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A profile of Professor Jiro Tsuji Pioneering works on palladium mediated C–C bond forming reactions[☆]

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J. Tsuji, born in central Japan in 1927, graduated from Kyoto University. After spending several years in a pharmaceutical company, he went to the US as a Fulbright Fellow, and obtained a Ph.D. degree from Columbia University in 1960, working on total synthesis of natural products with Professor G. Stork. After returning to Japan, he joined Toray Industries, Ltd. In 1974, he was invited to Tokyo Institute of Technology as a Professor. After the mandatory retirement from a National University, he joined Okayama University of Science in 1988. During the past 2 years he has been a Professor at Kurashiki University of Science and Arts.

Realizing the great potential of transition metal chemistry in organic synthesis, he started his independent research on organometallic chemistry and homogeneous catalysis in the early 1960s at the Basic Research Laboratories of Toray. Pd has been his most favourite metal from that time when almost nothing was known about the use of Pd in organic synthesis.

One of his pioneering works in Pd chemistry is the discovery of the facile C–C bond formation by the reaction of COD–PdCl₂ complex with carbon nucleophiles such as malonate and acetoacetate under extremely mild conditions. This is the first example of C–C bond formation by the carbopalladation. He also discovered the reaction of the π -allylpalladium complex with nucleophiles, such as malonate and enamines (1965), opening the new fruitful field of π -allylpalladium chemistry. The C–C bond formations by the reaction of carbon nucleophiles are significant because conventional organometallic compounds, typically Grignard reagent, react with carbon electrophiles, generating Mg(II) at the same time. On the other hand, Pd complexes react with the nucleophiles, and the genera-

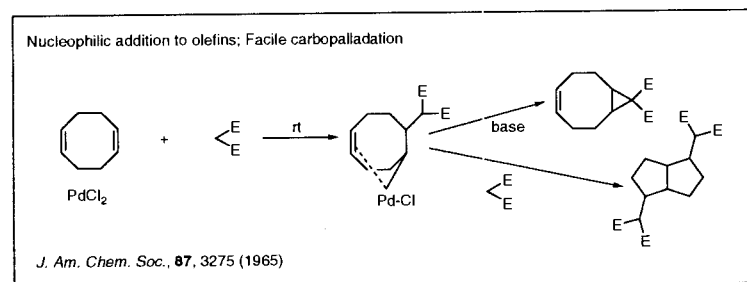
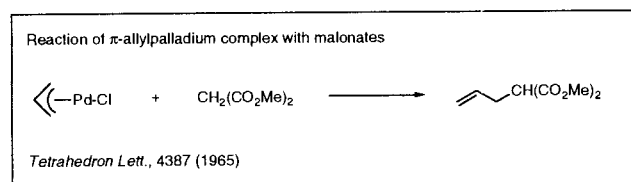
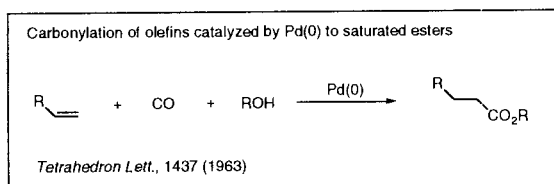
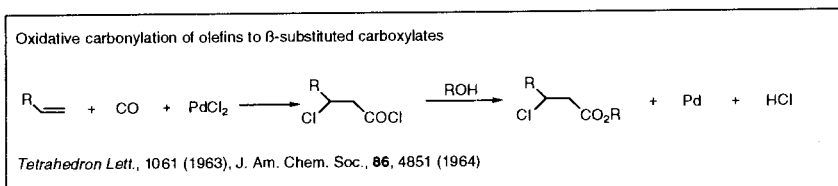
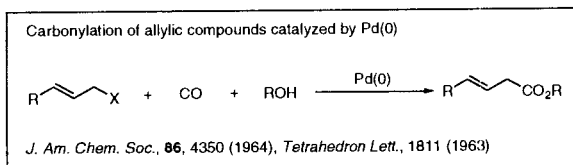
tion of Pd(0) species after the C–C bond formation indicates the possibility of catalytic reactions. He discovered the Pd-catalyzed carbonylation of allylic compounds. As a result of these discoveries, he has established himself as a pioneer in the field of Pd chemistry, and has continued his life long research.

Among numerous contributions he has made to organopalladium chemistry, he carried out extensive and pioneering research on π -allylpalladium chemistry including attack of nucleophiles, carbonylation, diene formation by elimination, regioselective hydrogenolysis, and dimerization of conjugated dienes. In particular reactions under neutral conditions using allylic carbonates and vinyl oxides are noteworthy. He has expanded the usefulness of β -keto esters and malonate by developing several new Pd-catalyzed reactions of allylic esters of these acids under mild neutral conditions with smooth decarboxylation, opening a new generation of β -keto esters and malonates chemistry. Based on π -allylpalladium chemistry, he showed the usefulness of allyl as the protecting group of carboxylic acids, amines, and alcohols, introducing the facile deprotection method of the allyl group by Pd-catalyzed hydrogenolysis using formic acid. He also explored the organopalladium chemistry of propargylic compounds by using propargylic carbonates as highly favorable substrates.

