Chemistry Chat -Focusing on the Elements-

New Allotropes of Main Group Elements (2)

Kentaro Sato

Continuing from the previous time, let us take a look at some of the recently discovered allotropes of main group elements.

Silicon

Silicon, having Clarke number 25.8, is the second most abundant element in the Earth's crust next to oxygen. Its most famous allotrope is one in which silicon atoms are bonded in a diamond-like network and it is a gray, hard but weak solid. This material is essential to our contemporary society as it is used everywhere to make semiconductors.

Another allotrope of silicon that is stable under ambient pressure is amorphous silicon. It consists of a random three dimensional reticular network of silicon atoms and appears as a brown powdery solid. Because it has a larger energy gap than crystalline silicon and is easier to be processed into a film, it is used for thin-film transistors and solar batteries. In a strict sense, though, amorphous silicon is not an allotrope since it is thought to contain hydrogen atoms attached to the silicon skeleton.

Other than these two, it is known that crystalline silicon undergoes pressure-induced phase transition into other structures such as β-tin form. The application of these new crystalline forms is yet to be explored.

New Three Dimensional Cage

Recently, the synthesis of a new three dimensional reticular allotrope of silicon was reported (*Nat. Mater.* **2015**, *14*, 169.). Timothy Strobel and his coworkers at Carnegie Institution of Washington treated silicon with sodium under high thermal and pressure conditions and obtained a compound with the composition $NaSi_6$, in which sodium atoms were trapped in silicon-based cages. Then, it was found that by heating it to 400 K in a vacuum, the sodium atoms were gradually removed, leaving the caged structure intact.

The newly obtained silicon allotrope consists of a network based on 5, 6, and 8-membered rings and contains 24 silicon atoms per unit cell. It is stable in air up to around 750 K and has a band gap of 1.3 eV, which are desirable characteristics as a material for solar batteries. And importantly, the synthetic methodology used by the Strobel group has a potential to yield even more silicon allotropes, and therefore further development is expected.

Silicene

Can't we synthesize silicon-based nanomaterials that correspond to those nanocarbon materials? When it comes to Si_{60}, the silicon analogue of fullerene, It has been evaluated by theoretical calculations but has yet to be synthesized. The relative weakness of π-conjugation among silicon atoms is considered to be the obstacle. The silicon equivalent of graphite has not been known either.

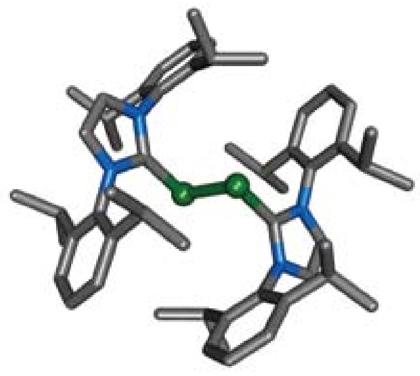
On the other hand, in recent years, the silicon version of graphene called silicene has been drawing an attention. Similar to graphene, it has a honeycomb structure. Although silicene had long been the subject of theoretical research, its first synthesis was achieved in 2010 by vapor deposition of silicon onto silver surface (*Appl. Phys. Lett.* **2010**, *97*, 223109.).

Since sp^2 hybridization of silicon is not as stable as that of carbon, silicene is not completely planar and has a rippled surface, and it is also unstable to air. However, expectations are high because it can have functions that are not possible with graphene. In 2015, a transistor using silicene was already introduced. It is a new exciting material toward the realization of ultrafast computers.

Holding Si(0) with NHC

In 2008, Gregory Robinson and his coworkers at University of Georgia reported the synthesis of carbene-stabilized diatomic Si(0) compounds. (*Science* **2008**, *321*, 1069.). The reduction of $SiCl_4$-NHC (NHC=*N*-heterocyclic carbene) complex with KC_8 led to the formation of stable compounds containing a Si=Si bond. Interestingly, the bond angle of C-Si-Si is almost perpendicular (about 93 degrees).

Diatomic silicon species had hitherto been detected only spectoroscopically at ultralow temperature, but now, it can be isolated as a crystalline solid in carbene-stabilized form. Since the carbene is merely a ligand, the central Si_2 unit can be regarded as a new allotrope of silicon. This is recognized as a landmark achievement in main group chemistry.



