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Historical mini-review

Discovery of the cross-coupling reaction between Grignard reagents and $C(sp^2)$ halides catalyzed by nickel–phosphine complexes

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Abstract

This mini-review traces the initial ideas, discoveries and significant features of the cross-coupling reaction between Grignard reagents and $C(sp^2)$-halides such as aryl and alkenyl halides in the presence of a nickel–phosphine complex as a catalyst, which was first reported by Kohei Tamao, Koji Sumitani, and Makoto Kumada in 1972. © 2002 Published by Elsevier Science B.V.

Keywords: Cross-coupling reaction; Nickel–phosphine complex; Grignard reagent; Aryl halide; Alkenyl halide; Catalytic cycle; Oxidative addition; Reductive elimination; Transmetallation

1. Discovery

In 1972, myself, together with K. Sumitani and M. Kumada reported the cross-coupling reaction between Grignard reagents and $C(sp^2)$-halides such as aryl and alkenyl halides in the presence of a nickel–phosphine complex as the catalyst [1]. Publication of our paper was so dramatic that shortly after we had submitted our manuscript for publication, a closely related paper by R.J.P. Corriu and J.P. Masse reached us [2]. Thus it has been generally recognized that the nickel-catalyzed Grignard cross-coupling reaction was discovered independently in France and Japan in 1972.

How did our group discover the nickel-catalyzed Grignard cross-coupling reaction? One must look back to the year 1970, because this year was very special for us and for organo-nickel chemistry. In 1970, I finished my Dr thesis work in the field of organosilicon chemistry and started my academic career as a coworker of M. Kumada, who asked me to switch my research project from organosilicon chemistry to organotransition metal chemistry. A few years before, Kumada and his coworkers discovered the first example of the nickel–phosphine complex-catalyzed hydrosilylation of olefins and published the first communication in the same year [3]. Therefore, it was quite natural that my research group was involved in the mechanistic studies on the nickel-catalyzed hydrosilylation. For this purpose, we prepared a series of nickel–phosphine complexes such as $Ni(PR_3)_2Cl_2$, $Ni(dppe)Cl_2$, $Ni(dppp)Cl_2$, $Ni(dppb)Cl_2$, $Ni(dmpe)Cl_2$, and $Ni(dmpf)Cl_2$, where dppe, dppp, dppb, dmpe and dmpf denote $Ph_2P(CH_2)_2Ph_2$, $Ph_2P(CH_2)_3PPh_2$, $Ph_2P(CH_2)_4PPh_2$, $Me_2P(CH_2)_2PMe_2$, and 1,1′-$(Me_2P)_2$-ferrocene, respectively. At the same time, I comprehensively studied organo-nickel chemistry and listed all the known σ-organo-nickel complexes to determine their synthetic routes, properties, and reactivity. Up to 1970, only about 20 isolated σ-organo-nickel complexes were known, which were grouped into the following three types: $NiX(Ar)(PR_3)_2$ [4], $CpNi(C_2H_5)(PPh_3)$ [5], and $Ni(C_2H_5)_2(bpy)$ [6]. I learned three main ideas from the literature. First, the reaction of nickel halides with Grignard reagents is the general method for the synthesis of σ-organo-nickel complexes, the process now being generally called ‘transmetallation’. Second, σ-alkyl-nickel complexes containing the β-hydrogen atom(s) can be stabilized by a bidentate ligand such as bpy even in the coordinatively unsaturated complexes [7]. Third, a diorgano-nickel complex undergoes the coupling of two organic groups (now called ‘reductive

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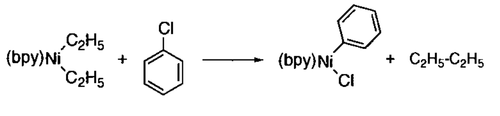
elimination') by the action of an aromatic halide, which subsequently undergoes 'oxidative addition' [7] to the resulting Ni(0) species, as first reported by Akio Yamamoto in 1970 [8] and as shown in eq. 1

