# Richard Heck

## *(1931–2015)*

Organic chemist who won a Nobel for palladium catalysis.

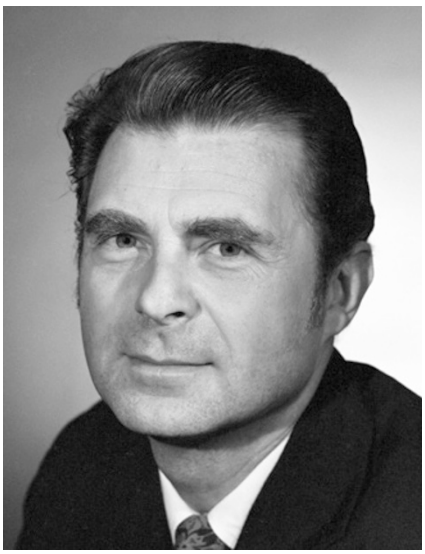
"Do something with transition metals," quipped the research director of the Hercules Powder Company to Richard Heck in 1958, two years after he had joined. After consulting with Pat Henry, an organometallic chemist across the hall, and with some bold thinking, Heck discovered a new method for clicking together carbon atoms in a single step (R. F. Heck *Synlett* **18,** 2855–2860; 2006).

The carbon–carbon bond is a prerequisite for life: nature catalyses it with enzymes; Heck used palladium. It was the dawn of a new era in organic synthesis, the field dedicated to constructing a vast array of compounds, from simple building blocks to bewildering mega-atom frameworks. Heck had taken the first step on the path that led him to the 2010 Nobel Prize in Chemistry.

Ask an organic chemist today about products of the Heck reaction and they'll name smartphone displays, sunscreens, perfumes, pesticides and medicines. One example is the over-the-counter pill naproxen for pain, fever, stiffness and inflammation. A biologist will recognize the reaction as the basis for the coupling of fluorescent dyes to DNA bases, allowing the automation of DNA sequencing and the elucidation of the human genome.

Richard Heck died on 9 October 2015 in Manila. He was born in Springfield, Massachusetts, on 15 August 1931. Aged eight, he moved with his parents, both professional dancers, to Los Angeles in California. His interest in chemistry was stirred by the vivid colours and abundant fragrances of flowers in the vacant lot near their home. Following a PhD with the prominent physical organic chemist Saul Winstein at the University of California, Los Angeles, and a postdoctoral fellowship with the future Nobel laureate Vladimir Prelog at the Swiss Federal Institute of Technology in Zurich, the 25-year-old Heck joined Hercules (now Ashland) in Wilmington, Delaware, in 1956.

After two years of working on the development of a commercial process for producing polyethylene using the newly discovered Ziegler–Natta catalysts, Heck was given the fateful mission by research director David Breslow. "They left us alone to try anything we want," Heck later said. So, appreciating that discovery proceeds stepwise from scattered observations in the literature, Heck studied the alkene hydroformylation reaction. He proposed the first correct



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mechanism for a reaction catalysed by a transition metal. It illuminated many other unexplained organometallic reactions, and produced a rich harvest of new cobalt organometallic chemistry.

The hydroformylation technology is currently used to produce 6.8 million tonnes of basic carbon building blocks (alcohols and aldehydes) each year for the synthesis of everyday materials. Perhaps less known today are Heck's other forays into cobalt carbonyl chemistry to establish reactions with a variety of organic molecules (carbon monoxide, alkenes, dienes, epoxides and ketones). With, as he put it, "no immediate ideas" on how to employ this chemistry profitably for Hercules, he took a new direction.

In 1968, the chemical community was astounded by Heck's flurry of seven consecutive single-author papers in the *Journal of the American Chemical Society*. In hindsight, these heralded the innovative work to follow when he moved down the road to the University of Delaware in 1971. The next year, Heck's seminal paper appeared (R. F. Heck & J. P. Nolley *J. Org. Chem.* **37,** 2320–2322; 1972). With characteristic generosity, he begins by acknowledging Tsutomu Mizoroki for preceding his discovery. He goes on: "We have independently discovered this reaction and find that it can be carried out under much more convenient laboratory conditions."

The discovery, now also widely known as the Mizoroki–Heck reaction, involves the palladium catalyst slipping into a carbon–halogen bond to give a fleeting species. This intermediate clutches another reactive molecule to form, after more contortions, a product in which a new carbon–carbon bond is established. Although this paper led to the Nobel prize in 2010 (with Ei-ichi Negishi and Akira Suzuki), it lay mostly unappreciated in the literature. Heck continued on his innovative path with two further publications, in 1975, which revealed two other new ways of carbon–carbon bond formation that are harbingers of the Sonogashira and Suzuki–Miyaura cross-coupling reactions. "I reported the copperless Sonogashira," Dick Heck said to me unpretentiously.

During this prodigious run of groundbreaking research, he and his co-workers established two other mainstays of the synthetic chemists' toolbox: palladium-catalysed carbonylation of aryl halides and transfer hydrogenation with formate as a reductant.

Today, undergraduates learn the Heck reaction in class and laboratory; industrial chemists practise it to make tonnes of drugs against asthma, diabetes and AIDS, among others. Thus, Heck's work may be considered as a forerunner of a cornucopia of transition-metal-catalysed technologies that are in operation worldwide.

In 1989, he retired to Florida with his Filipino wife Socorro Nardo. In 2006, I invited him to Queen's University, Canada, to follow up on his cobalt work. Students overcame their awe to work alongside him, striving to arrive before his customary 8 a.m. start. Seventeen years after retirement and 45 years after opening the door to organocobalt chemistry, Dick entered the lab again, prepared the complexes and measured their infrared spectra ("you get all of the information you need"). With the assistance of a postdoc, he obtained nuclear magnetic resonance and high-resolution mass spectrometry data, interpreted them, and took the next step.

Dick returned later in 2006 to the Philippines with Socorro. A handwritten letter to me noted that he had returned to his two passions: "I have some room to grow orchids again so I will have something to do," and "Have you found anyone to work with cobalt carbonyl?" He had drawn chemical structures of potential next steps along the palladium-paved path that he had established. ■

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