A new iron age

Iron has important roles in areas as diverse as physiological processes and industrial activities, but has traditionally been eclipsed by other transition metals in synthesis processes. **Carsten Bolm** looks at how iron is now also becoming an increasingly sought-after catalyst.

Gold is for the mistress — silver for the maid —
Copper for the craftsman cunning at his trade.
"Good!" said the Baron, sitting in his hall,
"But Iron — Cold Iron — is master of them all."

Rudyard Kipling, 1907 Nobel Prize winner in Literature, begins his poem 'Cold Iron' with these lines. Indeed, iron does appear in many different facets of our lives: from the band Iron Maiden to the Ironman championships in triathlon; in history with the Iron Curtain, or when we refer to the Iron Lady, ruling with an iron hand.

Iron is a transition metal that melts at 1,539 °C, and its appearance can be described as lustrous and metallic, with a silver–grey tinge. It is the second most abundant metal on our planet — with the first being aluminium — and is mostly present in its dense metal core as an alloy with nickel. It is also ubiquitous in the Earth's crust, and constitutes about a third of its entire mass.

More and more chemists are now working with iron catalysts and are finding it most rewarding.

For almost all living organisms iron is an essential trace element. For example, haem — an iron–porphyrin complex — is key to the activity of a few proteins, including haemoglobin where it participates in the binding and transport of molecular oxygen. Iron is not eliminated by any physiological processes, and its uptake, transport and storage is highly regulated. It is so important to living organisms that iron deficiency due to an uncontrolled loss can lead to cell damage, and eventually even death.

Only rarely can iron be found in its pure, elemental form, and iron(II) compounds are also rare. It is mostly found in hydroxides and oxides of iron(III), but these are hardly soluble in aqueous media at about neutral pH, and most organisms have developed specialist mechanisms to meet the essential iron demand. Bacteria, for example, release siderophores, which chelate iron and allow subsequent directed transport and uptake. A presentation on siderophores for the faculty at the University of Basel was, in fact, my first direct exposure to iron chemistry — it turned out to have a significant impact on my research interests, as well as being a pleasant challenge.

Iron chemistry was developed early on in the history of mankind. In prehistoric times, samples were likely to have been collected from meteors, and iron has been smelted since 2,000 BC. Pure metal can be obtained from iron oxides such as the mineral haematite (Fe_2O_3) by reduction with carbon at high temperature. Subsequent modifications with other metals (as well as a few non-metallic additives, such as silicon or carbon) lead to alloys with tunable properties — steels — which have become key components to the building, automotives and machinery industries, to mention a few.

Abundant and mostly non-toxic, iron could be expected to be found as a catalyst for many applications. The Haber–Bosch process — which uses a doped iron catalyst to synthesize ammonia from nitrogen and hydrogen — is well-known, and iron catalysis was introduced by Walter Reppe at the BASF laboratories in Ludwigshafen, Germany, for the synthesis of alcohols from olefins and carbon monoxide. However, iron is usually not the first metal of choice for catalysis, with precious metals such as palladium or rhodium often taking preference. This is probably because too many transformations have been shown to work with non-iron catalysts; why, then, should this approach be changed, and switched to the unknown?

Furthermore, iron's magnetic properties make standard mechanistic investigations difficult (for example, by NMR spectroscopy). Many iron complexes are paramagnetic, and reaction pathways often involve radical components. Theoretical studies can also be hampered by having to consider spin-state changes. Nevertheless, more and more chemists are now working with iron catalysts and are finding it most rewarding. As recent advances show, both reactivity and selectivity can often be controlled by judicious combination of iron source, ligand and additive.

This approach led to the discovery of unexpected cross-coupling activities, and even the functionalization of hydrocarbons with simple oxidants has become possible. Finally, it was also demonstrated that asymmetric synthesis with chirally modified iron complexes is feasible. More discoveries and breakthroughs will surely soon be reported, allowing the currently used precious metal catalysts to be efficiently substituted.

Is iron really cold, as noted by Kipling in his poem from the beginning of the last century? About 100 years later the scene has changed — iron is hot, and the fire has only recently been ignited. ❐

CARSTEN BOLM is at the Institute of Organic Chemistry at the RWTH Aachen University, Germany.
e-mail: carsten.bolm@oc.rwth-aachen.de