In Your Element – Cobalt

Cobalt compounds have featured regularly throughout history, and it remains an important and useful element within chemical synthesis in the 21st century. The name is thought to derive from the German *kobold*, meaning “goblin” or “evil sprite”. The difficulty in isolating this metal from its ore and the release of arsenic oxide, which often accompanied its smelting process, were both attributed to the work of evil spirits by the miners who were tormented by this element. Undoubtedly, cobalt’s relative scarcity also played a part – it makes up only 29 ppm of the earth’s crust, making it the 30th most abundant element on earth, and the second rarest transition metal after Scandium.

The confirmation of cobalt as a new element took place over a forty year period, with Brandt’s isolation of the metal in 1735, and Bergman’s confirmation that this was indeed a new element in 1780. Cobalt’s history goes back much further, however, as its ore was being used as a blue dye in the Middle East over four thousand years ago. Even today, almost 30% of cobalt produced is used in the ceramic and paint industries. Cobalt is an essential trace element for humans, and is found at the centre of vitamin B12 and a range of other co-enzymes called cobalamins. Even though the body contains only 2-5 mg of vitamin B12, its involvement in the production of red blood cells means it is vital to life. Vitamin B12 is notable for its cobalt-carbon bond, making it the only known naturally-occurring organometallic complex. In this respect, many new developments in cobalt chemistry employ organometallic compounds of cobalt. In the field of catalysis, for example, cobalt has been found to also mediate many of the cross-coupling reactions dominated for years by palladium and nickel.

Developing new and environmentally-benign energy sources represents one of the most critical challenges currently facing society. One potential solution lies in the development of methods to harness the energy of the sun. Amongst the possibilities for harvesting solar energy directly into clean fuels is the solar energy-driven conversion of water into hydrogen and oxygen. Such a process, when broken down into fundamental steps, requires the oxidation of water to oxygen, and the concomitant reduction of protons to hydrogen, and would provide an incredibly clean and efficient entry into the hydrogen economy. The key to this technology is the so-called oxygen evolution reaction (OER), and this aspect of water-splitting still remains a challenge due to the sensitive redox balance inherent in the process. Cobalt-based catalysts are now amongst the many systems under active investigation to mediate this challenging process.

Historically, the most important application of organocobalt complexes in catalysis has been in the hydroformylation of alkenes. The classical catalyst for this reaction is the protonated derivative of the tetracarbonylcobaltate anion – hydridotetracarbonylcobaltate. Although more selective catalysts, often rhodium-based, have been developed over the years, the cobalt system is still used for many applications. Being a group 9 element, cobalt does not form a neutral monometallic carbonyl. Instead a dimer forms – dicobalt octacarbonyl – with a bent cobalt-cobalt bond. Dicobalt octacarbonyl is also employed as a hydroformylation catalyst, and it reacts with alkenes, with loss of two molecules of carbon monoxide, to give alkynehexacarbonyldicobalt complexes. These air-stable, deep red solids and oils can catalyse the cyclotrimerisation of alkynes to substituted benzenes, but their main preparative use is in the formation of substituted cyclopentenones.

The use of alkyne-cobalt complexes in such synthetically-direct and –economical cyclopentannulation processes was serendipitously discovered at the University of Strathclyde in 1971. Following on from the establishment of ferrocence synthesis and reactivity, and as an internationally-leading contributor to many aspects of metallo-organic chemistry as the field emerged through the 1950s and 1960s, Professor Peter L. Pauson and his co-workers became engaged in attempts to establish the fundamental aspects of cobalt-mediated alkyne trimerisation processes. Believing that sufficiently reactive alkenes may be as applicable with alkyne-cobalt complexes as (other) alkynes, the appreciably strained alkene norbornene was employed. The main organic products isolated were cyclopentenones, from inclusion of one unit each of alkyne, alkene, and carbon monoxide. This accidental, yet extremely fortunate, discovery then led to vigorous research efforts within the Strathclyde laboratories over the subsequent years in efforts to establish the scope and limitations of this process for the direct formation of selectively substituted cyclopentenones. Indeed, such is the importance of substituted ketonic five-membered ring products in organic chemistry, that many related metal-mediated annulation processes have now evolved from these initial discoveries, and remain the focus of intense international research effort.

To (almost) all organic chemists the world over, this now renowned class of annulation process is known as the Pauson-Khand reaction; this is, except to one chemist: Pauson himself. The co-worker who discovered the cyclopentannulation process was Ihsan U. Khand, a postdoctoral researcher and ex-PhD student of Professor Pauson's. Accordingly, and typical of the generosity and support which he showed to his many students and co-workers, coupled with his remarkable, yet characteristic, modesty, Professor Pauson only ever referred to this reaction in spoken or written communications as "The Khand Reaction".

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