Cooperativity Between Metal Centers in Homogeneous Catalysis: Hydroformylation as a Model Reaction

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Cooperativity between metal centers can be defined as two or more metal centers working together through concerted activation of substrates or as one metal center serving as a ligand or electron source for another metal center. Alternately, cooperativity between metal centers can be defined as one metal center influencing the electronic and steric properties of another metal center by inducing "extended ligand effects" [1].

Hydroformylation is the catalytic conversion of olefins to aldehydes. Cooperativity between metal centers in the homogeneously cobalt catalyzed hydroformylation reaction was first proposed by Heck in the early 1960's [2]. It was thought that cooperativity in the rate determining step of this reaction, the oxidative addition of H_2 to the metal acyl species, which is followed by reductive elimination of product aldehyde, acted to increase the reaction rate. For this reason hydroformylation is often viewed as a model reaction to examine cooperativity between metal centers.

Recently, Stanley and coworkers developed a bimetallic Rh cation, [Rh₂(nbd)₂(et, ph-P4)](BF₄)₂, which is extremely active and selective in the catalysis of the hydroformylation reaction [3]. While the high selectivity of linear aldehyde products over branched aldehyde products by this complex is not well understood, the high activity can be explained in terms of cooperativity between metal centers via an intramolecular hydride transfer [3,4]. Although kinetic and spectroscopic evidence firmly establishing this mechanism is lacking, there is convincing evidence based upon modeling studies. In particular the activity of the catalyst prepared with the racemic linear tetratertiary phosphine ligand as compared to the activity of these complexes to perform an intramolecular hydride transfer.



Intramolecular hydride transfer for the racemic (left) and meso (right) complex.

In the late 1970's Pittman reported hydroformylation under mild conditions catalyzed by both tricobalt and tetracobalt clusters [5,6]. Complete recovery of intact clusters at the end of the hydroformylation reaction was taken as evidence that the clusters had remained intact during the catalytic process [5,6]. It was soon realized that the tricobalt cluster readily fragmented under hydroformylation conditions to produce the catalytically active monometallic species [7,8]. The fate of the tetracobalt cluster during the catalytic process remained uncertain. With the development of cylindrical internal reflectance (CIR)-FTIR for *in situ* spectroscopic studies of working catalytic systems [9], the tetracobalt cluster catalyzed hydroformylation reaction has been examined in greater detail [10-12]. At 130 °C the Co(CO)₈-(μ_2 -CO)₂(μ_4 -PPh)₂ cluster appears to remain intact during the hydroformylation process. At 150 °C both spectroscopic and kinetic studies indicate the cluster fragments to a catalytically active monometallic species [10].

Spectroscopic studies of the phosphine substituted clusters $Co_4(CO)_8(\mu_4-PPh_2)$ -[P(OMe)3]2 and $Co_4(CO)_8(\mu_4-PPh_2)(PPh_3)_2$ indicate they become catalytic upon conversion into the parent cluster, $Co_4(CO)_8(\mu_2-CO)_2(\mu_4-PPh)_2$ [11]. This is supported by recovery of the parent complex as the only Co containing product at the end of the hydroformylation reaction [13]. Further, while the parent cluster decomposes at 150 °C when it is introduced directly to the reaction, the $Co_4(CO)_8(\mu_2-CO)_2(\mu_4-PPh)_2$ cluster produced from the decomposition of the phosphine substituted clusters now appears both active and stable at 150 °C [12].



Spectroscopic studies of bi-dentate phosphine substituted cluster $Co_4(CO)_8(\mu_4-PPh_2)$ -(dmpe) [12] indicate it does not decompose at 150 °C and is catalytic ally active at temperatures as low as 130 °C. Kinetic studies of the phosphine substituted clusters have not yet been performed.

There has been extensive work done concerning several other homometallic [14,15] and heterometallic systems [10,16-18] which catalyze the hydroformylation reaction. The study of heterometallic systems is of interest as polar metal-metal bonds are introduced and the possibility exists to tailor the functionality of the metal centers. Some mixed metal systems have been reported to exhibit synergism as compared to the homometallic counterparts [16,18]. There are also reports concerning mixed metal systems performing catalysis at conditions much milder than one would expect fragmentation to occur [17]. However, to date there have been no heterometallic systems for which cooperativity between metal centers has been firmly established.

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