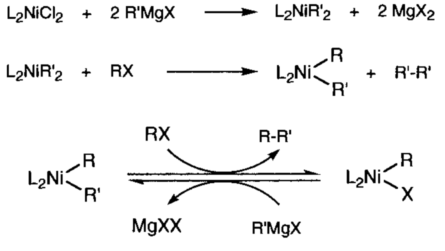


(1)

During 1970 and 1971, one of our able graduate students, Koji Sumitani, was devoting his efforts to clarifying the mechanism of the nickel-catalyzed hydrosilylation, which included the preparation of nickel(0)-ethylene complexes by the reaction of $NiCl_2(PR_3)_2$ with the ethyl Grignard reagent [9]. Based on these our own experiences, along with the features of the organo-nickel chemistry mentioned above, we came to the conclusion that nickel–phosphine complexes should act as good catalysts for the selective cross-coupling reaction between Grignard reagents and aromatic halides. In early October 1971, he started to examine our new project and soon found our expectation correct. It took only a few months at the end of 1971 for us to obtain sufficient results for our first communication [1], which included the ligand effect on the catalytic activity because we had already had synthesized a series of nickel–phosphine complexes in our group.

2. Some characteristic features

Since 1972, we have examined the scope and limitations of the nickel–phosphine complex-catalyzed Grignard cross-coupling reaction [10]. Some characteristic features are summarized below.



Scheme 1.

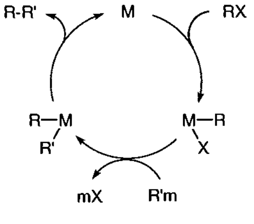
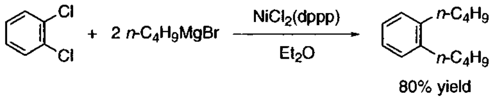


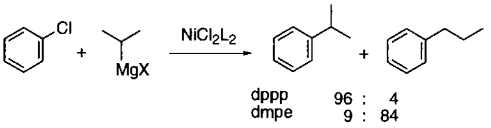
Fig. 1. A generalized catalytic cycle: M, low-valent metal species such as Ni(0) and Pd(0), RX, C(sp^2)-halides, triflates, etc., and R′m, Organometallic reagents containing Li, Mg, B, Al, Si, Sn, Zn, Cu, Zr, etc.

1. In the first communication [1], we proposed the catalytic cycle shown in Scheme 1, by combining Yamamoto's elegant chemistry shown in eq. 1 and the reaction chemistry of the nickel-halogen bond with the Grignard reagents previously mentioned. This catalytic cycle has become the prototype for other various transition metal (mostly palladium) catalyzed cross-coupling reactions which have been developed by other groups since 1975 [11]. The catalytic cycle has now been more generalized as shown in Fig. 1, which involves a Ni(0) or Pd(0) species as the key catalytically active species and a series of 'oxidative addition', 'transmetallation', and 'reductive elimination' steps.
2. Another important point is that our results provided the first case where transition metal–phosphine complexes were employed for the traditional Kharasch-type Grignard reactions [12]. This concept of 'molecular catalysis' has opened many new possibilities of Grignard cross-coupling reactions, which were impossible by the catalysis with simple transition metal salts, as will be mentioned below.
3. The catalytic activity significantly depends on the nature of the phosphine ligands and the following order is generally observed: $Ni(dppp)Cl_2 > Ni(dppe)Cl_2 > Ni(PR_3)_2Cl_2 \sim Ni(dppb)Cl_2$.
4. Even alkyl-Grignard reagents containing β-hydrogen atom(s) can selectively undergo the cross-coupling reaction, as exemplified by the synthesis of *o*-dibutylbenzene (eq. 2) [10c]. This is the most significant feature attained for the first time by the nickel–phosphine molecular catalysis.



