Journal of Organometallic Chemistry, 473 (1994) xi–xvii

Introduction

Organometallic chemistry in Japan — how it has developed

Akio Yamamoto

Department of Applied Chemistry, School of Science and Engineering, Waseda University, Okubo, Sinjuku, Tokyo 169 (Japan)

1. Introduction

On the occasion of this special issue of the *Journal of Organometallic Chemistry* focussing on the contributions of Japanese chemists, the author was asked to contribute an essay for non-Japanese readers to provide a background to the development of organometallic chemistry in Japan. Having been deeply committed to this, I am not confident that I can afford a proper, balanced perspective but I have accepted the invitation for several reasons. Firstly, I felt organometallic chemists of our age group have a responsibility to the organometallic pioneers in Japan from whose contributions we have benefitted. Most of these people have already retired due to the Japanese system of letting professors retire from research at an early stage to make room for younger people. Secondly, our experiences in building up this new discipline in Japan may provide some hints for those who are coping with the task of building up organometallic chemistry in countries where this fascinating field is still in the developing stage. Thirdly, I thought that the essay might elicit some interest among organometallic chemists in developed countries as well following the pattern of the reminiscences published in commemorative issues of the *Journal of Organometallic Chemistry*, which appear in every hundredth volume.

2. A short sketch of the development of science and engineering in Japan

To make this essay comprehensible for non-Japanese readers I suppose it is appropriate to give some background of recent Japanese history.

2.1. Japan was a late comer in science and engineering

When the US fleet led by Admiral Perry entered Edo Bay (the present Tokyo Bay) in 1853, the demonstration of the mighty power of advanced western technology in the form of steam-driven iron warships with their thundering cannon caused electrifying horror among the Japanese who still lived in premodern situations. It shook Japan awake from her peaceful sleep of seclusion in the Far East which she had entered over two hundred years before. Pressure from foreign countries and the ensuing turmoil in Japan led to the eventual collapse of the Shogun Government to be replaced by the Meiji Government in 1868. This newly founded government had many things to do to catch up with the west — in education, technology, industry and in military matters. This transition took place when the industrial revolution was already complete in Europe, but before the foundations of modern chemistry were laid. It was only one year after the Meiji Restoration that the Periodic Table was proposed by Mendeleev in 1869. The cyclic structure for benzene was proposed by Kekulé in 1863 and the tetrahedral structure of the carbon compounds in 1864.

It was fortunate for Japan that the essential basis for the rapid building up of the educational system existed already, although in a primitive way, in the Edo Period before Japan entered the new era. Although a modern educational system was absent, there were numerous small private schools teaching reading, writing and arithmetic everywhere in Japan. Thus the illiteracy rate was already quite low. The clearest indication that Japan was ready for an educational transition can be found in the surprising number, 25,000, of primary schools established within 10 years all over Japan after the political upheaval. This number is not very far from that of primary schools in Japan today.

The efforts of the Meiji government in upgrading education were remarkable. They invited first-class educators from the US and Europe, paying extraordinarily high salaries similar to those of top government ministers, to educate young and motivated students. At the same time the government sent selected students, loyal to their mission, to advanced western countries to bring the most advanced western scientific ideas back to Japan. The educational transition from the old sys-

0022-328X/94/$7.00
SSDI 0022-328X(94)24535-P

tem to the new proceeded smoothly. After only ten years or so the new generation took charge of teaching and research in the newly established universities with little help from the foreign teachers hired previously. Several academic societies were founded in this period, including the Chemical Society of Japan which was established in Tokyo in 1879, just 10 years behind the American Chemical Society [1].

Among those who were later sent to Europe was Yuji Shibata who went to Alfred Werner's laboratory in Switzerland. He published a joint paper with Werner in 1912 and later brought back the concept of coordination chemistry to Japan, to Tokyo University. Shibata had a strong influence on the later development of inorganic chemistry in Japan and trained many excellent inorganic chemists including Ryutaro Tsuchida who formed a strong group at Osaka University and contributed to raising the standard of coordination chemistry in Japan. Early workers in coordination chemistry were involved in syntheses and properties of various coordination compounds using UV-visible spectrometers with photographic plates as their main tools. Most of these coordination chemists belonged to faculties of science and were involved with static aspects of coordination chemistry. One notable achievement in the prewar period was the discovery by T. Tsumaki of Kyushu University in 1938 of reversible binding of O_2 with cobalt complexes having the ligand of Schiff bases of salicylaldehyde with diamines [2]. His work stimulated Melvin Calvin in Berkeley to start his intensive study on reversible oxygen carriers which became the forerunner of bioinorganic chemistry.

