

Developing Binuclear Metal Complexes for Catalysis

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In order to develop improved synthetic methods, chemists have long been interested in catalyzing reactions by using bimetallic complexes that contain two or more different metal centers. Bimetallic catalysts can promote a variety of reactions, but it is not always clear whether the metal centers are actually acting synergistically.^{1,2} For the present purposes, the following discussion will be confined to bimetallic catalysts that react in one of the following three ways: a) the substrate is coordinated to both metal ions simultaneously, b) the substrate is bound to one metal and the reactant is bound to the other, and c) the second metal does not participate in the reaction but electronically stabilizes the reacting metal and acts as a redox partner (Figure 1).¹

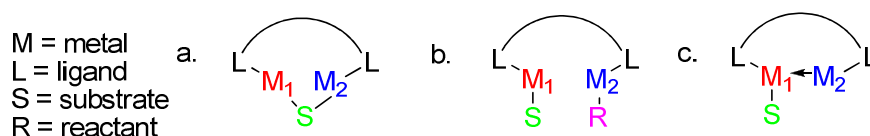


Figure 1. Reactivities of binuclear complexes

Some homodinuclear complexes are far more catalytically active than their mononuclear counterparts. Stanley's $\text{Rh}_2(\text{norbornadiene})(\text{P}_4)$ complex, where P_4 is $(\text{PEt}_2\text{CH}_2\text{CH}_2\text{PPhCH}_2)_2$,³ catalyzes the hydroformylation of terminal olefins at a rate of 640 h^{-1} with a linear:branched selectivity of 27.5 for the aldehyde product (Figure 2). This turnover rate is comparable that of 540 h^{-1} for the mononuclear, commercial $\text{Rh}(\text{acac})(\text{CO})_2$, but the selectivity is much higher: the mononuclear catalyst gives a linear to branched ratio of only 17.

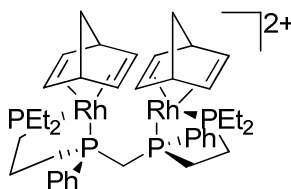


Figure 2. Rh_2 hydroformylation pre-catalyst

Following oxidative addition of H_2 and insertion of the olefin and CO to form an acyl intermediate, reductive elimination of the aldehyde product is proposed to be enhanced by an intramolecular hydride transfer from one Rh center to the other. If a less flexible bridging phosphine is introduced, the turnover rate decreases by a factor of 10 or more.

Homobinuclear palladium complexes catalyze the hydration of nitriles to acetamide under ambient conditions.⁵ When acrylonitrile is used as a substrate in this system, the Pd_2 catalyst can selectively form the acrylamide product without the generating the regioisomers and

overoxidized products commonly seen for mononuclear catalysts. The two metals help orient the incoming hydroxide nucleophile and activate the electrophilic carbon center, which are held in close proximity to one another (Figure 3). A mononuclear catalyst requires basic conditions to generate the hydroxide nucleophile, but this dinuclear catalyst displays rate acceleration in the presence of acid, corresponding to faster protonation and release from the metal center.

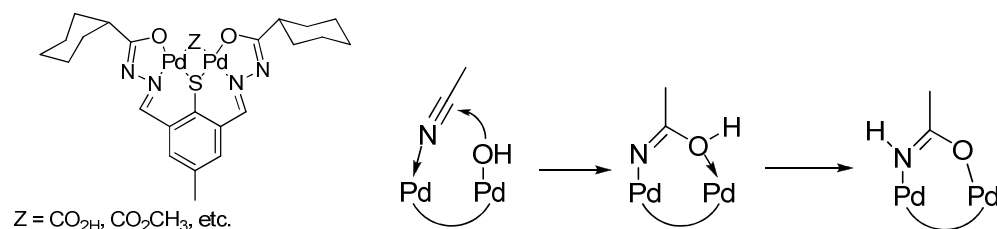


Figure 3. Pd₂ catalyst and its orientation of electrophile and nucleophile in hydration of acetonitrile

Though they are more challenging to synthesize than homobinuclear complexes, heterobinuclear complexes may enhance reactivity due to the cooperation of two metals with different chemical properties. In the mid-1990s, the Bergman group investigated dinuclear methylene-bridged tantalum-iridium complexes that catalyze the hydrogenation, hydrosilylation, and isomerization of olefins.⁶ After the oxidative addition of H₂ to the Ir center, tantalum is believed to promote the reversible reductive elimination of one of the methylene bridges to open a coordination site on the Ir center for olefin binding (Figure 4).

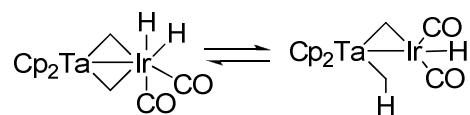


Figure 4. Ta-Ir -CH₃ reductive elimination

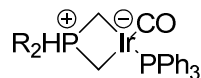


Figure 5. Mononuclear Ir ylide complex

This mechanistic proposal is supported by the observed deuterium exchange of the methylene hydrogens in the presence of D₂.⁶ When the Ta center is removed and replaced by a phosphine in a model Ir ylide complex, H/D exchange at the methylene bridge is not observed, and hydrogenation proceeds via dissociation of PPh₃ prior to olefin coordination (Figure 5).⁷

Recent studies from the Marks group present some of the most compelling evidence for catalysis by a discrete binuclear complex. In studying the copolymerization of ethylene with styrene, it was noted that the bimetallic “constrained geometry catalyst” C1-Ti₂ enchaind 15% more styrene than a corresponding mononuclear titanium catalyst (Figure 6).⁸

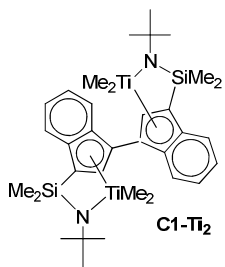


Figure 6. C1-Ti₂ complex

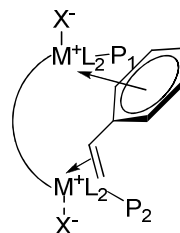


Figure 7. Dinuclear M₂-substrate interaction

Further studies led the authors to propose a stabilizing interaction in which the styrene monomer binds simultaneously with both metal centers (Figure 7). An increasing amount of styrene enchainment is observed when the electron density on the styrene unit is increased.

Binuclear catalysts have the potential to outperform existing mononuclear catalysts, but their use is hampered by a number of difficulties. The complexes suffer from challenging syntheses, a tendency to form inert metal-metal bonds from reactive intermediates, and a tendency to fragment to mononuclear species. Addressing these issues, as well as designing ligands that can accommodate two metal centers, are challenges that must be met to further expand the utility of these catalysts.

References

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