Another important contribution is Pd-catalyzed carbonylations. He discovered Pd(II)-promoted oxidative carbonylation of alkenes, dienes, and alkynes. In addition, he found Pd(0)-catalyzed hydroesterification of alkenes, dienes, alkynes, allylic and propargylic compounds, offering novel synthetic methods for carboxylic esters of many interesting types.

He paid attention to the application of the Wacker reaction to organic synthesis. In particular he pointed out the usefulness of the preparation of methyl ketones,

[☆]This profile is based on the information kindly provided by Professor J. Tsuji.



a very important functional group, from terminal olefins by the Wacker reaction.

He has shown the usefulness of the Pd-catalyzed reactions he discovered by elegant synthetic applications to natural products such as steroids, pheromones, and terpenoids. As one practical application, methyl jasmonate is produced commercially by applying the new method of enone formation from allyl β -keto carboxylate. Needless to say, his catalytic reactions are used extensively both in academia and in industry.

He has indeed been a true pioneer of organopalladium chemistry, and he has been a major contributor to this field for more than 30 years. In addition, based on his broad experience in Pd chemistry, he has written two comprehensive books on Pd chemistry in 1980 (Springer) and 1995 (John Wiley). In particular the latter book published in 1995, covering the broad field of Pd chemistry from its beginning to the present, has been well received by many synthetic organic chemists in academia and industry alike who are actively using

or wishing to use Pd catalysts for their synthetic works. This is a tremendous accomplishment no one else in the field has achieved.

He has given plenary and invited lectures in numerous international conferences, and received awards such as the Chemical Society of Japan Award, the Society of Synthetic Organic Chemistry Award, National Medal of Purple Ribbon, and Grand Prix of the Synthetic Organic Chemistry Award, Japan.

The following is a list of selected papers, books, and reviews on palladium chemistry by J. Tsuji.

I. Papers

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2. J. Tsuji, M. Morikawa, J. Kiji, Reaction of Olefin Palladium Chloride Complexes with Carbon Monoxide, *J. Am. Chem. Soc.* **86** (1964) 4851 ~ 4853.

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4. J. Tsuji, H. Takahashi, M. Morikawa, Reaction of π -Allylpalladium Chloride with Nucleophiles, *Tetrahedron Lett.* (1965) 4387 ~ 4388.
5. J. Tsuji, H. Takahashi, Reactions of the Cyclooctadiene Palladium Chloride Complex with Ethyl Malonate, *J. Am. Chem. Soc.* 87 (1965) 3275; 90 (1968) 2387 ~ 2392.
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7. J. Tsuji, T. Nogi, Palladium-catalyzed Carbonylation of Propargyl Alcohols and Propargyl Chloride, *Tetrahedron Lett.* (1966) 1801 ~ 1804.
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9. J. Tsuji, T. Yamakawa, A Convenient Method for the Preparation of 1-Olefins by the Palladium Catalyzed Hydrogenolysis of Allylic Acetates with Ammonium Formate, *Tetrahedron Lett.* (1979) 613 ~ 616.
10. J. Tsuji, I. Shimizu, I. Minami, Y. Ohashi, Facile Palladium-catalyzed Decarboxylative Allylation of Active Methylene Compounds under Neutral Conditions Using Allylic Carbonates, *Tetrahedron Lett.* 23 (1982) 4809 ~ 4812.
11. I. Shimizu, J. Tsuji, Palladium Catalyzed Decarboxylation-Dehydrogenation of Allylic β -Keto Carboxylates and Allyl Enol Carbonates as a Novel

Synthetic Method of α -substituted α,β -Unsaturated Ketones, *J. Am. Chem. Soc.* 104 (1982) 5844 ~ 5846.

II. Books

1. J. Tsuji, *Organic Synthesis by Means of Transition Metal Complexes*, Springer Verlag, 1975.
2. J. Tsuji, *Organic Synthesis with Palladium Compounds*, Springer Verlag, 1980.
3. J. Tsuji, *Palladium Reagents and Catalysts, Innovations in Organic Synthesis*, Wiley, 1995.

III. Reviews

1. J. Tsuji, Carbon-Carbon Bond Formation via Palladium Complexes, *Acc. Chem. Res.* 2 (1969) 144 ~ 152.
2. J. Tsuji, Decarbonylation Reactions using Transition Metal Compounds, *Synthesis* (1969) 157 ~ 169.
3. J. Tsuji, Synthetic Application of Palladium-catalyzed Oxidation of Olefins to Ketones, *Synthesis* (1984) 369 ~ 384.
4. J. Tsuji, I. Minami, New Synthetic Reactions of Allyl Alkyl Carbonates, Allyl β -Keto Carboxylates, and Allyl Vinylic Carbonates-catalyzed by Palladium Complexes, *Acc. Chem. Res.* 20 (1987) 140 ~ 145.
5. J. Tsuji, T. Mandai, Palladium-catalyzed Synthetic Reactions of Propargylic Compounds, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2589 ~ 2612.
6. J. Tsuji, T. Mandai, Palladium-catalyzed Hydrogenolysis of Allylic and Propargylic Compounds with Various Hydrides, *Synthesis* (1996) 1 ~ 24.