Laboratory of Organometallic Chemistry

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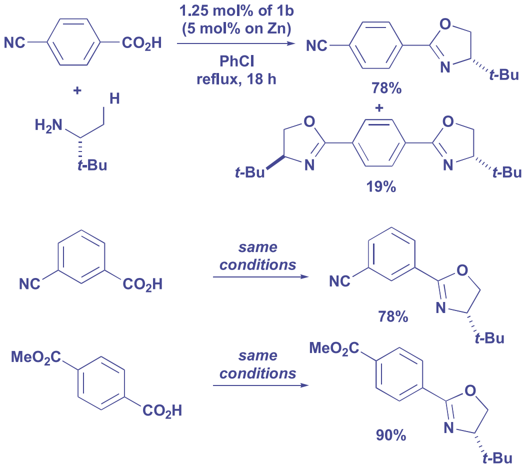
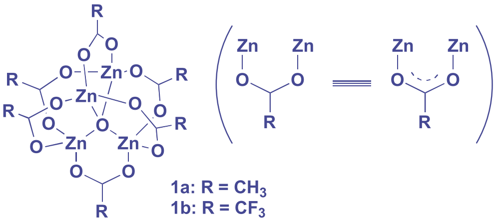
Artificial, Enzyme-like Multimetal Catalysts

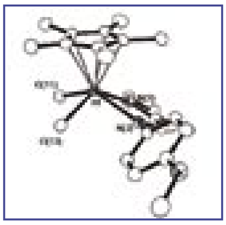
We are focusing our interest on developing homo- and hetero-multimetallic clusters for use as artificial enzyme-like catalysts which can lead to unique organic reactions without forming any waste, thereby facilitating environmentally benign processes and green chemistry. The μ-oxo-tetranuclear zinc cluster $Zn_4(OCOCF_3)_6O$ (**1b**) was found to be a catalyst for the direct catalytic conversion of esters and lactones to oxazolines, which are commonly found in natural products, and their use for pharmaceutical drug discovery has stimulated great interest in recent years. This catalysis is applicable to the reaction of carboxylic acids and does not require azeotropic dehydration. In addition, we found remarkable chemoselectivity suitable for the synthesis of bis(oxazoline) that contains different oxazoline moieties. Acylation of alcohol (esterification) and amine (amidation) is one of the most fundamental and widely used reactions in both organic and biological processes. Because of the much higher nucleophilicity of the amino group compared to the hydroxyl group, and the higher thermodynamic stability of amides compared to esters, *N*-acylation proceeds entirely in organic synthetic reactions. Only enzymatic catalysis can promote highly selective *O*-acylation reactions. We have found that acylation using the μ-oxo-tetranuclear zinc cluster **1b** efficiently catalyzes highly chemoselective acylation of hydroxyl groups in the presence of primary and secondary alkyl amino groups to produce high yields of the corresponding esters. This method can be applied to the direct conversion of aminoalcohols to the corresponding aminoesters, opening up the option of developing a new transformation without using protecting groups. Thus, we are also studying hetero-multimetal catalysts that show enzyme-like selectivity and reactivity.





1a: R = CH_3
1b: R = CF_3

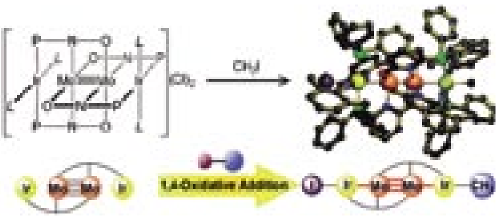
Organometallic Chemistry and Catalysis of Early Transition Metals

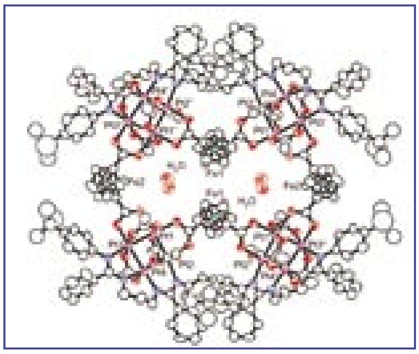


We have been carrying out long-standing fundamental research in the area of organometallic chemistry involving group 5 metals and other early transition metals, aiming to develop new polymerization catalysts through the design and synthesis of new ligand systems able to support and promote the novel chemistry of early transition metals. Recent achievements include finding that nonbridged half-metallocene dimethyl-hafnium complexes with *N*-substituted (iminomethyl)pyrrolyl ligands show unique catalytic performance for the isoselective living polymerization of 1-hexene upon treatment with $[Ph_3C][B(C_6F_5)_4]$ below 0 °C, and that $M(CH_2Ph)_4$ (M = Zr and Hf) reacts with α-diimine ligands to selectively afford tribenzyl amido–imino complexes of zirconium and hafnium, whose treatment with $B(C_6F_5)_3$ then produces the corresponding cationic dibenzyl complexes capable of polymerizing 1-hexene.

Development of Nano-scale Clusters Containing Metal-Metal Bonds

We have synthesized linear and cyclic tetrametal clusters with metal-metal bonds on their main skeletons forming unique cluster units suitable for constructing nano-scale cluster molecules. We are developing a new type of chemistry based on the shape, kind, and number of metals. The hetero-metallic linear tetrametal clusters react with RX to undergo unusual 1,4-oxidative addition reactions. The assembly of the cisoid-capped Pt_4 complex $[Pt_4(\mu\text{-}OCOCH_3)_6(\kappa^4\text{-}N_4\text{-}DAr\text{-}Bp)]$ with an equimolar amount of 1,1'-ferrocenedicarboxylic acid undergoes stereoselective self-assembly to produce a tetramer, which is a unique precursor of immobilized catalysts.





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For other papers, see: http://cobalt.chem.es.osaka-u.ac.jp/organomet/english/publications.htm