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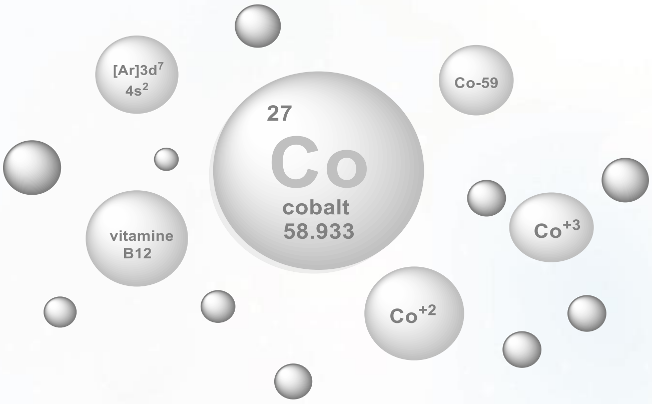
Radiance NEWSLETTER

Cobalt in Catalytic Transfer Hydrogenation

Salini S.
MSc Chemistry
Fourth semester
School of Chemical Sciences,
Mahatma Gandhi University, Kottayam
Salinisatheesh200q@gmail.com

Modern research emphasizes sustainable technologies for renewable energy conversion and environmental purification. Environmentally friendly, ecologically sustainable, and economically viable methodologies for catalysis are under study, marking a shift from precious metal catalysts to first-row, earth-abundant metal catalysts. This transition is primarily motivated by the use of cost-effective materials that can support the scaling up of relevant technologies. Among the first-row transition metals, cobalt has gained special attention. It has become a crucial element in various areas of catalysis, offering a low-cost alternative to precious metal catalysts. Being the 27th element in the periodic table, cobalt commonly exists in +2 and +3 oxidation states. It has moderate abundance and is often found in the same deposits as nickel and iron ores.

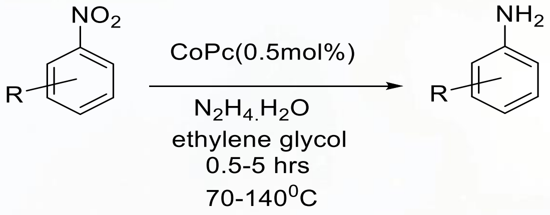


Like other first-row transition metals, cobalt is significantly less toxic than second- and third-row transition metals. Due to its abundance in the Earth's crust, it is more economical than rarer and more expensive noble metal catalysts, making it a promising option for developing new catalytic systems. This has spurred interest in cobalt bifunctional catalysts in recent years. Cobalt-based catalysts have been applied in the transfer hydrogenation of nitriles, unsaturated systems, imines, nitroarenes, carbonyl compounds (such as aldehydes, ketones, and esters), and heterocyclic compounds. In response to its growing demand, the European Union has classified cobalt as a critical raw material.

Cobalt's exceptional catalytic activity is attributed to its partially filled d-orbitals and its ability to exist in Co(+2) and Co(+3) oxidation states. This feature facilitates the formation of composites and complexes with other elements or supports. Cobalt can easily exchange electrons with external species, enabling it to participate in varied oxidation states and act as a source or sink for electrons. Among transition metals like iron and nickel, cobalt's three unfilled d-orbitals provide an optimal balance in forming bonds, aiding in the adsorption and desorption of reactants and products. Its semiconductor nature makes cobalt oxide suitable for photocatalysis, and it can be easily separated in heterogeneous catalytic systems, minimizing product contamination.

Cobalt is highly reactive in hydrogenation under mild conditions and exhibits good functional group tolerance, making it effective in hydrogenating a broad range of substrates. Asymmetric hydrogenation, a popular synthetic method that uses sustainable molecular hydrogen, has typically relied on noble metals like Ru, Rh, and Ir. These metals, however, are scarce and costly. In contrast, first-row transition metals like cobalt offer better reactivity and abundance. As a result, cobalt-mediated hydrogenation has become an active research area, drawing interest from both industrial and academic fields.

In 2010, cobalt catalysts were used for the regioselective reduction of nitroarenes. Upendra Sharma and colleagues developed a copper/cobalt phthalocyanine catalyst that efficiently reduced nitroarenes, providing chemoselective and regioselective products with various functional groups such as carbonyl compounds, nitriles, and heterocycles, achieving over 99% selectivity.[1]

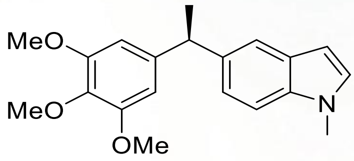


scheme 1 : regioselective reduction of nitroarenes
using Co-phthalocyanine complex

Asymmetric hydrogenation of non-functionalized olefins has long been a challenging process. The enantioselectivity of functionalized or unfunctionalized olefins depends on the coordination of the substrate with the catalyst. Functionalized olefins typically enable better enantioselectivity through chelation, which reduces the number of possible transition states. In contrast, non-functionalized olefins often coordinate as monodentate ligands, making it harder to achieve enantioselectivity. This challenge was addressed in 2012 when Chirik and colleagues demonstrated the first successful asymmetric hydrogenation of unfunctionalized olefins using affordable cobalt catalysts.

