

## Chemistry between Carbon and Other Elements

Kentaro Sato

Numerous research articles are published every day in the field of organic chemistry. Come to think of it, in the genre that deals with only one element - carbon, considering such high pace of publication, one might wonder how researchers manage not to run out of new ideas. Apparently, the possibility of carbon chemistry has a large space left to be explored after hundreds of years of history, and the horizon even continues to expand.

In the CAS database, the largest chemical database in the world, close to 70 million compounds are registered. Of those, 80 percents are carbon-based organic compounds. Within the periodic table consisting of more than 100 elements, carbon has a special status which may be called the “king of all elements.”

There are several reasons why carbon is such a special element, and one of them is because of its ability to form stable bond(s) with a number of other “heteroatom” elements. Carbon forms bonds with not only common non-metal elements such as hydrogen, oxygen, nitrogen, sulfur, phosphorus, and halogens, but also with most metallic elements. Many of the compounds based on carbon-heteroatom bond are common reagents found in the shelves of chemistry laboratories.

Without needing to mention such prime examples as Grignard reagent, hydroboration, and Wittig reaction, carbon-heteroatom bond has always been trailblazing the development of organic chemistry. Even relatively less familiar heavy metal elements such as hafnium, rhenium, and bismuth have been utilized for organic synthetic reactions. Molybdenum and ruthenium carbenes used to be somewhat exotic compounds until not too long ago, but became mainstream regulars after the advent of Grubbs olefin metathesis catalyst. The development of new chemical

bond is always the most important frontier of chemistry, and as such, it continuously draws a great deal of interest and energy from scientific community.

### Organic Noble Gas Compounds

The synthesis of the first xenon-containing compound XePtF<sub>6</sub> by Neil Bartlett in 1962 is a renowned accomplishment listed in many textbooks. Since then, xenon compounds of different oxidation numbers (II, IV, VI, VIII) have been known to date and many of those are fluorides and oxides. Among them, for example, XeF<sub>2</sub> is a useful (and commercially available) fluorination reagent.

Xenon is also known to form a bond with carbon. It has a surprisingly long history, with the first preparation of its kind reported back in 1989 [1]. For Xe(II) compound, C<sub>6</sub>F<sub>5</sub>XeF has been used to synthesize several organic xenon compounds including Xe(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> [2].

In 2000, the first organic xenon(IV) compound was synthesized [3]. For example, [C<sub>6</sub>F<sub>5</sub>XeF<sub>2</sub>]BF<sub>4</sub> was made by the reaction between XeF<sub>4</sub> and C<sub>6</sub>F<sub>5</sub>BF<sub>2</sub>. Reported to act as a strong fluorinating agent, this compound perhaps has an interesting chance to develop into a reagent.

For krypton, which is one size smaller family member of xenon, it is known that photo irradiation in the presence of acetylene under low temperature conditions produces HC≡CKrH [4]. There might be similar possibility for radon, but so far only Rn(II) fluoride is known and the synthesis of organic radon compound has not been realized. How about argon and neon? To find out whether they can react with carbon, there is probably a competition going on among laboratories around the world.

## Hot Organic Compounds

High sociability of carbon extends to the realm of radioactive elements. For example, short-lived astatine (having a half-life of maximum 8.1 hours) forms organic compounds such as  $C_6H_5At$ . Actinide elements such as uranium, neptunium, plutonium, and americium also complex with cyclooctatetraene to form sandwich-shaped molecules commonly called “hot sandwiches” (picture shown below) [5]. These complexes are rare molecules having a symmetry feature known as  $D_{8h}$ . For uranium, there is  $Cp_4U$  complex, in which four cyclopentadienyl ligands are bonded to the uranium in tetrahedral fashion [6]. Big atoms have surprising properties indeed.

To the best of my literature search, the heaviest element that forms a bond with carbon is einsteinium with atomic number 99. In 2005, the synthesis of an alkene-einsteinium complex was reported [7]. Among smaller elements than this, there are only a few which are not known to bond with carbon; the examples are some of noble gases like helium, neon, and argon, and extremely short-lived species such as francium.

