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**INDUSTRIAL CHEMISTRY**

**ICH 321**

**APPLICATIONS OF TRANSITION ELEMENTS TO ORGANIC CHEMISTRY**

**SCANDIUM**:

* . Scandium(III) triflate is sometimes used as a Lewis acid catalyst in organic chemistry.

**TITANIUM:**

* Titanium can be alloyed with iron, aluminium, vanadium, and molybdenum, among other elements, to produce, agri-food, medical prostheses, orthopedic implants, dental and endodontic instruments and files, dental implants, etc.
* Titanium tetrachloride can accelerate numerous organic reactions. Valuable syntheses of, e.g., allyl sulfides, amides, enamines, and ketones are based upon transformations of functional groups with TiCl4. Particular mention should also be made of carbon-carbon linkage with TiCl4 which permits the synthesis of hydroxy ketones and carbonyl compounds of the Michael adduct type. TiCl4 reduced in situ is suitable for the reduction of chloroarenes or the linkage of two aldehyde molecules to give an alkene.

**VANADIUM:**

* Organometallic chemistry of vanadium is well developed, although it has mainly only academic significance. Vanadocene dichloride is a versatile starting reagent and even finds some applications in organic chemistry.[[25]](https://en.wikipedia.org/wiki/Vanadium#cite_note-wilkinson-25) Vanadium carbonyl, V(CO)6, is a rare example of a paramagnetic metal carbonyl. Reduction yields V(CO)−  
  6 (isoelectronic with Cr(CO)6), which may be further reduced with sodium in liquid ammonia to yield V(CO)3−  
  5 (isoelectronic with Fe(CO)5).
* The vanadium-containing metal-organic frameworks (MOFs) MIL-47 and MOF-48 are found to have high catalytic activity and chemical stability. They convert methane selectively to acetic acid with 70% yield (490 TON) based on K(2)S(2)O(8) as an oxidant. Isotopic labeling experiments showed that two methane molecules are converted to the produced acetic acid. The MOF catalysts are reusable and remain catalytically active for several recycling steps without losing their crystalline structures.

**CHROMIUM:**

* Chromic acid, H2CrO4, is a strong acid and a reagent for oxidizing alcohols to ketones and carboxylic acids.
* Paints and Dyes: This useful element is also found in paint and dyes and chemical makeup that is used for fabrics.
* Although organochromium chemistry is heavily employed in industrial catalysis, relatively few reagents have been developed for applications in organic synthesis. Two are the Nozaki-Hiyama-Kishi reaction (1977) (transmetallation with organonickel intermediate) and the Takai olefination (1986)(oxidation of Cr(II) to Cr(III) while replacing halogens). In a niche exploit, certain tricarbonyl(arene)chromium complexes display benzylic activation.

**MANGANESE:**

* Organomanganese halides react with aldehydes and ketones to the alcohol, with carbon dioxide to the carboxylic acid (tolerating higher operating temperature than corresponding RLi or RMgBr counterparts), sulfur dioxide and isocyanates behaving like soft Grignard reagents.
* Methylcyclopentadienyl manganese tricarbonyl is a half-sandwich compound used as a gasoline additive.
* Manganese is essential to plant growth and is involved in the assimilation of nitrates in green plants and algae.
* t is an essential trace element in higher animals, in which it participates in the action of many enzymes.
* Lack of manganese causes testicular atrophy. An excess of this element in plants and animals is toxic.

**IRON:**

* the color of blood is due to hemoglobin, an iron-containing protein
* Iron-containing enzymes and proteins, often containing heme prosthetic groups, participate in many biological oxidations and in transport
* Iron compounds are used as catalysts in organic reactions

**COBALT:**

* Organocobalt compounds are involved in several organic reactions and the important biomolecule vitamin B12 has a cobalt-carbon bond
* Many organocobalt compounds exhibit useful catalytic properties, the preeminent example being dicobalt octacarbonyl
* Animals use trace minerals to make essential enzymes which function as catalysts. These enzymes speed up changes that occur in the human body. Enzymes are needed for living cells to function properly For example cobalt is needed for the natural production of B-12 vitamins. B-12 vitamins ensure that enough red blood cells are produced in the human body.

**NICKEL:**

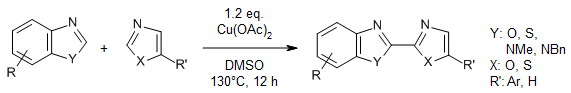
* Raney nickel is used in organic synthesis for desulfurization. For example, thioacetals will be reduced to hydrocarbons in the last step of the Mozingo reduction:
* It is typically used in the reduction of compounds with multiple bonds, such as alkynes, alkenes, nitriles, dienes, aromatics and carbonyl-containing compounds. Additionally, Raney nickel will reduce heteroatom-heteroatom bonds, such as hydrazines, nitro groups, and nitrosamines. It has also found use in the reductive alkylation of amines and the amination of alcohols.