(2)

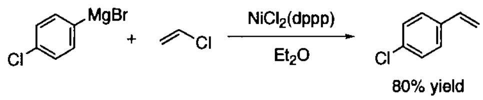
5. With *sec*-alkyl Grignard reagents, alkyl group isomerization occurs from secondary to primary, the extent of isomerization highly dependent on the basicity of the phosphine ligands [13a], as well as the electronic nature of the aromatic halides [13b], as exemplified by the following results eq. 3.



(3)

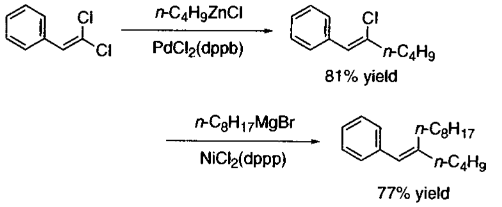
6. The asymmetric cross-coupling reaction is possible with catalysts containing optically active phosphine ligands [14].
7. Chlorobenzenes are the aromatic halides of first choice rather than the bromo- and iodo-benzenes in view of the high reactivity and high product

yields. It is noted that even fluorobenzene undergoes the nickel-catalyzed cross-coupling reaction, although the reactivity is rather low. It is also mentioned that vinyl chloride is one of the most reactive C(sp^2)-halides; the cross-coupling reaction occurs very fast and has been used for the industrial production of certain *p*-substituted styrene derivatives as shown in eq. 4 [15].



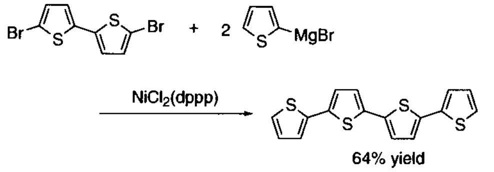
(4)

8. The olefin geometry of the *E*- and *Z*-alkenyl halides are retained in the cross-coupling reaction.
9. Nickel catalysts are generally more reactive toward C(sp^2)-halides than palladium catalysts which were developed later [11,16]. This feature can be used for the stepwise cross-coupling reaction of aromatic or alkenyl dihalides [17,18], as exemplified by the following transformation (eq. 5).



(5)

10. The nickel-catalyzed cross-coupling has provided the first practical method for the tailor-made synthesis of heteroarene homo-oligomers [10b] and mixed-oligomers [18], as exemplified by eq. 6.



(6)

3. Epilogue for future progress

We are now in 2001, 30 years after the discovery of the nickel–phosphine complex-catalyzed Grignard cross-coupling reaction. Obviously, the importance of the cross-coupling reaction has been and will be increasing as a general synthetic method for the C–C bond formation at sp^2-carbon atoms. Here are some interesting data demonstrating this point. Thus, the citation numbers of our original communication [1] and two full papers published in 1976 [10a] and 1982 [10b] are still steadily increasing, as shown in Fig. 2. In particular, the full paper dealing with the tailor-made heteroarene oligomers such as oligothiophenes [10b] has been attracting much attention from the view point of the conducting π-conjugated material science. This clearly represents a typical and general trend in future developments of the cross-coupling reactions.

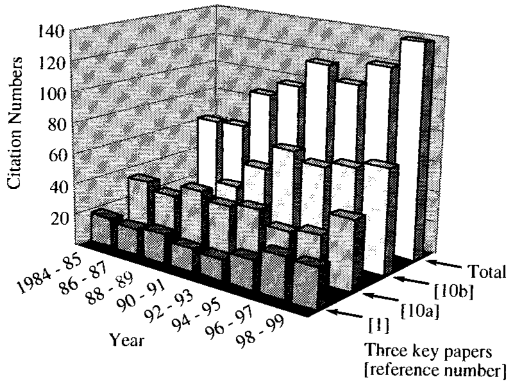


Fig. 2. Plots of citation numbers of our three key papers concerning the nickel–phosphine complex-catalyzed cross-coupling reaction during 1984–1999.

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