Si_2 (the green atoms in the center) stabilized by the coordination of two NHC ligands

Complex Allotropes of Phosphorus

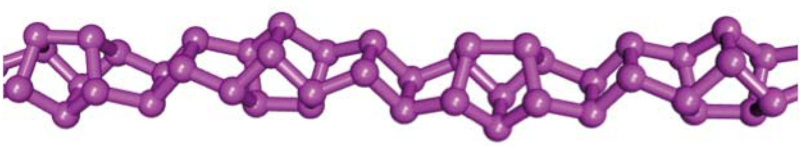
The allotrope of phosphorus includes yellow phosphorous and red phosphorous, according to high school textbooks. It is explained that yellow phosphorus exists as P_4 and a flammable pale yellow solid, and red phosphorus is a less reactive powder used in matches.

However, the more recent understanding is that there is no such pure substance as yellow phosphorus and it is actually white phosphorus that contains impurities including red phosphorous. Similarly, even though there are other phosphorus “allotropes” such as black, violet, and scarlet phosphorous according to some literature, it has become clear that these do not qualify as true allotropes either. Scarlet phosphorus, for example, is considered to be fine crystals of red phosphorus. The world of phosphorus allotropes is rather complex.

One dimensional polymeric form of phosphorus allotrope was discovered after the turn of the 21st century. The research team led by Pfitzner and Eckert in Germany obtained a reddish brown solid composed purely of phosphorus, when they treated the adduct of red phosphorous and copper(I) iodide with aqueous solution of potassium cyanide, which removed copper. The analysis revealed that it was a polymer with a unit structure composed of 12 phosphorus atoms connected in tubular fashion (*Angew. Chem. Int. Ed.* **2004**, *43*, 4228.). One of them is shown below. By exploring the variation of synthetic conditions, there seems to be a good possibility for the discovery of more new allotropes.

Stabilization by NHC

Nitrogen sits above phosphorus in the periodic table and is most stable in diatomic N_2 form. As one might wonder, the diatomic form of phosphorus (P_2) is also known. The phosphorus atoms are triply bonded to each other and the bond length is 189.5 pm, which is significantly shorter than ordinary P-P single bond (roughly 220 pm). This “diphosphorus” is formed when white phosphorus is heated



One dimensional polymer composed of phosphorus atoms

to 1100 K, but is also extremely unstable and difficult to be handled. It has been found recently that it undergoes hetero-Diels-Alder reaction with dienes, which could be developed into an effective synthetic strategy for phosphorus-containing compounds.

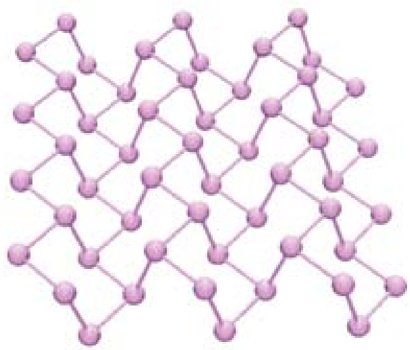
Then, can the diatomic phosphorus be stabilized by the coordination of NHC just like the aforementioned diatomic silicon? In fact, the Robinson group has already synthesized a stabilized diatomic phosphorus molecule by the almost same approach they employed for silicon (*J. Am. Chem. Soc.* **2008**, *130*, 14970.). These are truly the significant impacts that NHC ligands have had in the world of chemical science.

Sheet of Phosphorus

Black phosphorus is one of the allotropes known for a long time and it forms when white phosphorus is heated under 12,000 atm. It consists of stacked sheets of phosphorus-based honeycomb structure and resembles carbon-based graphite.

Graphene, the popular substance in materials science today, was first created by peeling a single layer of sheet off of graphite. Then, could we do the same for black phosphorus and obtain a phosphorus analogue having unique properties? This question was answered by Peide Ye of Purdue University and his coworkers in 2014 and the answer was yes (*ACS Nano* **2014**, *8*, 4033.).

The new two dimensional material, named phosphorene, has a wave-like structure unlike flat graphene. And interestingly, while graphene is a good electric conductor, phosphorene behaves as a semiconductor. It is already drawing a major attention and the initial report has been referenced more than 800 times in just a couple of years. Phosphorene has a potential to be developed into high-performance electronic devices and it can be prepared from inexpensive phosphorus. Therefore, it is counted as one of the promising materials for future application.



The structure of phosphorene (extracted from Wikipedia)

Silicon and phosphorus, the two elements so familiar to us, still offer this many opportunities for new discovery. This serves as a great reminder of the vast possibility of chemistry.

Introduction of the author :

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[Brief career history] He was born in Ibaraki, Japan, in 1970. 1995 M. Sc. Graduate School of Science and Engineering, Tokyo Institute of Technology. 1995-2007 Researcher in a pharmaceutical company. 2008-Present Freelance science writer. 2009-2012 Project assistant professor of the graduate school of Science, the University of Tokyo. 2014-present Publicist for π-system figuration, scientific research on innovative areas.
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