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APPLICATION OF TRANSITION METAL IN ORGANIC CHEMISTRY

The term transition metal (sometimes also called a transition element) has two possible meanings: In the past it referred to any element in the d-block of the periodic table, which includes groups 3 to 12 on the periodic table. All elements in the d-block are metals (In actuality, the f-block is also included in the form of the lanthanide and actinide series).

It also states that a transition metal is "an element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell

Application of Transition Metals:

The application of transition metals is as follows:

1. Transition metals are applied in the organic reactions.

Transition metals complex under goes a series of reactions that are generally unlike those main group compounds. The most fundamental is the simple coordination and dissociation of ligands.

Dissociation may also be achieved by destruction of a ligand. This is often done by the oxidation of co and co2 using an amide oxide.

2. Transition metals are applied in the synthesis of metal hydride.

M=C=O + OH- ====> M-H + CO2

Here metal carbonyl group reacts with hydroxide to give metal hydride and carbon dioxide.

Hydrides such as, sodium borohydride, lithium aluminium hydride, diisobutylaluminium hydride (DIBAL) and super hydride, are commonly used as reducing agents in chemical synthesis. The hydride adds to an electrophilic center, typically unsaturated carbon.

Hydrides such as sodium hydride and potassium hydride are used as strong bases in organic synthesis. The hydride reacts with the weak Bronsted acid releasing H2.

Hydrides such as calcium hydride are used as desiccants, i.e. drying agents, to remove trace water from organic solvents. The hydride reacts with water forming hydrogen and hydroxide salt. The dry solvent can then be distilled or vac transferred from the "solvent pot".

Hydrides are of important in storage battery technologies such as Nickel-metal hydride battery.

Various metal hydrides have been examined for use as a means of hydrogen storage for fuel cell-powered electric cars and other purposed aspects of a hydrogen economy.

Hydride intermediates are key to understanding a variety of homogeneous and heterogeneous catalytic cycles as well as enzymatic activity. Hydroformylation catalysts and hydrogenase both involve hydride intermediates. The energy carrier NADH reacts as a hydride donor or hydride equivalent.

3. Transition metal used in the complexes in fluorescence cell imaging.

Transition metal complexes have often been proposed as useful fluorophores for cell imaging due to their attractive photo physical attributes, but until very recently their actual applications have been scarce and largely limited to ruthenium complexes in DNA and oxygen sensing.

4. Transition metal used as Catalysts.

Some transition metals are good catalysts. For example: most automobiles have an emissions-control device called a catalytic converter. This device contains a screen of platinum or palladium along with rhodium, a metal. The presence of the transition metals, along with the heat of combustion generated by an automobile engine causes an exhaust coming from an internal combustion engine to be broken down from partially burned hydrocarbon compounds into less harmful compounds such as water vapour and carbon dioxide.

Catalytic applications of transition metals in organic synthesis:-

OXIDATION REACTIONS:

The epoxidation, dihydroxylation and aminohydroxylation reactions of alkenes, especially their asymmetric variants, continue to attract considerable attention. The basic principles were covered in the previous review. The use of fluorous solvents has now been demonstrated formany transition metal catalysed reactions. One advantage that they offer for catalyticepoxidation is the fact that molecularoxygen has a high solubility in fluorous solvents. The combination

of O2 with pivalaldehyde and manganese catalysts hasbeen shown to be effective for epoxidation of alkenes in aracemic and enantioselective sense. The fluorous soluble ligand afforded a manganese complex which was insoluble incommon organic solvents, but soluble in the fluorous phase.Indene was converted into indene oxide with high enantioselectivity,although other substrates afforded low selectivity The fluorous phase, containing the active catalyst,could be recycled. Manganese salen complexes have also now been successfullyimmobilised within polymer supports, and still provide high

Whilst the enantiomerically pure manganese salen complexes are still often the most enantio selective available for epoxidation of unfunctionalised alkenes, alternative systems are often reported. For example, End and Pfaltz have used rutheniumbis (oxazoline) complexes to provide up to 69% ee in the epoxidation of stilbene.

The use of methyltrioxorhenium as a catalyst for epoxidationcontinues to attract attention. Herrmann and co-workershave shown that a combination of methyltrioxorhenium withpyrazole affords a highly efficient catalyst for the epoxidation of alkenes. Styrene was converted cleanly into styrene oxide with this catalytic combination.

Reduction reactions

The reduction of various functional groups can often be achieved using transition metal catalysts and a suitable reducing agent: often molecular hydrogen, silanes, boranes orhydrides. Amongst all of the possibilities, metal-catalysed hydrogenation has been the most widely studied, especially asan asymmetric process.Some recently reported examples of rhodium-catalyse dasymmetric hydrogenation of alkenes include the conversion ofthe enamide into the derivatised amino alcohols and the regioselective hydrogenation of dienyl acetate into the allyl acetate both using the Me-DuPhos ligand .Reports of new ligands for asymmetric hydrogenation of alkenes continue to appear, often providing highly selective examples.Ruthenium catalysed hydrogenation of alkenes is also popular,and an interesting example has been provided by Bruneau,Dixneuf and co-workers. The achiral substrate is hydrogenatedwith an enantiomerically pure ruthenium complex into compound , which behaves as propionic acid attachedto a chiral auxiliary. The achiral auxiliary in the substrate is converted into an enantiomerically enriched one prior to a subsequent auxiliary controlled functionalisation.

