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Preface

Until 30 years ago, chemists did not have any practically useful methodology for the carbon–carbon bond formation by the nucleophilic substitution-type cross-coupling reaction between organometallic reagents and C(sp²)-halides and related compounds. Several revolutionary findings were made during 1970–1972 by A. Yamamoto, J.K. Kochi, R.J.P. Corriu, and M. Kumada and K. Tamao, which made the cross-coupling reactions available as a new synthetically powerful tool. A catalytic cycle consisting of oxidative addition, transmetallation, and reductive elimination was explicitly proposed by Kumada and Tamao in 1972 for their nickel–phosphine complex-catalyzed cross-coupling between organomagnesium reagents and C(sp²)-halides, based on Yamamoto's important observations on organonickel complexes. Based on this catalytic cycle, several types of palladium-catalyzed cross-coupling reactions have been developed. A brief historical survey of the cross-coupling reactions is summarized in Fig. 1, which contains the schematic representations of each reaction together with the discoverers and their first papers.

The International Symposium 'Thirty Years of the Cross-Coupling Reaction' was held during July 27–29, 2001, in Kyoto, Japan, as the Post-Conference of the 11th International Symposium on Organometallic Chemistry directed towards Organic Synthesis (OMCOS-XI) which was held during July 22–27, in Taipei, Taiwan.

The cross-coupling symposium celebrated, by gathering roughly 230 attendants, the 30th anniversary of the discovery of the transition metal-catalyzed cross-coupling reaction and the proposal of the catalytic cycle, both made at the beginning of 1970s. The symposium was historically the first big event where all key scientists in this field met together.

This special volume of JOM has been edited as the Proceedings of the commemorative symposium, the logo of the symposium being shown as the cover picture. A picture of all invited speakers and a collection of their signatures are reproduced in Figs. 2 and 3. In addition

to most of the invited lectures by key scientists, a selected number of contributed papers are published in this special volume: A series of Historical Mini-reviews presented by the key scientists listed in Fig. 1 are compiled separately in the first part of this volume. All other invited papers are roughly grouped in the order of development of new catalysts including new ligands, new combinations of organometallic reagents and electrophiles, synthetic applications to π -conjugated materials, applications to pharmaceutical materials, and industrial applications. We are convinced that this special volume of JOM is useful as an official document of a variety of cross-coupling reactions developed during the first 30 years in the history of cross-coupling reaction, together with other related monographs published recently, which include F. Diederich, P. Stang (Eds.), "Metal-Catalyzed Cross-Coupling Reactions", Wiley-VCH, Weinheim, 1998, and N. Miyaura (Ed.), "Cross-Coupling Reactions: A Practical Guide", Topics in Current Chemistry No. 219, Springer-Verlag, Berlin, 2002.

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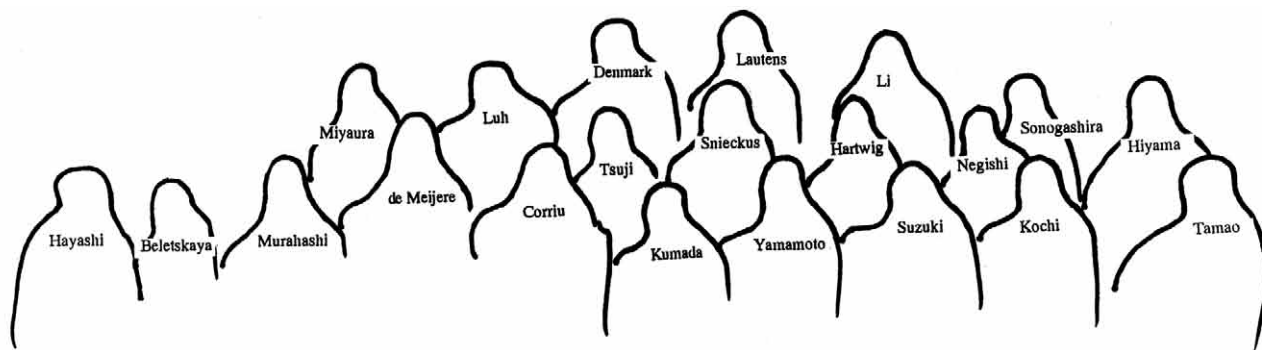
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A Brief Historical Survey

