

Silver: The Cultured and Versatile Element

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Unlike other elements discovered in the recent centuries where modern chemistry emerged from the world alchemy, we cannot name the first person who discovered silver.^[1] Indeed, mankind's long association with silver is evident from both its name and its symbol. The former originates from the Anglo-Saxon word 'seolfor' while the latter, 'Ag', comes from the Latin word 'argentum'.^[2]

Silver, one of the coinage metal elements, is found in the Earth's crust at around 0.07 parts per million (ppm), making it rarer than copper (around 55 ppm), but not as rare as gold (around 0.004 ppm).^[3] In nature, silver can be found in both its free form and in combination with other elements in over 40 different minerals of which argentite (cubic silver sulfide (Ag₂S)) is one of the most common.^[4] Silver is often found and mined with other metal ores such copper, lead, zinc, and gold. Australia is the fifth largest producer of silver (1400 tons in 2016).^[4] Indeed BHP-Billiton, one of Australia's largest and oldest companies, started out as the 'Broken Hill Proprietary' company aimed at developing a silver, lead and zinc mine in Broken Hill, Australia.^[5]

Silver was one of the first elements to have been mined, refined, and fashioned into objects. This is reflected in the more than 80 Bible verses that mention silver, most from the Old Testament, including 'For you, God, tested us; you refined us like silver' (Psalm 66:10). In the New Testament we learn that Judas betrays Jesus for 30 silver coins: 'And asked, "What are you willing to give me if I deliver him over to you?" So they counted out for him thirty pieces of silver' (Matthew 26:15).

The relative access to silver and gold was not the same in different ancient societies. For example, silver was much closer in value to gold in ancient Egypt compared with other ancient states (1:2 instead of the more typical 1:13).^[6] Each of the ancient societies revered silver and used it to fashion a range of different objects.

In Book XVI of Horace's Odes Pythia, the Delphic Oracle advises Philip of Macedonia to 'fight with silver spears and you will conquer all things'. Philip interpreted this to mean that he could master all Greece through economic means, including bribery, silver spears being equivalent to silver coins.^[7] The silver coins of the ancient Greeks are amongst the most beautiful coins to have ever been made. Fig. 1a shows one of the largest silver coins made by the ancients, a Silver Dekadrachm of Syracuse.^[8] The obverse shows the nymph Arethusa appropriately surrounded by dolphins. The reverse shows a charioteer whom we might imagine as taking part in a race from one of the

Ancient Olympic games. The first coin manufactured in Australia, the Holey Dollar (Fig. 1b), was initiated by Governor Lachlan Macquarie to replace the unofficial rum currency. The notorious convict forger William Henshall was tasked with preparing the dies and producing the coins by cutting out the centres of around 40000 silver Spanish dollars to produce two types of coins – the Holey dollar as well as the central plug, called the dump.^[9,10]

Silver is one of few elements widely used in everyday language, where it is often used to describe the colour of objects. Everyone knows about silver wedding anniversaries (marking 25 years of marriage), silver prizes in Olympic competitions (for coming second), and silver bullets (one of the few weapons effective against a werewolf, witch, vampire, or other monster^[11]). At some stage, we have all used the expressions 'every cloud has a silver lining' and 'born with a silver spoon in his/her mouth'. Books and the 'silver screen' (movies) are home to characters such as Long John Silver (from Robert Louis Stevenson's *Treasure Island*) and some of us may recall the Lone Ranger's catchphrase 'Hi Ho, Silver'. Argentina is the only country named after an element.

There are two naturally occurring stable isotopes of silver: ¹⁰⁷Ag and ¹⁰⁹Ag. These produce distinct isotope patterns in mass spectra that can be exploited. For example, mass spectrometry can be used to study the fractionation of silver isotopes in coinage, thereby quantifying monetization in ancient Mediterranean and Near-Eastern societies through the identification of silver mineral sources, monetary sinks, and major transfer routes.^[12] Mass spectrometry allows ready identification of silver complexes and clusters since the distinctive isotope envelope can be used to 'count' the number of silver atoms,^[13] just like the number of bromines can be counted in organic compounds.

Silver is a soft metal with a shiny metallic finish and has the highest electrical and thermal conductivity of the metals. It is both ductile and malleable, so that it can be pulled into wires or hammered into sheets. Each of these characteristics makes silver a valuable element in a wide range of applications including: in the electronics industry, in long life batteries, manufacture of mirrors and musical instruments, and dental fillings.^[4] A noteworthy historical example of the application of the electrical conductivity of silver is the building of the calutrons used to refine the ²³⁵U isotope used to build the first atomic bomb.^[14] Since the copper needed for brass shell casings received a higher priority than calutron construction, the scientists and engineers



