ELSEVIER

Journal of Organometallic Chemistry 653 (2002) 20–22

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Historical Note

Catalytically assisted carbon–carbon coupling reaction: a French–Japanese 'cuisine'

Robert J.P. Corriu *

Laboratoire de Chimie Moléculaire et Organisation du Solide, Université Montpellier II, Case 007 Place E. Bataillon, 34095 Montpellier Cedex 05, France

Received 6 September 2001; accepted 19 October 2001

Abstract

The metal assisted carbon–carbon cross coupling reaction has a long history in which Japanese and French chemists have been strongly involved. The French have been working in this area since the 19th century. The Japanese contribution started in 1972 and has strongly developed since this time. This paper is focused on the historical part before 1972. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carbon–carbon bond; Coupling reaction; Synthetic organic chemistry

The formation of carbon–carbon bonds is one of the key steps in organic synthesis and chemists have been highly interested in finding new routes for reaching this goal in the most general way. The catalytic metal-assisted cross coupling reaction was first used in 1972 as a synthetic tool with the publication of the so-called Kumada–Corriu reaction. It was the beginning of a explosion of new synthetic routes permitting the coupling of two organic radicals thanks to the formation of one carbon–carbon bond.

The aim of this short paper is to present briefly the history or more precisely the genesis of the catalytically assisted coupling reactions which started in the 19th century. Although many other distinguished chemists from countries other than Japan and France have been involved in the discovery of new methods in this area, I have selected a humoristic title for this short presentation of the genesis of the reaction.

The genesis of the Kumada–Corriu reaction corresponds to the description of the different steps which have been followed by chemists in achieving the idea of using a catalyst for the activation of the reaction between an organometallic reagent and an electrophilic carbon. Such a sophisticated idea is the result of a long story in which the experimental results and the scientific concepts have been in permanent evolution and in permanent interaction.

The first organometallic compounds were prepared in 1852 by Frankland who isolated $Et{\cdot}Zn{\cdot}I$ and $Et_2{\cdot}Zn$ and who prepared in 1855 PR_3, AsR_3 and SbR_5. However, he was mainly interested in the study of the organic radicals and organic chemistry was not developed enough for using these products as reagents. Later Wurtz (born in Strasbourg in 1817, died in Paris in 1888) succeeded in the coupling of two radicals using Na as coupling reagent for the formation of a saturated carbon–carbon bond.

$$2RX + Na \rightarrow R{-}R + 2XNa$$

This reaction, which since long is no longer used, is still taught because of its historical importance in spite of the fact that students like it very much and overuse it in examinations.

At this stage of the development of chemistry, the atomic theory was still not accepted and concepts were not clear enough to allow the development of synthetic ideas. Moreover, new ideas were very often not easily accepted. One of the best example, is for instance the concept of substitution reaction proposed by J.-B. Dumas which was strongly criticised. At this time the conceptual background was not sufficiently developed to permit the beginning of organic synthesis which occurred several decades later.

---

* Tel.: +33-467-143-801; fax: +33-467-143-852.
E-mail address: corriu@univ-montp2.fr (R.J.P. Corriu).

PII: S0022-328X(02)01172-5

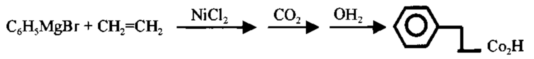
As Urbain (1872–1938) (the French chemist who succeeded in the separation of the rare earths), wrote about Grignard's discovery: "The Grignard reagent vitalises organic chemistry as blood does for the body: all chemists are 'Grignarding' more and more". Grignard reagents (which are called organomagnesiens in France) were discovered by Victor Grignard (1858–1935) who received the Nobel Prize in 1912, sharing it with Paul Sabatier who made the discovery of heterogeneous catalysis. They were two very important tools and concepts for organic chemistry. There is a funny coincidence that these two discoveries which are the two fundamental concepts involved in the chemistry we are talking about, were discovered at the same time.

