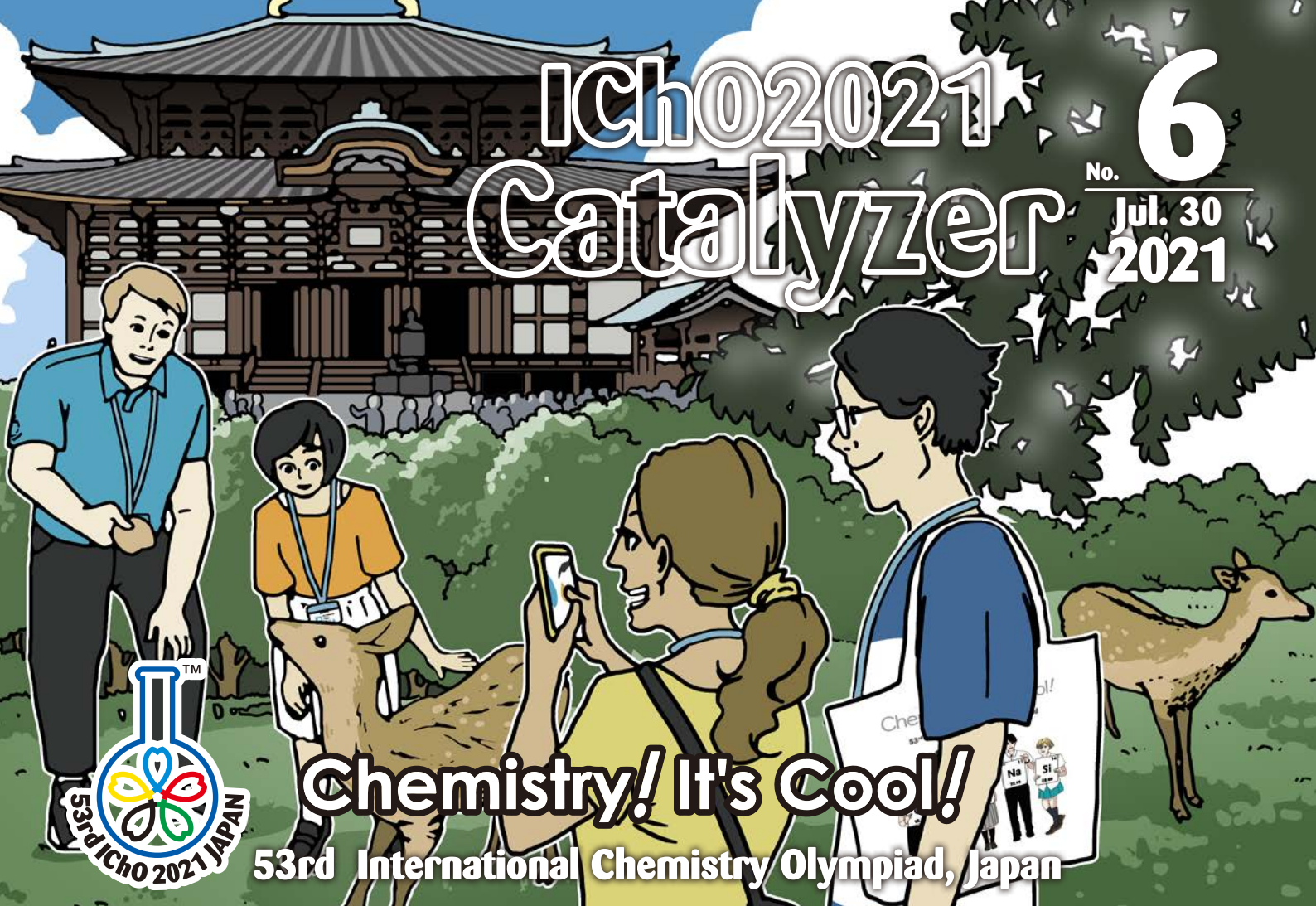