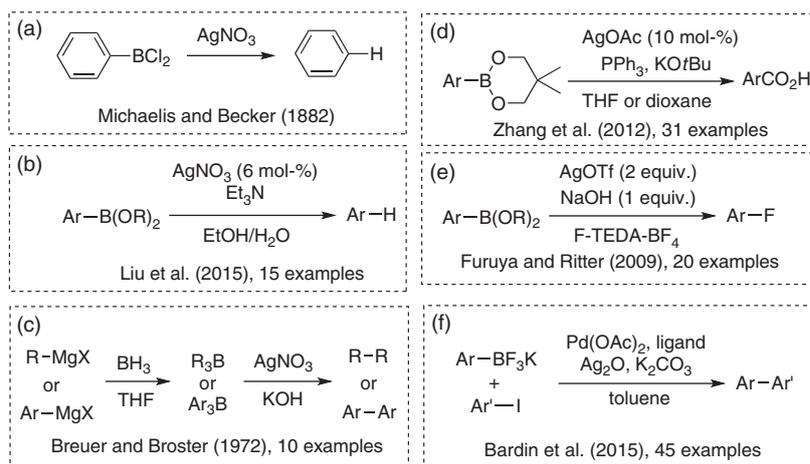
Fig. 1. Two historically significant silver coins: (a) Sicily, Syracuse. Dionysios I. 405–367 BC. AR Dekadrachm. Unsigned dies in the style of Euainetos. Struck ~405–400 BC. Obverse: Wreathed head of Arethusa (left), wearing triple pendant earring and necklace, surrounded by four dolphins swimming; star to right. Reverse: Charioteer driving galloping quadriga (left), holding kentron and reins; above, Nike flying right and crowning charioteer; below, heavy exergual line: a military harness, shield, greaves, cuirass, and Attic helmet all connected by a horizontal spear; (b) New South Wales, five shillings or holey dollar, 1813, struck on a Charles III Mexico City Mint eight reales, 1792FM. Images reproduced with permission.

involved in the construction of the magnetic coils turned to silver. The federal treasury repository at West Point had large stores of silver and 15000 tons of the metal were loaned to the Manhattan Engineering District and shipped, under guard, to Detroit for preparation of the wire. Guards were constantly present to pick up filings and scrap. Upon completion of the project, the silver was melted down and returned to the Treasury with virtually no loss.

Apart from the uses of metallic silver described above, silver exhibits a diverse chemistry. Indeed, silver salts have a rich history in organic chemistry and continue to enjoy widespread use. Most students of chemistry will have performed the Tollens' 'silver mirror' test, which provides a simple visual and qualitative assay for the presence of aldehyde functional groups and formally involves oxidation via C-H bond activation.^[15] Other stoichiometric and catalytic Ag^+ promoted C-X bond activation reactions play key roles in organic synthesis and new variants continue to be sought.^[16] In 1882, Michaelis and Becker reported on the silver nitrate promoted protodeborination of phenyl borate (Scheme 1a),^[17] a reaction commonly employed in early arylboron chemistry^[18] and more recently developed for applications in solid-phase synthesis^[19] and into a

catalytic protocol (Scheme 1b).^[20] Silver salts have also been used to promote C-C (Schemes 1c, d),^[21] C-F (Scheme 1e)^[22] and C-O bond^[23] formation from organoboron compounds. Alternatively, silver salts can be employed in conjunction with other transition metal catalysts to develop robust C-C coupling protocols. For example, the Suzuki-Miyaura reaction^[24] between weakly nucleophilic organoboron reagents and C-electrophiles often benefits from the addition of stoichiometric amounts of Ag_2O , as illustrated in the biaryl synthesis employing aryltrifluoroborates (Scheme 1f).^[25] Indeed, silver salts are common co-additives in many newly developed gold(I) catalysed organic reactions.^[26]

Since there is often a dearth of mechanistic information on these reactions, the exact role of silver is poorly understood. In some instances, organosilver intermediates formed via transmetalation have been invoked, but rarely have they been isolated and characterised. While the formal oxidation states of silver in silver compounds and complexes can range from 0 to +3, changes in silver oxidation states during reactions used in organic synthesis are also often difficult to discern. We recently used a combination of electrospray ionisation and direct injection NMR experiments to monitor the formation of



Scheme 1. Examples of Ag^+ promoted C-B bond activation reactions of organoboron compounds for use in organic synthesis: (a) stoichiometric protodeboration; (b) catalytic protodeboration; (c) stoichiometric deboration with C-C bond coupling; (d) catalytic deboration/carboxylation; (e) catalytic deboration/fluorination; and (f) Pd catalysed biaryl synthesis employing aryltrifluoroborates and stoichiometric amounts of Ag_2O .

organoargentate(I) and (III) complexes and to show that these were key intermediates in silver-mediated cross-coupling reactions.^[27]

The low solubility of silver halides is widely exploited to abstract halides from organohalides or transition metal complexes by reactions with silver(I) salts. The former reactions give rise to carbocations,^[28] while the latter yield either cationic solvent complexes or complexes with coordinating anions.^[29]

Aside from silver being used in catalytic reactions of interest for the synthesis of fine chemicals, silver catalysts underpin two important processes used to manufacture commodity chemicals on a vast scale: (1) the vapour phase oxidation of ethylene to ethylene oxide; (2) the oxidative dehydrogenation of methanol to formaldehyde.^[30]

Apart from chemical applications, silver compounds have found uses in other areas. Up until the recent development of digital cameras, around a quarter of silver production was used in the preparation of the light-sensitive compounds for photography.^[31] Work by the CSIRO in the 1940s–1990s confirmed that silver iodide (AgI) can be used in cloud seeding to produce rain.^[32] Silver compounds and nanoparticles have long been used as antibacterials to prevent the growth of fungi and bacteria.^[33] Indeed, silver has been used to store and purify water, including during Alexander the Great's military campaigns and aboard the Apollo spacecraft, the MIR space station and the NASA space shuttle.^[33]

For its beauty, and its many practical uses, I propose we raise a glass of any one of at least five silver named cocktails^[34] and make the toast 'To silver: the cultured and versatile element'.

Conflicts of Interest

The author declares no conflicts of interest.

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