Another important work which is not well known outside Japan but should be mentioned here for the sake of historical interest is the discovery of homogeneous hydrogenation of sodium cinnamate with molecular hydrogen in the presence of a mixture of cobalt(II) chloride and KCN reported in 1942 by M. Iguchi, another student of Y. Shibata at Tokyo University [3].

3. Postwar development

World War II ended with the devastating defeat of Japan which left the Japanese in misery and starvation. It widened even further the big gap that already existed between western science and that of Japan. Japanese could have no confidence in being able to survive with so many mouths to feed and so very few natural resources. I remember the time when we were discussing if we would ever catch up with the US level of science, with our so meagre resources. Later, however, the people, well-trained and hard working, proved to be an indispensable resource as well as providing a good-sized market, leading to the reform of Japan as a powerful industrial country that could supply the world with excellent high-tech products to an extent which lead to friction with other countries.

3.1. Organosilicon chemistry

The first impetus toward starting organometallic chemistry in Japan after the end of the war came from organosilicon chemistry. Chemical factories producing silicones, then dubbed "magic sand", were built in Japan under licence from US companies. It was somewhat ironic that it had been silicone oils that enabled the B-29 bombers to fly up in the stratosphere to attack Japanese cities at will, reducing most of them to ash.

A small society was founded in 1950 in Osaka to exchange information and views on organosilicon chemistry and this was followed in 1952 by initiation of an academic meeting. In 1954 the Annual Symposium on Organosilicon Compounds was instituted whose scope was later broadened to include other organometallic compounds. Since 1972 the abstracts of the symposium have been printed only in English, a rather exceptional practice in Japan. We have now seen the 40th annual symposium, in which over 600 people participated including academic as well as industrial chemists interested in the basic aspects as well as in applications covering transition metals and non-transition metals.

Notable participants from universities in the organosilicon symposium in its early days were Rokuro Okawara and Makoto Kumada [4], who were in the first generation of organometallic chemists, concerned mainly with main group elements. The late Yoshio Ishii who was concerned first with organotin compounds joined later and then explored further organotransition metal chemistry. Hideki Sakurai [5], who joined the Kumada group as associate professor, then at Kyoto University and later at Tohoku University, represents the second generation of organosilicon chemists together with other researchers such as the late Yoichiro Nagai at Gumma University. They helped to bring Japanese organometallic chemistry of non-transition metals to the international forefront.

One remarkable example of the application of organosilicon chemistry which was achieved in Japan was the invention of Si-C fibre, developed by Seishi Yajima of Tohoku University in 1975. He thermolyzed polysilane to form Si–C fibres that can be processed to produce highly thermostable and extremely strong polymeric materials of use in commercial products as well as in spacecraft.

3.2. Organotransition metal chemistry

This discipline took a different course from that of the main group elements. The most influential western models for researchers were two Germans, W. Reppe and K. Ziegler. Reppe's influence can be seen in the work of the pioneer of organotransition metal chemistry in Japan, Nobue Hagihara. Hagihara started as an associate professor working jointly with Shunsuke Murahashi at Osaka University. Although he may have been influenced by Reppe's work at first, Hagihara made several original contributions working with excellent graduate students, including Hiroshi Yamamzaki, Akira Nakamura, Kenkichi Sonogashira, and Shigetoshi Takahashi. Some of Hagihara's papers were published in Japanese journals and have not been well recognized outside Japan. But he was the first to point out possible mechanisms of conversion of acetylene into cyclooctatetraene and benzene catalyzed by zerovalent nickel catalysts, modified or unmodified by nitrogen base [6]. Also worth mentioning are their studies on monometallic chromium catalyst systems to polymerize ethylene and on the palladium-catalyzed telomerization of butadiene and alcohol. Besides application-type work they synthesized the first alkyl-nickel and cobalt complexes coordinated with cyclopentadienyl ligand [7] and developed cobalt metallacycle chemistry [8]. Toward the end of his tenure at Osaka University Hagihara turned his attention to preparation of polymeric materials containing transition metals in the backbone [9]. These metal-containing polymeric materials were the first of this type of compound later to be studied in the rest of the world.

