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Historical Note

International Symposium on ‘30 years of the cross-coupling reaction’—summarizing remarks

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Ladies and Gentlemen,

First of all, I heartily appreciate your attendance at this memorial Symposium: 30 Years of the Cross-Coupling Reaction.

The cross-coupling reaction of organic halides with organometallic reagents to form the carbon–carbon *sigma* bond is a reaction of tremendous importance in organic synthesis. Although the reaction can be effected in various ways, transition metal salt or complex-catalyzed coupling is by far the most practical one. The systematic, but largely mechanistic, study of the influence of catalytic amounts of transition metal salts (mostly cobalt(II) chloride) on the interaction of Grignard reagents with organic halides dates from the researches by Morris S. Kharasch at the University of Chicago, but it was not until 1971–1972 that such catalytic reactions received much attention owing to their very wide applicability in organic synthesis. In 1971, Tamura and Kochi published the first paper on a series of studies and described that some ‘soluble catalysts’ containing silver, iron, or copper in tetrahydrofuran were extremely effective for coupling of Grignard reagents with organic halides. In 1972, Corriu and Masse at the University of Montpellier, and Tamao, Sumitani, and Kumada at Kyoto University disclosed almost simultaneously a very efficient method for selective carbon–carbon bond formation by nickel complex-catalyzed cross-coupling of Grignard reagents with sp^2-carbon halides.

The latter method has aroused wide-spread interest in related reactions as well, which involve other organometallics than Grignard reagents, such as those of lithium (Li), zinc (Zn), boron (B), aluminum (Al), silicon (Si), tin (Sn), and zirconium (Zr) and Pd(0) complexes such as $Pd(PPh_3)_4$ have proved to be by far the most suitable of catalyst precursors in many cases where these reagents are employed. Use of a variety of combinations of reagent and catalyst has made it possible to prepare in good yields and with high selectivity, a vast range of organic compounds, even containing various functional groups, which cannot be realized by the use of Grignard reagents.

Last but not the least, it is not too much to say that Akio Yamamoto’s important observation in 1970 at Tokyo Institute of Technology about the reaction between $Ni(C_2H_5)_2(bpy)$ with chlorobenzene, giving rise to elimination of the two ethyl groups to form *n*-butane and production of chloro(phenyl)(bpy)-Ni(II), was the key which motivated Tamao’s clever idea of the Ni complex-catalyzed Grignard cross-coupling reaction, and further, today’s remarkable development of transition metal complex-catalyzed cross-coupling reactions in general.

Finally, I beg to avail myself of this opportunity to submit my great esteem to all the chemists who have devoted themselves to developments in this field of chemistry, and also to governmental as well as many non-governmental organizations that have supported their investigation.

Thank you very much for your kind attention!

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