Lewis acid catalysed reactions:-

Lewis acids are able to catalyse a wide range of reactions. Theaddition of cyanide to aldehydes is one such reaction and hasbeen studied by many groups. Recently, North, Belokon andco-workers have used a titanium (salen) complex to catalyse

the addition of trimethylsilylcyanide to benzaldehyde withlow catalyst loadings. Less work has been reported on theenantioselective addition of cyanide to imines, although it providesa useful route to Î±-amino acids (Strecker synthesis). However, there have been several reports of the enantio selective variant of this reaction by aluminium catalysts,non-metallic catalysts, and with the zirconium catalysts, reported here. The imine is converted into the Î±-aminonitrile with good yield and enantio selectivity Scandium triflate is a good catalyst for the allylation of aldehydes with allylsilanes and stannanes. Aggarwal and Vennallhave detailed the allylation of aldehydes followed by in situ acylation.36 Benzaldehyde allylsilane and acetic anhydride undergo coupling to provide the homoallylic acetate withscandium triflate as the catalyst Kobayashi and co-workers have shown that a three component system comprising of benzaldehyde an amine,such as aniline and allylstannane affords the homoallylicamine The reaction works more quickly in the presence of sodium dodecylsulfate SDS, which provides amicellar system .The allylation of isolated imines with enantiomerically pure palladium complexes has been achieved with up to 82%enantiomeric excess.

Catalytic coupling reactions:-

The formation of C-C bonds, as well as C-X bonds can becatalysed by many transition metals, although palladium complexesseem to have a greater scope than other metals. The useof catalytic coupling reactions to provide biaryls has recently been reviewed.

5.REAL LIFE APPLICATIONS:

The fact that the transition elements are all metals means that they are lustrous or shiny in appearance, and malleable, meaning that they can be molded into different shapes without breaking. They are excellent conductors of heat and electricity, and tend to form positive ions by losing electrons.

Generally speaking, metals are hard, though a few of the transition metals-as well as members of other metal families-are so soft they can be cut with a knife. Like almost all metals, they tend to have fairly high melting points, and extremely high boiling points.

Many of the transition metals, particularly those on periods 4, 5, and 6, form useful alloys-mixtures containing more than one metal-with one another, and with other elements. Because of their differences in electron configuration, however, they do not always combine in the same ways, even within an element. Iron, for instance, sometimes releases two electrons in chemical bonding, and at other times three.

ABUNDANCE OF THE TRANSITION METALS:

Iron is the fourth most abundant element on Earth, accounting for 4.71% of the elemental mass in the planet's crust. Titanium ranks 10th, with 0.58%, and manganese 13th, with 0.09%. Several other transition metals are comparatively abundant: even gold is much more abundant than many other elements on the periodic table. However, given the fact that only 18 elements account for 99.51% of Earth's crust, the percentages for elements outside of the top 18 tend to very small.

In the human body, iron is the 12th most abundant element, constituting 0.004% of the body's mass. Zinc follows it, at 13th place, accounting for 0.003%. Again, these percentages may not seem particularly high, but in view of the fact that three elements-oxygen, carbon, and hydrogen-account for 93% of human elemental body mass, there is not much room for the other 10 most common elements in the body. Transition metals such as copper are present in trace quantities within the body as well.

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DIVIDING THE TRANSITION METALS INTO GROUPS.

There is no easy way to group the transition metals, though certain of these elements are traditionally categorized together. These do not constitute "families" as such, but they do provide useful ways to break down the otherwise rather daunting 40-element lineup of the transition metals.

In two cases, there is at least a relation between group number on the periodic table and the categories loosely assigned to a collection of transition metals. Thus the "coinage metals"-copper, silver, and gold-all occupy Group 9 on the periodic table. These have traditionally been associated with one another because their resistance to oxidation, combined with their malleability and beauty, has made them useful materials for fashioning coins.

Likewise the members of the "zinc group"-zinc, cadmium, and mercury-occupy Group 10 on the periodic table. These, too, have often been associated as a miniature unit due to common properties. Members of the "platinum group"-platinum, iridium, osmium, palladium, rhodium, and ruthenium-occupy a rectangle on the table, corresponding to periods 5 and 6, and groups 6 through 8. What actually makes them a "group," however, is the fact that they tend to appear together in nature.

Iron, nickel, and cobalt, found alongside one another on Period 4, may be grouped together because they are all magnetic to some degree or another. This is far from the only notable characteristic about such metals, but provides a convenient means of further dividing the transition metals into smaller sections.

To the left of iron on the periodic table is a rectangle corresponding to periods 4 through 6, groups 4 through 7. These 11 elements-titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, and rhenium-are referred to here as "alloy metals." This is not a traditional designation, but it is nonetheless useful for describing these metals, most of which form important alloys with iron and other elements.

One element was left out of the "rectangle" described in the preceding paragraph. This is technetium, which apparently does not occur in nature. It is lumped in with a final category, "rare and artificial elements."

It should be stressed that there is nothing hard and fast about these categories. The "alloy metals" are not the only ones that form alloys; nickel is used in coins, though it is not called a coinage metal; and platinum could be listed with gold and silver as "precious metals." Nonetheless, the categories used here seem to provide the most workable means of approaching the many transition metals.

GOLD.

Gold almost needs no introduction: virtually everyone knows of its value, and history is full of stories about people who killed or died for this precious metal. Part of its value springs from its rarity in comparison to, say iron: gold is present on Earth's crust at a level of about 5 parts per billion (ppb). Yet as noted earlier, it is more abundant than some metals.