- 1970** **A. Yamamoto:**
Reductive Elimination and Oxidative Addition in a Diorganonickel Complex NiEt₂(bipy)
 M. Uchino, A. Yamamoto, S. Ikeda, *J. Organomet. Chem.* **1970**, *24*, C63.
- 1971** **J. K. Kochi:**
Fe(acac)₃; RMgX + R'X
 M. Tamura, J. K. Kochi, *J. Am. Chem. Soc.* **1971**, *93*, 1487.
- 1972** **R. J. P. Corriu:**
Ni(acac)₂; RMgX + R'X
 R. J. P. Corriu, J. P. Masse, *Chem. Commun.* **1972**, 144.
- 1972** **M. Kumada, K. Tamao:**
Ni(PR₃)₂Cl₂; RMgX + R'X
The first introduction of the concept of "Molecular Catalysis"
(Ni-phosphine catalysts) in this field.
Proposal of a Catalytic Cycle.
-
- K. Tamao, K. Sumitani, M. Kumada, *J. Am. Chem. Soc.* **1972**, *94*, 4374.
- 1973** **G. Consiglio &**
1974 **K. Tamao, K. Yamamoto, M. Kumada:**
Ni(-)-DIOP / Catalytic Asymmetric Grignard Cross-Coupling Reaction
 G. Consiglio, C. Botteghi, *Helv. Chim. Acta* **1973**, *56*, 460.
 Y. Kiso, K. Tamao, N. Miyake, K. Yamamoto, M. Kumada, *Tetrahedron Lett.* **1974**, 3.
- 1975** **S.-I. Murahashi:** **Pd(PR₃)₂Cl₂; RLi + R'X**
 M. Yamamura, S. Murahashi, I. Moritani, *J. Organomet. Chem.* **1975**, *91*, C39.
- 1975** **K. Sonogashira, N. Hagihara:** **Pd / CuI / R₂NH; RC≡CH + R'X**
 K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, 4467.
- 1976** **E.-i. Negishi:** **Pd / R₃Al, R₂Zn, Cp₂ZrClR**
 E.-i. Negishi, S. Baba, *J. Chem. Soc., Chem. Commun.* **1976**, 596.
 E.-i. Negishi, A. O. King, N. Okukado, *J. Org. Chem.* **1977**, *42*, 1821.
 E.-i. Negishi, D. E. van Horn, *J. Am. Chem. Soc.* **1977**, *99*, 3168.
- 1976** **T. Hayashi, M. Kumada:**
Ni-FcPPh₂* / Catalytic Asymmetric Grignard Cross-Coupling Reaction
 T. Hayashi, M. Tajika, K. Tamao, M. Kumada, *J. Am. Chem. Soc.* **1977**, *98*, 3718.
- 1977** **M. Kosugi, T. Migita:** **Pd / R₄Sn**
 M. Kosugi, Y. Simizu, T. Migita, *Chem. Lett.* **1977**, 1423.
- 1979** **J. K. Stille:** **Pd / R₄Sn**
 D. Milstein, J. K. Stille, *J. Am. Chem. Soc.* **1979**, *101*, 4992.
- 1979** **N. Miyaura, A. Suzuki:** **Pd / R₃B**
 N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Lett.* **1979**, *20*, 3437.
- 1981** **N. J. A. Alexakis, J. F. Normant:** **Pd / RCu / ZnCl₂**
 N. J. A. Alexakis, J. F. Normant, *Tetrahedron Lett.* **1981**, *22*, 959.
- 1982** **K. Tamao, J. Yoshida, M. Kumada:** **Pd / RSiF₅²⁻**
 J. Yoshida, K. Tamao, M. Kumada et al., *Organometallics* **1982**, *1*, 542.
- 1988** **T. Hiyama, Y. Hatanaka:** **Pd / RSiF_nR'_{3-n} / F⁻**
 Y. Hatanaka, T. Hiyama, *J. Org. Chem.* **1988**, *53*, 918.

Fig. 1. A brief historical survey of the cross-coupling reactions developed during 1970s and 1980s.



**PostOMCOS - II Symposium—Thirty Years of the Cross-Coupling Reaction—
July 27 - 29, 2001, Kyoto Research Park, Japan**

Fig. 2. A picture of key scientists who attended the International Symposium on 'Thirty Years of the Cross-Coupling Reaction' which was held on July 27-29, 2001, in Kyoto.

30 Years of the Cross-Coupling Reaction
July 27-29, 2001, Kyoto

70スカツ70リソ7反応究見30周年
 Tani/Hayashi Masamori Kosugi 梶山隆治
 林 茂生 小杉正純 Tamaguchi
 Ohyama 山本明夫 鈴木 隆
 Ohyama Manoto Kumada S. Murahashi
 山口 直樹 熊田 誠 杉橋 俊一
 矢口 直樹 Robert Corriu 根岸 英一
 和 夫 辻 二郎 玉屋 隆平
 U Beneyeva Jiro Tanji Kohatomo
 (Belotskaya) Y. Fukuroi Viktor Snieckus
 P. B. Kholodovskiy
 Georgiy Anis de Vries Sette Dumark
 Telenkin 宮浦 忠夫 Tienyan Lu
 Mahajan 浦和 雄雄 着能 志 潘 天 亮

Fig. 3. A collection of signatures by key scientists at the International Symposium in Kyoto in 2001.