Ruthenium one of the rarest elements on Earth, so it is perhaps not surprising that it has no known biological role. Yet it is not without its uses in making large organic molecules, such as its remarkable ability to catalyze the chemical reaction known as olefin metathesis, which in recent years has become a standard tool of organic chemistry.

In the current Hot Ten, at #10, is a paper by Robert Grubbs and colleagues at the Arnold and Mabel Beckman Laboratory of the California Institute of Technology, who have discovered a ruthenium catalyst that will effect ring-closure reactions rapidly, cleanly, and completely by means of olefin metathesis. Just below the Hot Ten, at #12, is a second paper by them revealing modified versions of the catalyst, plus further data showing that they can be made to produce better yields with even smaller amounts. This second paper appeared in the new journal Organic Letters (see M. Scholl, et al., 1[6]:953-6, 23 September 1999; the paper collected 10 citations this period).

What is noteworthy about the new catalysts is that they are stable in air, will tolerate water, and will operate at elevated temperatures compared to earlier ruthenium catalysts that were only stable at room temperature. This extra stability is the key to Grubbs’s work and has been achieved by replacing one of the attached groups of the earlier catalysts with an imidazole ring.

Olefin metathesis is the reaction of two olefinic bonds, i.e. carbon-to-carbon double bonds, which thereby form two new olefins, one of which is likely to be the simplest olefin of all, ethylene gas, and thereby easily removed. When the original two double bonds are at the opposite ends of a chain of carbons, their reaction might be expected to form polymers, which is what often happens, but they might also interact with each other to produce a ring compound. This is what papers #10 and #12 are all about.

They describe the preparation of the new ruthenium catalysts for promoting this reaction and the results they obtain using them—results
that are quite remarkable. A 5% solution of one of the new catalysts, in refluxing methylene chloride (40 degrees C), not only gave higher yields of ring products, and in shorter times (30 minutes) than the older system, but also caused ring closure to occur with compounds that had previously resisted cyclization because of their bulkiness, although they required 90 minutes to achieve this. Paper #12 extends the use of this catalyst to even bulkier systems, still giving high yields, and also demonstrating that some systems would cyclize completely within 10 minutes—an with as little as 0.05% of the catalyst present.

According to Grubbs, the new catalysts have commercial potential: "They are being explored for application in large-scale polymer synthesis, for the synthesis of pharmaceutical intermediates, and for the synthesis of insect pheromones. Some commercial products that rely on them are already on the market (e.g., polymeric pipes for chemical processing) and a number of others are anticipated in the near future. The catalysts are commercially available and a reasonable volume has been sold over the past few years."

Meanwhile, since paper #10 appeared, Grubbs and his team have extended their researches to other compounds, and in Organic Letters they recently published developments in olefin cross-metathesis (see C.W. Lee and R.H. Grubbs, 2 [14]:2145-7, 13 July 2000). This is a type of reaction in which two linear olefins couple to form new linear olefins but in which the molecular fragments of the original two are scrambled. Examples of cross-metathesis are described in the Journal of the American Chemical Society (see H.J. Blackwell, et al., 122[1]: 58-71, 12 January 2000; and A.K. Chatterjee, et al., 122[15]: 3783-4, 19 April 2000). Grubbs is also known for his work on using olefin metathesis to open rings to form chains, again using ruthenium catalysts (e.g., see C.W. Bielawski and R.H. Grubbs, Angew. Chemie, Int. Ed. Engl., 39[16]:2903-6, 2000).

And there should be plenty more to come. "I was attracted originally to olefin metathesis because it provided a unique method of forming carbon-to-carbon double bonds," he tells Science Watch. "The new catalysts are now allowing us to fulfill the promise of this reaction. We are just beginning to realize the opportunities that it opens up in the areas of polymer synthesis and in the production of bioactive molecules."