Asymmetric transfer hydrogenation has been explored since 2013, when Friedfeld and co-workers reported the asymmetric alkene hydrogenation using a cobalt catalyst with bidentate phosphine ligands, achieving 96.1% enantiomeric excess at 22°C.[2] In 2015, Waterman and co-workers developed a sandwich cobalt complex using amine-borane as a hydrogen donor for the hydrogenation of alkenes like styrene, phenylacetylene, and cis-cyclooctene.[3]

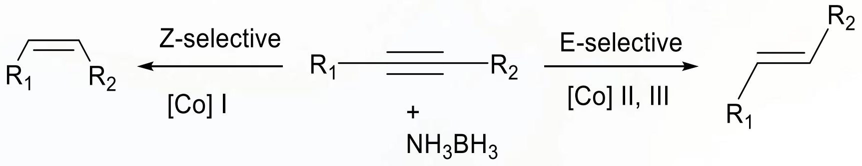
In 2016, Lu and co-workers used a chiral oxazoline-N-pyridylimine ligand with a cobalt catalyst for the asymmetric hydrogenation of simple unfunctionalized olefins. They found that adding a chloro substituent at the ortho position of the aryl alkene enhanced enantioselectivity. Screening various cobalt complexes with NaBHEt3 as an additional reductant showed that sterically bulky substituents on the oxazoline ligand increased reactivity and enantioselectivity compared to less hindered imine precursors. The reaction was effective with 1,1-diarylethenes containing electron-donating and electron-withdrawing groups, yielding products with high optical purity. This method was also applied to the gram-scale synthesis of an anti-cancer compound.



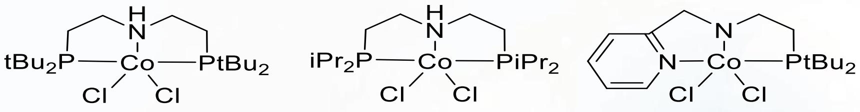
(*S*)-1-methyl-5-(1-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-indole

Anti-cancer agent

The challenge of alkyne reduction was addressed in 2016 by Liu and E. Balaraman, who reported the first cobalt-based catalyst for alkyne reduction via transfer hydrogenation. They used a cobalt dichloride phosphine pincer complex with amine-borane as a hydrogen source, achieving selective Z- and E-alkene products with a 99:1 Z/E ratio. The E-selectivity was enhanced using less bulky phosphine ligands, while Z-selectivity was maintained with bulkier ligands.[4]



scheme 2 : selective reduction of alkyne using Cobalt complexes



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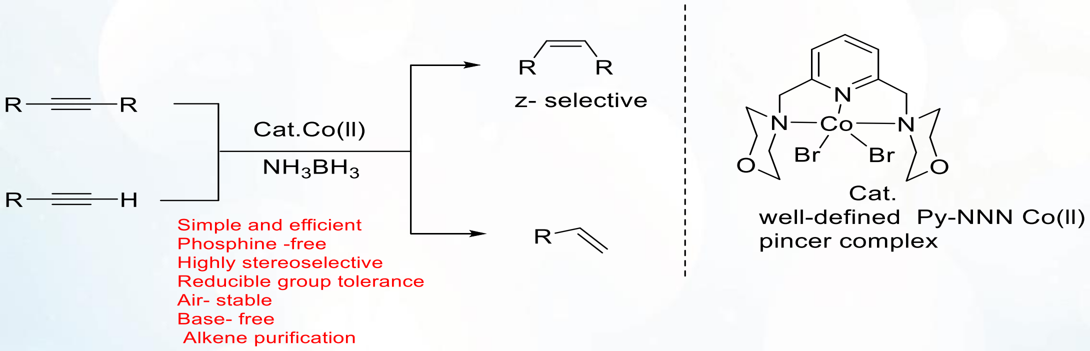
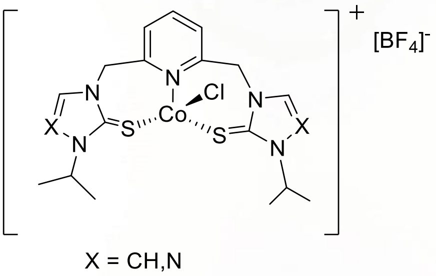
cobalt catalysts by Liu and co-workers

Balaraman’s group further explored selective hydrogenation of alkynes to Z-isomers in 2018 using phosphine-free cobalt(II) pincer complexes with NNN-ligands and ammonia-borane as the hydrogen source.[5]



scheme 3 : selective reduction of alkynes to alkene using cobalt-NNN complex

In 2016, Liu's team also reported on cobalt-catalyzed hydrogenation of nitriles using PNP- and NNP-based cobalt-pincer complexes with amino-borane, yielding mono- and disubstituted amines. Beller followed up in 2017 with a homogeneous cobalt-catalyzed transfer hydrogenation strategy for quinoline derivatives using formic acid as the hydrogen donor in isopropanol without a base, showing tolerance for a range of functional groups like acids, esters, and alkenes. Miecznikowski and co-workers developed Tri-dentate ligand precursors coordinated with cobalt(II) to form three- and five-coordinate complexes.[6]



cobalt-SNS complex by Miecznikowski and co-workers

Recent studies have highlighted the potential of cobalt as a catalyst due to its unique properties, with 90% of cobalt production being used in catalytic applications. However, despite its advantages as a substitute for noble metals, cobalt's inclusion in the European Union's list of critical raw materials indicates potential availability challenges. Additionally, concerns about the health hazards of cobalt suggest that its usage should be closely monitored to prevent environmental contamination, particularly in water sources. Understanding cobalt toxicity, especially from spent catalysts, through life cycle analysis is crucial for developing mitigation strategies and ensuring sustainable use of this valuable metal.

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