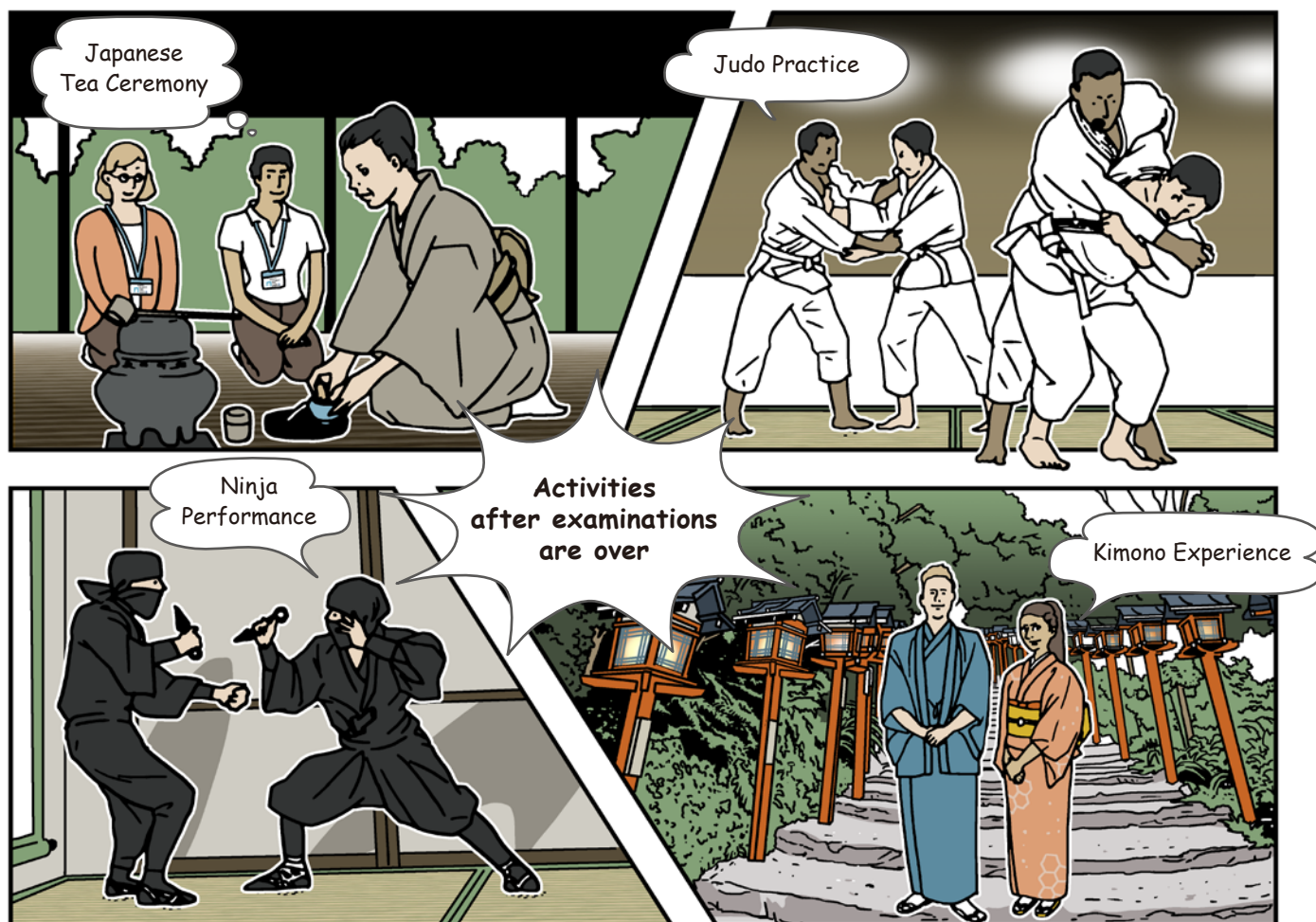


