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Editorial Note on Metal Ligand Cooperation

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Editorial

Metal Ligand Cooperation (MLC) is a kind of reactivity in which a metal and ligand of a complex both participate during a reaction in the disruption or the bonding of a substratum. This ligand is an actor rather than a spectator, and the reaction is often considered to comprise MLC only if the actor ligand is doing more than simply leaving to provide an open coordination site. MLC is also known as "metal-ligand bifunctional catalysis."

Modes of metal-ligand binding

This cooperative behaviour has been proven in a variety of ways. MLC normally accepts four fundamental modes: the ligand can

- (1) Act with Lewis acidity
- (2) Act with Lewis basicity
- (3) Participate in aromatization and de-aromatization or
- (4) Be redox non-innocent

As it binds to the metal, the ligand can serve as a Lewis acid, accepting electrons from the incoming substrate, as in dehydrogenation catalysis. The ligand, on the other hand, can be Lewis basic and bind the substrate; this Lewis basicity is most commonly seen in hydrogenation catalysis. The ligand can also be redox non-innocent in order to enhance reactions that the metal would otherwise be incapable of activating.

The ligand can operate as an electron reservoir, which is enabled when ligands contain sufficient energy frontier orbitals to participate in the redox event, and can take or donate electrons throughout the reaction, allowing the metal to adjust its oxidation state. This enables metals that are ordinarily only involved in one electron regime to be employed in two electron regimes with a redox non-innocent ligand to store electrons during the reaction. Dithiolate ligands have been widely employed in metal complexes as one electron redox active ligands.

Mechanism

MLC is most commonly utilised in hydrogenations, but it also has several uses in asymmetric catalysis and chemical process scale production. A hydride and hydrogen are transferred to a substrate during a hydrogenation. Aldehydes, ketones, and imines are common substrates. Because this is a typical use for MLC, it is useful in understanding the mechanism of metal-ligand cooperativity. MLC arises as a result of an outer spherical process.

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An outer sphere method does not involve oxidative addition or reductive removal of the metal. Thus, H_2 is supplied across a ligand rather than across the metal; alternatively, the metal complexes are prepared to contain a hydride ligand as well as a ligand with a hydrogen alpha to the metal. As a result, the hydride and hydrogen are nearby, allowing transfer to the substrate; this transfer occurs without the substrate ever attaching to the metal itself.

The substrate will be injected into the metal in an inner spherical mechanism, and the reaction with hydrogen will yield the hydrogenated product. This technique does not make use of MLC. Cobalt hydrogenation with an amine pincer ligand exemplifies the distinction between an outer sphere mechanism that relies on MLC and an inner sphere mechanism. The hydrogen on the pincer ligand is added to the ketone together with a hydride ligand on the metal in the outer sphere process. It is worth mentioning that there is considerable controversy about the concertedness of the transition state of this outer sphere hydrogenation phase, and different reactions and catalysts may be concerted or stepwise, and in some scenarios, multiple pathways may be at work. Unlike ketone hydrogenation, an olefin passes through an inner sphere mechanism under the identical reaction circumstances, in which the olefin inserts straight into the metal.

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