When reducing a carbon-carbon double bond, Raney nickel will add hydrogen in a *syn* fashion.

* They are used in chemical vapor deposition

**COPPER:**

* . Copper(I) acetylide is highly shock-sensitive but is an intermediate in reactions such as the Cadiot-Chodkiewicz coupling and the Sonogashira coupling
* Conjugate addition to enones and carbocupration of alkynes can also be achieved with organocopper compounds
* The use of Cu(OAc)2 enables a dehydrogenative cross-coupling between two heteroarenes via disproportionation of the copper mediator. This synthetic protocol provides a concise and "green" access to unsymmetrical biheteroarenes bearing structural motifs of substantial utility in organic synthesis.

[](http://www.organic-chemistry.org/abstracts/lit3/736.shtm)

**ZINC:**

The Frankland-Duppa Reaction in which an oxalate ester (ROCOCOOR) reacts with an alkyl halide R'X, zinc and hydrochloric acid to form the α-hydroxycarboxylic esters RR'COHCOOR[[144]](https://en.wikipedia.org/wiki/Zinc#cite_note-146)

* The Reformatskii reaction in which α-halo-esters and aldehydes are converted to β-hydroxy-esters
* The Simmons–Smith reaction in which the carbenoid (iodomethyl)zinc iodide reacts with alkene(or alkyne) and converts them to cyclopropane
* The Addition reaction of organozinc compounds to form [carbonyl](https://en.wikipedia.org/wiki/Carbonyl) compounds
* The Barbier reaction (1899), which is the zinc equivalent of the magnesium Grignard reaction and is the better of the two. In presence of water, formation of the organomagnesium halide will fail, whereas the Barbier reaction can take place in water.
* On the downside, organozincs are much less nucleophilic than Grignards, and they are expensive and difficult to handle. Commercially available diorganozinc compounds are [dimethylzinc](https://en.wikipedia.org/wiki/Dimethylzinc), [diethylzinc](https://en.wikipedia.org/wiki/Diethylzinc) and diphenylzinc. In one study,[[145]](https://en.wikipedia.org/wiki/Zinc#cite_note-147)[[146]](https://en.wikipedia.org/wiki/Zinc#cite_note-148) the active organozinc compound is obtained from much cheaper [organobromine](https://en.wikipedia.org/wiki/Organobromine_compound) precursors
* The [Negishi coupling](https://en.wikipedia.org/wiki/Negishi_coupling) is also an important reaction for the formation of new carbon-carbon bonds between unsaturated carbon atoms in alkenes, arenes and alkynes. The catalysts are nickel and palladium. A key step in the catalytic cycle is a transmetalation in which a zinc halide exchanges its organic substituent for another halogen with the palladium (nickel) metal center.
* Zinc has found many applications as catalyst in organic synthesis including asymmetric synthesis, being cheap and easily available alternative to precious metal complexes. The results (yield and ee) obtained with chiral zinc catalysts are comparable to those achieved with palladium, ruthenium, iridium and others, and zinc becomes metal catalyst of choice.
* The Fukuyama coupling is another coupling reaction, but it uses a thioester as reactant and produces a ketone.

**MOLYBDENUM:**

* Though molybdenum forms compounds with various organic molecules, including carbohydrates and amino acids, it is transported throughout the human body as MoO42
* In some animals, and in humans, the oxidation of xanthine to uric acid, a process of purine catabolism, is catalyzed by xanthine oxidase, a molybdenum-containing enzyme.
* In animals and plants, a tricyclic compound called molybdopterin (which, despite the name, contains no molybdenum) is reacted with molybdate to form a complete molybdenum-containing cofactor called molybdenum cofactor.

**SILVER:**

* Silver-NHC complexes are easily prepared, and are commonly used to prepare other NHC complexes by displacing labile ligands. For example, the reaction of the bis(NHC)silver(I) complex with bis(acetonitrile)palladium dichloride or chlorido(dimethyl sulfide)gold(I)
* ilver carbonate is used as a reagent in organic synthesis such as the Koenigs-Knorr reaction. In the Fétizon oxidation, silver carbonate on celite serves as an oxidising agent to form lactones from diols. It is also employed to convert alkyl bromides into alcohols.[[8]](https://en.wikipedia.org/wiki/Silver_carbonate#cite_note-OS-8) As a base, it has been used in the Wittig reaction.