Ich02021 Catalyzer

No. **6**
Jul. 30
2021



Cover illustration : Excursion to Nara



Development of Palladium-Catalyzed Cross Coupling Akira Suzuki / Ei-ichi Negishi

Many of the functional materials and pharmaceuticals that are indispensable to modern life are created by organic synthetic reactions. In order to synthesize such useful materials, carbon-carbon bond formation reactions are indispensable to link the carbon atoms of organic molecules. A typical example of such a cross-coupling reaction is the chemical transformation of benzene rings. This reaction is difficult to achieve by traditional methods using carbocations and carbanions, but was found to be more easily accomplished by using transition-metal catalysts. It is no exaggeration to say that the field

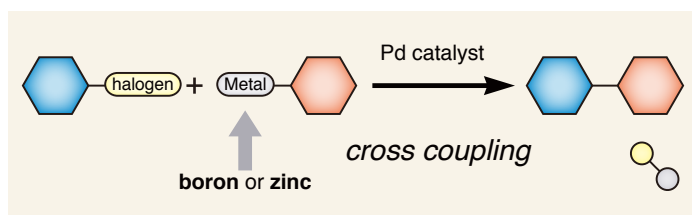
of cross-coupling reactions has been led by Japanese researchers, and in particular, the palladium-catalyzed cross-coupling reactions of aryl halides with arylmetal (boron or zinc) reagents developed by Akira Suzuki and Ei-ichi Negishi in the 1970s are extremely versatile. They have a wide range of applications, and are currently being used in the synthesis of numerous pharmaceuticals and organic electroluminescent materials. In 2010, Akira Suzuki and Ei-ichi Negishi were awarded the Nobel Prize in Chemistry, together with Richard F. Heck, for the development of such a truly practical synthetic reaction.



Photo by Hokkaido University



Dr. Akira Suzuki (1930-) **Dr. Ei-ichi Negishi (1935-2021)**



... IChO2021 Problem Q5 ...

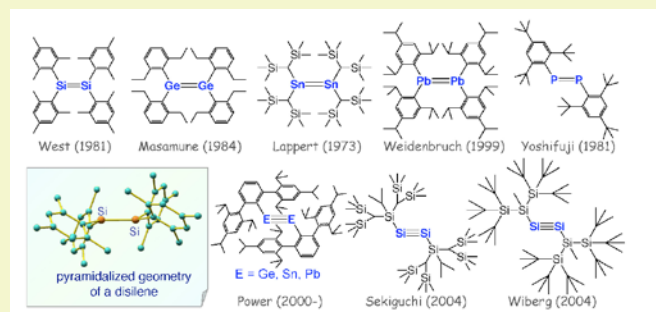
Unsaturated bonds between heavier main-group elements

In the late 1800s, the periodicity of the properties of elements was discovered; this concept suggests that elements that exhibit similar properties appear in a periodic order when arranged according to their atomic numbers. Ultimately, the stringent application of this principle resulted in the creation of the periodic table of elements by Mendeleev in 1869. In general, elements in the same group, *i.e.*, those located in the same column in the periodic table, are thus expected to exhibit similar properties. *What do you think about this statement? Is this true for all the elements in the same group?*

Silicon is the heavier homologue closest to carbon in the periodic table, and the analogies between carbon and silicon have been discussed controversially for a long time. For example, while the chemistry of unsaturated compounds of the main-group elements of the second row such as olefins ($R_2C=CR_2$) is plentiful, that of the heavier-element homologues of these multiple-bond compounds has remained underdeveloped in comparison, which is predominantly due to their extremely high reactivity and inherent instability under ambient conditions. Prior to the 1970s, all attempts to synthesize compounds with multiple bonds between heavier main-group elements were unsuccessful, and only cyclic oligomers or polymers with single covalent bonds between the main-group elements were obtained. Accordingly, the scientific consensus at the time was that such heavier main-group elements are probably not able to form π -bonds ('double-bond rule'). However, ambitious chemists were ultimately able to isolate and characterize several kinds of such compounds with unsaturated bonds between heavier main-group elements using bulky substituents for steric



