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A profile of Professor Richard F. Heck
Discovery of the Heck reaction[☆]

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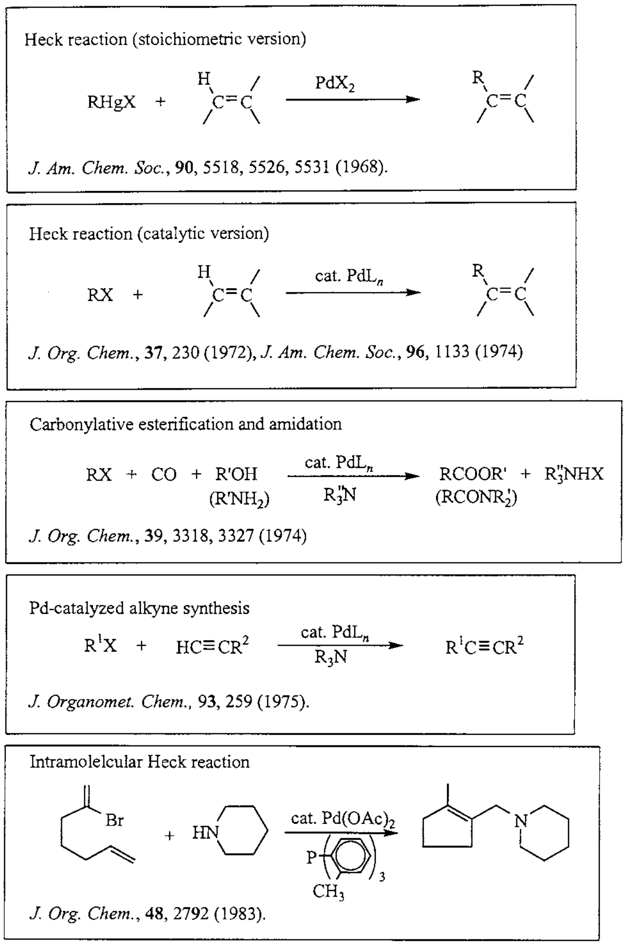
Richard F. Heck was born on 15 August 1931, in Springfield, Massachusetts, USA. At the age of eight he moved with his parents to Los Angeles, California. Eventually, he attended the University of California at Los Angeles (UCLA) and majored in chemistry. After obtaining a Bachelor's Degree in 1952 he continued his studies at UCLA and did graduate research with Professor S. Winstein in the area of neighboring group participation in the solvolysis of arylsulfonates. After graduation in 1954, he obtained a National Science Foundation Post-Doctoral Fellowship at the Swiss Federal Institute of Technology in Zurich with Professor V. Prelog. There he carried out research on the solvolysis of medium sized cycloalkyl arylsulfonates. In 1955 he returned to Professor Winstein's laboratory and carried out further research on neighboring group effects.

In 1956 he obtained employment at the Hercules Powder Company in Wilmington, Delaware. Initially, his research was concerned with efforts to form crystalline polymers from various polar monomers. After about 2 years he began research on organotransition metal chemistry with Dr David Breslow. The work began with an investigation of the hydroformylation reaction. Ultimately, the study led to a proposed mechanism for the reaction, which is considered to be the first correct mechanism suggested for a transition metal catalyzed reaction. The chemistry of organocobalt carbonyl complexes was then extensively studied. Many new reactions involving carbon monoxide, alkenes, dienes, epoxides and unsaturated carbonyl compounds were found, and a variety of new types of organocobalt complexes were prepared. It then became clear that many other unexplained reactions catalyzed by transition metals could be explained by reactions analogous to those found with cobalt. He also studied nickel carbonyl chemistry briefly and did find the expected analogies. However, the most interesting and potentially useful chemistry was discovered with palladium. The first experiment with this element was to combine palladium chloride dissolved in acetonitrile with phenylmercuric chloride at 25°C under one atmospheric


Heck reaction (stoichiometric version)

J. Am. Chem. Soc., **90**, 5518, 5526, 5531 (1968).

Heck reaction (catalytic version)

J. Org. Chem., **37**, 230 (1972), *J. Am. Chem. Soc.*, **96**, 1133 (1974)

Carbonylative esterification and amidation

J. Org. Chem., **39**, 3318, 3327 (1974)

Pd-catalyzed alkyne synthesis

J. Organomet. Chem., **93**, 259 (1975).

Intramolelcular Heck reaction

J. Org. Chem., **48**, 2792 (1983).

Scheme 1.

