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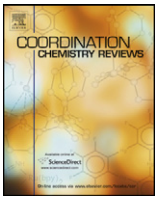

Review

Synthesis, reaction and catalysis of heterodinuclear organoplatinum or palladium complexes having M–M′ and M–C bonds without M–M′ connecting ligand

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ABSTRACT

Synthesis, reactions, and catalyses of heterodinuclear organometallic complexes without connecting ligands $L_2RM\text{-}ML'_n$ (M = Pt, Pd; M′ = Mo, W, Mn, Re, Fe, Co) are described. They are regarded as a simplest model for studying the cooperative effect of two transition metals in catalysis. Organic ligand R is found to move reversibly from M to M′ along M–M′ bond, which is accelerated by addition of electron-deficient olefins. The reaction is regarded as a reductive elimination of M′–R and the reverse process as oxidative addition reaction. The results may mimic the mobility of σ-bound organic group on heterogeneous surface. Visible light enhances reductive elimination (alkyl group transfer) in $(^tBu_2bpy)Me_2PhPt\text{-}Mn(CO)_5$. Enhanced CO insertion of heterodinuclear methylpalladium–cobalt system in comparison with mononuclear systems is presented and the mechanism is found to involve alkyl transfer followed by CO insertion into the Co–C bond and oxidative addition of σ-organic groups along heterometal–metal bond. Highly specific C–S bond cleavage reactions of heterodinuclear complex with thiiranes and thietanes are presented. Catalytic reactions such as carbonylation of thietane, copolymerization of aziridine and CO, and insertion of olefin or acetylene into Mo(or W)–H bond promoted by heterodinuclear complexes were described, where enhanced catalytic activity has been shown.

1. Introduction

Cooperative effect of different transition metals in catalysis is an interesting and intriguing unsolved research topic both in homo- and heterogeneous catalyses as well as in organometallic and coordination chemistry [1]. Many bi- or multimetallic heterogeneous catalysts are known to provide highly important industrial processes such as Ni-Mo and Co-Mo hydrodesulfurization catalysts

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[2], Pt-Re-S naphtha reforming catalyst etc. [3]. The high catalyst performance of these catalysts is expected to be the result of synergy effects of two or more different transition metals in their chemical processes. However origins of such effects are still far from understood at a molecular level even at present, though such fundamental insights are highly valuable for understanding their mechanisms and creating new high performing heterobimetallic catalysts. Synergy effects in catalysis are also observed in a few homogeneous systems. For example, selective hydroformylation has been achieved by Rh/Co mixed catalyst by Hidai and Ishii [4]. Smith also reported high regioselectivity in bimetallic hydroformyaltion catalyzed by $CpRu(\mu\text{-}CO)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}HC(PPh_2)_3\}RhCl_2$ [5]. Bimetallic synergism in alkyne silylformylation catalyzed by Co-Rh system is demonstrated by Ojima and Morokuma [6]. Polyethylene branching selective polymerization by Zr/B catalyst by Marks, and polymerization of ethylene [7] and ε-caprolactone by Ln/Al and Zr or Ti/Al oxygen bridged complexes by Roesky are also examples of homogeneous bimetallic catalysts [8]. Man et al. reported the coupling reaction of epoxide and carbon dioxide by heterobimetallic Ru–Mn complex [9]. Macrocyclization of thietanes using Os and Re carbonyl cluster complex catalysts by Adams is an unique catalytic reaction [10].