protection ('kinetic stabilization'). For example, the first distannene ($R_2Sn=SnR_2$, Lappert 1973), diphosphene ($RP=PR$, Yoshifuji 1981), disilene ($R_2Si=SiR_2$, West 1981), and disilynes ($RSi\equiv SiR$, Wiberg and Sekiguchi 2004) have been synthesized as stable compounds by using sterically demanding substituents, which disproved the double-bond rule. Since then, the unique features of unsaturated compounds of heavier main-group elements have been investigated in detail, attracting much attention to the area of main-group-element chemistry. For example, it has been reported that disilenes ($R_2Si=SiR_2$) and disilynes ($RSi\equiv SiR$) exhibit pyramidalized and bent geometries, respectively, which stands in sharp contrast to the planar geometry of ethylene and the linear structure of acetylene. These different structural features should in turn cause different reactivity and properties, and thus, the chemistry of unsaturated silicon compounds can be expected to be characterized by unprecedented functions and chemistry that is different from that of carbon. Thus, it should be noted here that the structure and chemistry of the second-row elements is considerably different in from those of the heavier main-group elements, as exemplified by the case of H_2O (bp: 100 °C; $\angle HOH \approx 104.5^\circ$) vs. H_2S (bp: -60 °C; $\angle HSH \approx 92^\circ$).



Discovery of Adrenaline

... Jokichi Takamine / Keizo Uenaka

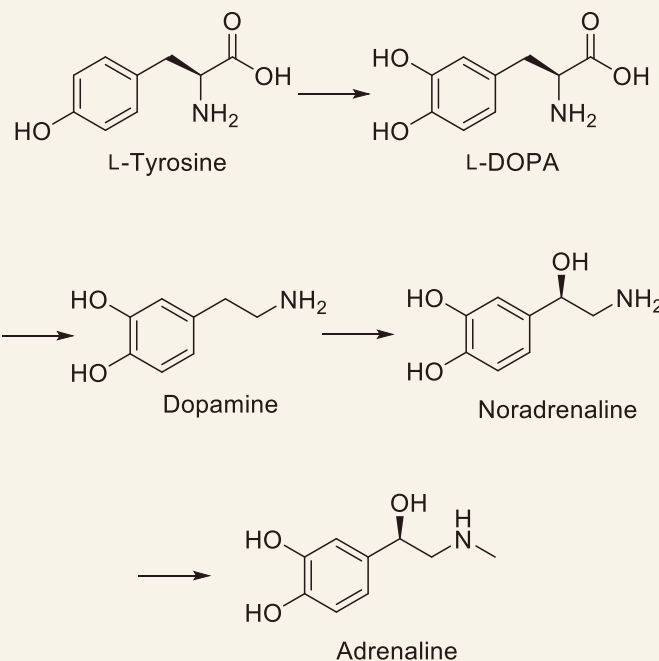
When one feels anxious, excited, or nervous, such as during important exams, public presentations, cheering on sports teams, muscle training, or when in love, our blood pressure rises and our heart rate increases. A hormone called adrenaline is secreted by the adrenal medulla when the sympathetic nervous system becomes dominant. Adrenaline was the first hormone to be isolated by scientists, in the year 1900. Jokichi Takamine and Keizo Uenaka (1876–1960) played key roles in this discovery. They succeeded in obtaining 7 grams of adrenaline crystals from 9 kilograms of bovine and sheep adrenal tissue by

repeated acid and base extraction. Only after the first successful isolation did the hormone become commercialized as adrenaline preparation. Since then, it has become an indispensable agent for raising blood pressure in surgery, ophthalmology, and internal medicine. The number of lives adrenaline has saved to date is testament to the importance of this achievement for humanity.



Dr. Jokichi Takamine
(1854–1922)

In vivo, adrenaline is biosynthesized via L-tyrosine, L-dopa, dopamine, and noradrenaline.



