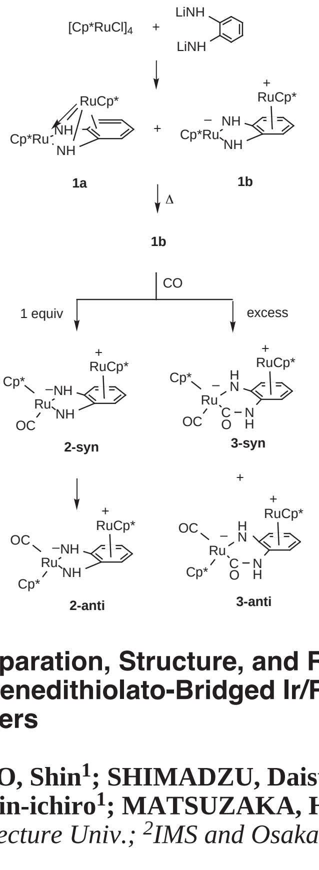
Novel dinuclear ruthenium 1,2-phenylenediamido complexes (**1a**) and (**1b**) were prepared and their reactivities have been examined in detail. Complex **1a** is cleanly converted to **1b** in refluxing acetonitrile. Treatment of 1b with 1 equiv of CO yields the carbonyl adduct (**2**), which further reacts with excess CO to form the amido/carbamoyl/carbonyl complex (**3**).



VII-H-2 Preparation, Structure, and Reactivity of the Benzenedithiolato-Bridged Ir/Ru Mixed-Metal Clusters

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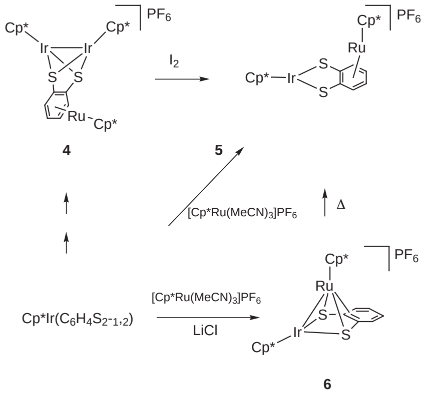
A series of the iridium/ruthenium mixed-metal clusters containing a bridging benzenedithiolato ligand were selectively synthesized in good yields and their chemical reactivities have been examined in detail. Oxidation of the Ir(II) centers in the novel Ir_2R mixed-metal cluster **4** with I_2 readily proceeded to give the IrRu cluster **5** together with [Cp*IrI(μ_2-I)]$_2$. Direct treatment of Cp*Ir(-$C_6H_4S_2$-1,2) with [Cp*Ru-(MeCN)$_3$]PF_6 alternatively afforded **5**, whereas similar reaction in the presence of LiCl selectively produced **6**, the isomeric form of **5**, which was quantitatively converted to **5** in refluxing acetonitrile.



VII-H-3 Selective Transformation of the Oligomeric Ru_2Rh Cluster to the Ru_3Rh_2 and the Ru_4Rh_4 Framework

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Selective heteronuclear metal-metal bond formation reaction readily proceeded to give the Ru_3Rh and Ru_4Rh_4 mixed-metal clusters (**7** and **8**) from mononuclear precursors *via* oligomeric Ru_2Rh complex (**9**).