In order to obtain better insights of synergy effects in catalyses, many studies on synthesis and reactivity of heterometallic transition metal complexes had been done in recent decades, though these complexes also attract other interests toward magnetism, new materials, new structures and etc. Previous accomplishments on the chemistry of heterodinuclear organotransition metal complexes are reviewed by Bruce, Chetcuti, Adams, Braunstein comprehensively [11]. Among them, the heterometallic complexes having metal-to-carbon bonds are the most closely related model complex to catalysis, since the mechanisms of catalytic organic transformation should generally involve interaction between transition metal and organic reactants, where σ and π bonding modes are important factors. In order to stabilize such heterometal–metal bond, a few strategies are developed [11]. The most well-established idea to create multimetallic structure is to use multidentate ligands such as diphosphine, polyamine, polyolefin, etc. to bring the two transition metals in close contact to give M–M′ bonds [12]. However it is difficult to predict whether a direct M–M′ bond is formed or not, though two metals stay in the same discrete dinuclear complex molecules. Chalcogen and halogen atoms are also capable to bind two metals by acting as a bridging ligand. Carbon ligands including carbonyl and hydrocarbyl also frequently act as bridging ligands to connect two or more metals [11]. On the other hand, metathesis reaction of transition metal complexes, reactions between different coordinatively unsaturated complexes and treatments of acidic metal complex with basic metal complex are alternative methods. These methods usually produce the direct M–M′ chemical bond between two metals, but sometimes heterolytic dissociation is accompanied to cause M–M′ bond ionization. Synthesis and chemical behavior of such heterodinuclear and cluster complexes of transition metals especially involving bond forming and cleaving processes are comprehensively reviewed by Ritleng and Chetcuti [11a], showing the importance of synergism of heterometals in organometallic reactions and catalyses. Braunstein's accomplishments in heterometallic chemistry including trimethoxysilyliron-transition metal complexes, which have been summarized in a few reviews [1a,11a,11c], are also notable. Bruce, Deeming, and Adams independently developed pioneering studies on structural and reactivity chemistry of organotransition metal carbonyl clusters having a M–C bond, which is summarized in many reviews [1,10,11]. Their pioneering works on cluster chemistry definitely inspired many scientists to work in this field, but their accomplishments are not dealt with in this review, since these carbon ligands mainly act as bridging ligands and have been described in other reviews.

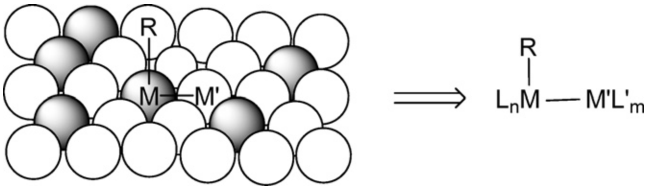

Fig. 1. Simplest model complex for organometallic active species in heterobimetallic catalyses.

In Chetcuti's review, the most simple heterodinuclear organotransition metal complexes $L_nRM–M'L_m$ having one M–C and one M–M′ bond with no connecting ligand for M–M′ atoms were excluded, unless the C–C and C–H bond forming and breaking steps were not included. These complexes are not focused to date in the previous reviews, though chemical reactivities of such complexes can be regarded as one of the simplest model for the active sites in heterogeneous heterobimetallic catalyst as shown in Fig. 1. The chemistry of such complexes would provide complimentary informations of these reviews on organoheterometallic chemistry.

Study on such simple heterodinuclear organometallic complexes without M–M′ connecting ligands, are more likely to provide essential features of the synergy effects by two transition metals, though the effects of the bridging ligands, the structural constraints due to cluster back bone, and the multi-interaction of carbon ligands with two or more metals also play important roles in producing the synergy effects in catalysis. However, the examples of such complexes are still very limited to date. Among them, the complex including group 10 transition metal alkyl bonds attracts interest, since previous fundamental studies using mononuclear organometallic complexes had already provided us detailed mechanistic insights of many important organometallic reactions such as reductive elimination, β-hydrogen elimination, oxidative addition and etc. [13–19]. Therefore, the present review deals with synthesis, reactivity and catalysis of the simplest heterodinuclear organotransition metal complexes represented as $L_nRM–M'L_m$ (M = Pt, Pd) having one M–C and one M–M′ bond without M–M′ connecting ligands, which are mainly developed by our group in recent decades [20]. This would provide ideas in understanding synergy of transition metals and creating new catalysis based on synergy of different transition metals.

As a result, two methods for preparation such as metathesis of organo(halido)transition metal complexes with different transition metalate complexes [20a,20b,20e] and oxidative addition of organotransition metal complexes to low-valent transition metal complexes [20r,20x,20C′] are mainly described after briefly showing other examples. These isolated heterodinuclear organotransition metal complexes show some interesting reaction features. The organic ligand on Pt transfers along transition metal linkage, presumably modeling the mobility of the σ-organic group on heterogeneous metal surface. Among them, allyl complexes show unexpected *E*-selective allyl transfer reaction [20A′]. Two interesting chemical reactions of heterodinuclear complexes are described in this account. One is the acceleration effect on the apparent CO insertion process in the dinuclear complex in comparison with the corresponding mononuclear complexes, and its molecular mechanism has been presented [20s]. Another example is regio- and stereo-selective C–S bond cleavage of thiiranes and thietanes by the heterodinuclear complexes [20q]. The reaction is applied to highly efficient catalytic carbonylation of thietanes to thiolactones promoted by heterodinuclear complexes [20t]. Palladium catalyzed hydrometalation of the transition metal hydride to olefin and acetylene is also described, where the heterodinuclear hydridotransition metal complexes act as important intermediates [20x].