Daibutsuden The world's largest wooden structure

Construction of the Great Buddha of Nara started in the year 745, after Emperor Shomu decided to build a huge statue of Buddha to placate social disturbances in the wake of multiple coups and rebellions. The Buddha statue was completed in 752. The current Buddha is approximately 14.7 meters tall, and the circumferences of the platform, the head, and the palm are 70 meters, 2.6 meters, and 2.6 meters respectively. The head was restored in the Edo (Tokugawa) period (1603 to 1868), and most of the body was restored during the Kamakura period (1185 to 1333), but parts of the original statue still remain. The amount of copper used for building the Buddha varies slightly, depending on the historical record, but it is estimated to be 500 tons. Mercury used as a solvent in the plating process and arsenic contained in copper are said to have caused poisoning of nearby residents, and a medical center was established to treat these patients. The Hall where the Great Buddha



(Daibutsuden) is enshrined today is 57.5 meters wide in the east-west direction, 50.5 meters deep, and 49.1 meters high to the ridge of the roof. It is the largest wooden frame building in the world, and was designated by the Japanese government as a National Treasure in 1952.

Today's schedule Jul. 30

Student


- **Video: Practical Examination explanation**

Mentor

- **Receive grading** (from Organizer, Request arbitration)
J 09:00 C 02:00 E 20:00 (Jul. 29)
- **Deadline of request, Jury meeting**
J 21:00 C 14:00 E 08:00

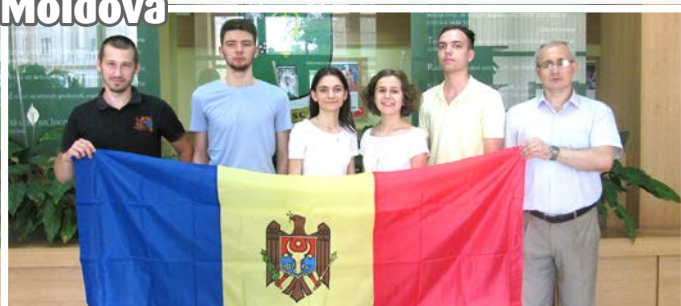
Have a nice day!

J: JST = UTC + 9 C: CET = UTC + 2 (summer time) E: EST = UTC - 4 (summer time)



Early Bird Communication

Moldova



Cyprus



Answer for Q5

2 Davy

Humphrey Davy discovered as many as six elements from nature in his lifetime by electrolyzing a huge number of substances using Volta batteries.

Element

5

Japanese mineral resources

Palladium

Basic Information

Origin of the name: Named after the asteroid Pallas
 Discovered by: W. H. Wollaston (the UK) [1803]
 Global production: 210 tons
 Major producers: Russia, South Africa, Canada

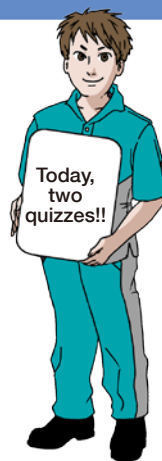
Palladium catalysts are vital to the efficient formation of carbon-carbon bonds. The compounds produced by cross-coupling reactions with these catalysts are indispensable to industry, from pharmaceuticals and agricultural chemicals to liquid crystals and organic light-emitting diodes. About 60% of palladium production is used in catalysts (three-way catalysts) for the removal of incomplete combustion products and unburned gasoline in automobile exhaust.



© Crystal Museum

ELEMENT QUIZ

Q6



① The 2001 Nobel Prize in Chemistry was awarded “for the development of catalytic asymmetric reactions”. Which catalytic metal was NOT used in the chemical reactions for which the prize was awarded?

- 1** Osmium **2** Palladium
3 Ruthenium **4** Rhodium

② Which of the following halogen elements is contained in vancomycin, a chemical widely known as an antibiotic?

- 1** Fluorine **2** Chlorine
3 Bromine **4** Iodine

Chemistry! It's Cool!



IChO2021

Catalyzer

No. 6

Official Website
<https://www.icho2021.org/>

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Jul. 30
1905

Published!

Special relativity
 by Albert Einstein

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