The discovery in 1953 of Ziegler catalyst to polymerize ethylene, with later reports from Natta's group on stereospecific polymerization of propylene and of other monomers had a tremendous impact on industrial as well as academic chemists in Japan. Many companies sent their people to Mülheim and Milan to have them negotiate the introduction of this new technology. This period coincided with the upsurge of the petrochemical industry along the coast of Japan and with restructuring industry from a coal base to oil base. This was when new polymeric materials were welcomed by Japanese who were ready to adopt any new products manufactured by new technologies from the west.

Chemists in universities were also fascinated by the dawning of the new era in polymer chemistry. The mechanism behind the stereospecific polymerization of propylene and related olefins was a challenging problem. Many sessions at the annual meetings of the Chemical Society of Japan and the Polymer Society of Japan were jam-packed by audiences expectant of reports of new findings. Particularly active in this initial period was the group led by Junji Furukawa at Kyoto University, with the collaboration of his excellent coworkers at the time, notably Teiji Tsuruta, Takeo Saegusa and Shohei Inoue; also the group led by Shu Kambara at Tokyo Institute of Technology with coworkers including Sakuji Ikeda, Noboru Yamazaki and Masahiro Hatano. It was a booming period. Many chemical companies, particularly those belonging to the petrochemical industry were eager to hire graduates of the chemistry-related departments of universities of good reputation.

The Ministry of Education, overseeing education from primary schools to universities, decided to expand the capacities of universities with emphasis on graduate schools to meet the demand from industries and from the public. In the 15 years from 1960 to 1975 the capacity of universities in Japan was expanded threefold.

Interest in coordination polymerization later waned in Japanese universities except for the group led by T. Keii and K. Soga at Tokyo Institute of Technology, while the research activity in industry has continued because of the strategic importance of polyolefin production in the petrochemical industry. The polyolefin manufacturing process is now in its third phase with the advent of Kaminsky–Brintzinger type catalysts using metallocene-based early transition metal complexes. The process, which requires the special design of catalysts is now attracting the renewed attention of certain organotransition metal chemists in Japan as in the rest of the world.

Other industrial processes which captivated the interest of academic as well as industrial chemists in Japan were the Hoechst–Wacker process and the Oxo process. Invention of these industrial processes and, most of all, the discoveries of ferrocene had a far reaching influence on the development of organotransition metal chemistry in Japan as well as in the west.

4. Development of organotransition metal chemistry related to organic synthesis in Japan

Although Japan was a latecomer in science and engineering, the situation in organotransition metal chemistry was different from that in other fields. Organometallic chemistry itself was a latecomer in the world of science and Japanese organometallic chemists were not so much behind the western chemists when the rapid development of organotransition metal chemistry started. This was dubbed the Renaissance of inorganic chemistry, as the discoveries of ferrocene, dibenzene chromium and metal-carbene complexes were reported one after another. Important concepts of fundamental processes involving organotransition metal complexes were established laying the foundations for subsequent development. These include oxidative addition, reductive elimination, olefin and CO insertion into the transition metal–carbon or the metal–hydride bond and the deinsertion processes, and attack of the coordinated ligands by nucleophiles.

It was also the period when new instruments such as those for IR, NMR and ESR followed later by automatic X-ray diffractometers were being introduced one after another. At that time some senior professors with their empirical knowledge of classic chemistry were not too confident how to supervise the younger ones, particularly those who had returned from the US and Europe. These people, who had been sent abroad mostly as post-doctoral fellows, were trained in the western way and had acquired invaluable experience there, returning to Japan to form nuclei in many universities for the task of developing the new field, organotransition metal chemistry. They have in their turn trained their young followers to bring organometallic chemistry in Japan to the higher international level.

We may note here the influence of another German, G. Wilke, in development of organotransition metal chemistry and homogeneous catalysis. He has clarified that the real active centres in those catalytic reactions which cause polymerization of butadiene as well as the oligomerizations of dienes and of other monomers are transition metal complexes and further established that the activity of the transition metal centre can be modified by choice of suitable ligands. He thus solved the long-standing question regarding the real active centre of Ziegler type catalysts and abolished myth from the mechanisms of catalytic reactions that had been incapable of clarification, by studying the surface of heterogeneous catalysts. His elegant work, which is organic in nature, had a strong influence on the methods of research of those who worked with him. His clear influence may be seen in the works of Sei Otsuka of Osaka University and Akio Yamamoto of Tokyo Institute of Technology and their coworkers. They followed the style of Wilke to isolate new types of organotransition metal complexes and find catalytic processes promoted by these species.