When Frankland made the discovery of organozinc reagents his personal aim was to study organic radicals in order to understand the formation of organic molecules by the combination of these building blocks. Moreover, the state of general knowledge was not sufficient for the development of diethyl zinc as a synthetic tool. Fifty years after, the atomic theory was well established, and most of the main building blocks of organic molecules were identified. The usefulness of a reagent allowing the introduction of a functional group and the formation of carbon–carbon bonds was welcomed. However, his genesis was not simple and it is not possible to talk about Grignard reagents without referring to Barbier who was the scientific director of Grignard. He succeeded in coupling reactions using Mg as reagent and was elected to the French Academy of Sciences. Moreover the Barbier/Calas reaction was published later when our distinguished colleague Calas from Bordeaux succeeded in coupling chloro silanes and C–X bonds using Mg under specific conditions:

$$R\text{–}X + Me_3SiCl \xrightarrow[Mg]{} R\text{–}SiMe_3$$

After Grignard's discovery the sentence of Urbain illustrates very well the great interest of chemists for these well identified reagents in solution and allowing the control of the introduction of a precise building, with the expected functionality, at the right place in the organic molecule. However, it was too early for combining both organometallic reagents and catalysis. These two wonderful tools were not followed by the appropriate theoretical concepts until another 50 years had passed.

The first person to successfully attempt the combination was JOB, a French chemist who published, between the two world wars (1920–1930), the activation of organomagnesium reagents with transition metal salts. In 1923 he reported that "a solution of C_6H_5MgBr in diethyl ether gives in the presence of $NiCl_2$ a derivative able to absorb CO, NO, C_2H_4, C_2H_2, and H_2". Predicting the activation of such molecules, he published in 1924 in more detail the reaction of C_6H_5MgBr and C_2H_4 in the presence of $NiCl_2$ and he succeeded in isolating $C_6H_5CH_2CH_2CO_2H$ after treatment with CO_2. In the same paper he demonstrated that the amount of $CH_2{=}CH_2$ fixed was not depended on the $NiCl_2$ ratio, thus demonstrating a catalytic effect. *He suggested the formation of phenyl nickel as the active species and concluded "Briefly, we believe progress has been made by introducing catalysis into the field of organometallics" (Comptes Rendus of French Academy of Science 1924 179 330)*. I would like to point out that this great chemist, who was in fact the grandfather of the chemistry we are talking about today in this symposium, was and is completely unknown even in France. He was too much in advance at this time, and French Chemistry which was declining at the end of the first world war was not in position to recognise the modernity of his ideas.



After these pioneering results obtained by JOB we have to wait until the middle of the sixties for the 'renaissance' of the ideas of JOB. However, before developing it is important to mention three very fundamental contributions. The first one from Karash who discovered the radical chemistry induced by Grignard reagents, by considering the chemistry obtained in the presence of transition metal salts. The second one is the wonderful contribution of Henri Normant (1907–1997) who extended the possibilities of Grignard reagents to the chemistry of vinyl groups. This discovery associated to the use of new solvents permitted the development of very wide synthetic possibilities. Finally Ashby succeeded in generalising the knowledge of mechanisms which control the reactivity of these reagents.

The renewal of JOB's chemistry occurred in Gif-sur-Yvette (France), when H. Felkin, helped by G. Swierczewski, decided to link coordination and organometallic chemistry. At this time the conceptual possibilities were wider. Reaction mechanisms were generally accepted and coordination chemistry had become much better understood than 40 years before. Moreover, the chemistry of Grignard reagents was better understood with appropriate theoretical concepts. Briefly, the conditions for a new start were optimal. The very nice contribution of H. Felkin was to use transition metal complexes as catalysts instead of transition metal salts. Working with $(PPh_3)_2{\cdot}NiCl_2$ as catalyst he considered the activation of Grignard reagents for different kinds of reactions by studying the mechanistic aspects. For the first time he was able to identify the organometallic species formed at nickel. Both theoretical and experimental aspects were now at an appropriate stage to allow the start of a new step corresponding to the development of a general synthetic chemistry: the catalytically induced cross coupling reaction between one nucleophilic and carbon one electrophilic together.

This new start occurred simultaneously in France and in Japan in 1972 when Kumada-Tamao in Kyoto and Corriu-Masse in Montpellier were working, without knowing each other, on the synthetic possibilities of the coupling reactions. The French chemists published first, but the Japanese contribution was the most important. However, the main phenomenon is the start of a new chemistry from their results. Japanese chemists were particularly successful in developing very beautiful cross coupling synthetic tools. However, some others also contributed to the wonderful development of this new chemistry which is still active 30 years after. This chapter of modern synthetic organic chemistry will be developed by my distinguished colleagues much better than I could and I am very happy to have contributed at the beginning of the history.