[☆] This profile is based on the information kindly provided by Professor R.F. Heck.

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pressure of ethylene. The presumed 'phenylpalladium chloride' formed, very rapidly absorbed one equivalent of ethylene, and produced styrene in high yield. (Discovery of the stoichiometric version of the Heck reaction). Extensive studies of reactions of organopalladium compounds, prepared as above, then followed. Reactions occurred easily under mild conditions with carbon monoxide, alkenes, dienes and alkynes even when functional groups were present. It was clear that this chemistry provided a potentially important new method for forming carbon–carbon bonds. The reactions were particularly exciting because of their tolerance of nearly all common organic functional groups (Scheme 1).

Two major problems of the reactions were addressed next: (1) the use of toxic and expensive mercurials; and (2) the need for stoichiometric quantities of expensive palladium. While cupric chloride could be added to the reaction mixtures to reoxidize the palladium metal formed and make the reactions catalytic, for various reasons, this procedure was not very attractive.

At about this time, 1971, he left Hercules and moved to the University of Delaware to continue the study of organopalladium chemistry. Literature reports of the successful formation of halo(aryl)palladium-phosphine complexes from palladium(0)-phosphine complexes and aryl halides suggested that this procedure might be a useful replacement for the arylmercurial–palladium chloride combination. Indeed, this proved to be not only possible but further brought a very important advantage that the reaction became catalytic in palladium when certain bases were added to take up the hydrogen halide produced in the reaction. (Discovery of the catalytic version of the Heck reaction). Many years were since devoted to studies on applications of this reaction in organic syntheses, and its many useful versions involving carbon monoxide, alkenes, dienes and alkynes were discovered and developed.

His own research at the University of Delaware in this area ended prematurely in 1989 with his retirement to Florida. Fortunately, these initial results stimuallated others to further advance organopalladium chemistry and uncover an amazing variety of additional applications in organic syntheses. Without a doubt the Heck reaction will remain as one of the several most important and widely used organopalladium reactions along with palladium-catalyzed cross coupling, carbonylation, and oxypalladation.

List of selected papers, books, and reviews on palladium chemistry by R.F. Heck.

I. Papers

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[3] R.F. Heck, Allylation of aromatic compounds with organopalladium salts, J. Am. Chem. Soc. 90 (1968) 5531.

[4] R.F. Heck, The mechanism of arylation and carbomethoxylation of olefins with organopalladium compounds, J. Am. Chem. Soc. 91 (1969) 6707.

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[8] A. Schoenberg, I. Bartoletti, R.F. Heck, Palladium-catalyzed caraboalkoxylation of aryl, benzyl, and vinylic halides, J. Org. Chem. 39 (1974) 3318.

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[10] H.A. Dieck, R.F. Heck, Palladium catalyzed synthesis of aryl, heterocyclic and vinylic acetylene derivatives, J. Organomet. Chem. 93 (1975) 259.

[11] C.K. Narula, K.T. Mak, R.F. Heck, Palladium-catalyzed cyclizations of bromo dienes, J. Org. Chem. 48 (1983) 2792.

II. Book

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III. Reviews

[1] R.F. Heck, Palladium-catalyzed reactions of organic halides with olefins, Acc. Chem. Res. 12 (1979) 146.

[2] R.F. Heck, Triarylphosphine-palladium complexes, Platinum Met. Rev. 24 (1980) 58.

[3] R.F. Heck, Palladium-catalyzed syntheses of conjugated polyenes, Pure Appl. Chem. 53 (1981) 2323.

[4] R.F. Heck, Palladium-catalyzed vinylation of organic halides, Org. React. 27 (1982) 345.[5] R.F. Heck, Vinyl substitution with organopalladium intermediates, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 4, Pergamon Press, Oxford, 1991, p. 833.