By the way, if the partner is not limited to carbon, the heaviest element ever prepared as a compound is hassium with atomic number 108. In 2002, hassium compounds including  $HsO_4$  were synthesized from just seven atoms and their properties have been studied [8]. The isotope used in the study had a half life of only 11 seconds, which tells us about the incredibly high level of experimental sophistication. Considering that, there may still be rooms in the list of elements that potentially make a bond with carbon.

## The Element Not Found in The Periodic Table

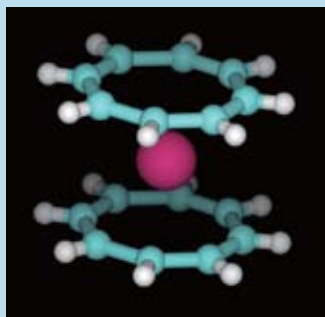
In 2008, an element called muonium emerged as a new chemical partner of carbon. Most people probably have never heard of this “element”, however, because it is not found anywhere in the periodic table. Muonium is not exactly an element which consists of proton, neutron, and electron.

There is an elemental particle called muon. This particle is 207 times heavier than electron and can have either a positive or a negative charge. A positively charged muon captures an electron upon encounter to form a hydrogen-like “atom” called muonium, which is considered one of the “exotic atoms” having neither proton nor neutron.

P. W. Percival and his group used muonium as an equivalent of hydrogen radical while studying the reactivity of carbon-silicon double bonds [9]. In this study, a compound in which muonium is bonded to carbon was observed. As a research method of organic chemistry, this is a very atypical but impressive approach.

You may wonder how stable the carbon-muonium bond is. Muon itself exists with an average longevity of only 2.2 microseconds, therefore, the organic muonium species is destined to vanish in split seconds literally.

It is surprising that any meaningful data can be collected in that instantaneous period of time, but according to the experts in the field of elemental particle research, muonium actually belongs to the group of long-lived particles and its analysis is relatively easy. For example, positronium (an exotic atom composed of an electron and a positron) is also known to form a compound but it lives for nanoseconds, therefore, its detection is “slightly difficult.” The physical chemists certainly have a very different perception about time, but this kind of interdisciplinary laboratory should be a great place where fascinating researches are born.



“Hot sandwiches”

**References**

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**Introduction of the author :****Kentaro Sato**

[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. 2007-Present Freelance science writer. 2009-2012 Project assistant professor of the graduate school of Science, the University of Tokyo.

[Specialty] Organic chemistry

[Website] The Museum of Organic Chemistry <<http://www.org-chem.org/yuuki/MOC.html>>

## Technical Glossary

### Carbene complex

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Carbene complexes are organometallic complexes with the carbene coordinated on the carbon atom to the metal center. There are two types which can be categorized as Fischer type carbene complexes and Schrock type carbene complexes.

Fischer carbene complexes show electrophilicity because the center metal is in an electron poor state. Therefore, the reactivity of it is similar to carbonyl compounds in which nucleophilic substitution of it with various nucleophiles proceeds. In addition one of substituents has to be an alkoxy group because of its electronic structure.

The chemical character of Schrock type carbene complexes is nucleophilic because of an electron rich state at the metal center. It shows especially high reactivities towards carbon-carbon and carbon-heteroatom multiple bonds. As typical chemical examples of Schrock type carbene complex usage, olefin metathesis and carbonyl olefination are well known. These synthetic characteristics are very useful so many suppliers have Schrock type carbene complexes as reagents.

### Olefin metathesis

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Olefin metathesis is a chemical reaction between double bonds of two separate olefin units in which double bonds exchange with each other to form two new olefin units. A Schrock type carbene complex is usually used for such a synthesis and Mo, Ru and Ti metals are generally used as active metals. The bulkiness of substituents on the olefins affects their reactivity in olefin metathesis, so the development of new carbene complexes showing higher reactivity has been studied since the 1990's.

### $D_{8h}$ symmetry

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A molecule having a  $C_n$  principal rotation axis and its perpendicular  $n$  elements of  $C_2$  rotation axes is in the  $D_n$  group. In addition, a molecule having a  $\sigma_h$  mirror perpendicular to the principal axis shows  $D_{nh}$  symmetry. The molecule satisfying the conditions in the figure drawn below is in  $D_{8h}$  group.