On the other hand, synthetic organic chemistry was also in transition. Some leaders in the field were quick to recognize the usefulness of transition metals as promoters and catalysts. Hitoshi Nozaki at Kyoto University was among those who influenced the development of organic synthesis using transition metal complexes, and also raised outstanding synthetic chemists such as Ryoji Noyori, Hidemasa Takaya, and Hisashi Yamamoto from the Kyoto school to name a few. Spurred by findings in the reactions of organometallic complexes, various techniques employing transition metal catalysts have been devised. Among many methodologies using transition metal complexes as catalysts, cross-coupling of alkyl and aryl groups catalyzed by nickel and palladium complexes, first reported by M. Kumada and K. Tamao of Kyoto University [10], ranks among the most utilized synthetic methodologies using transition metal complexes. The transition metal-catalyzed C–C coupling reaction was later developed by T. Yamamoto to synthesize polyarenes that can be modified on iodine doping to prepare conducting polymers [11]. Another development of the C–C coupling process is the coupling reaction using organoboron compounds, developed by Suzuki [12]. Together with the palladium-catalyzed C–C coupling process, allylation of nucleophiles catalyzed by palladium complexes, developed by J. Tsuji [13] and B. Trost, ranks among the most frequently adopted processes in organic syntheses. The other important palladium-catalyzed process arylation of olefins (the Heck reaction), first discovered by the late T. Mizoroki [14] independently of Heck [15] should also be noted. Also worth mentioning in the context of palladium-catalyzed arylation of olefins is one of the oldest examples [16], the pioneering work by the late I. Moritani and Y. Fujiwara in palladium-catalyzed arylation of olefins involving C–H bond activation. Together with western workers but with more emphasis on the catalytic aspect, the contributions on activation of alkanes and arenes by Tanaka [17] and Fujiwara [18] are to be noted.

The annual symposium of organometallic chemistry, which had been held in one session, is now divided into two, one being devoted to organic synthesis using transition metal complexes and the other to fundamental aspects of organometallic chemistry. There have been reasonably good interactions between the participants in the two sessions. Conversely, interactions with the classic coordination chemists have been weaker.

As we can judge by analysis of the number of particular transition metals dealt with in the annual symposia of organometallic chemistry, palladium is by far the favourite metal among Japanese organometallic and synthetic organic chemists followed by ruthenium and rhodium. The frequency of reports on other transition metals is much lower. Catalytic processes using ruthenium complexes have been studied extensively by the groups of Y. Watanabe at Kyoto University, S. Murahashi at Osaka University, and K. Ito at Toyohashi University of Technology, whereas Sonoda and Murai's group at Osaka University developed interesting processes to utilize carbon monoxide in organic synthesis using cobalt and rhodium complexes. Although fundamental aspects remain to be clarified, organocopper complexes have been extensively utilized by Japanese synthetic chemists. The contributions of Hisashi Yamamoto, Yoshinori Yamamoto, Yoshihiko

Ito, and Takeo Saegusa should be noted in this context.

A propensity that can be seen in the works of Japanese organometallic chemists, in the broad sense, is their readiness to application even if they were originally involved in fundamental aspects of organotransition metal chemistry. This pragmatic attitude may not be unrelated to the success in commercialization achieved in Japan of two of the three important asymmetric syntheses in the world using transition metal complexes as catalysts. These came after the first successful asymmetric synthesis commercialized by Monsanto to hydrogenate olefins to make L-dopa, the drug for Parkinson's disease. One asymmetric synthesis commercialized in Japan is the asymmetric cyclopropanation process based on original research by Nozaki and Noyori. This was industrialized at Sumitomo Chemical Industries for the production of pyrethroids, useful insecticides. The development was driven by Aratani who was also the student of Nozaki. The other commercialized asymmetric process is asymmetric isomerization catalyzed by rhodium-BINAP complexes. The process is based on the work of Ryoji Noyori, Hidemasa Takaya, Akira Miyashita, Takao Ikariya, Sei Otsuka and Kazuhide Tani in cooperation with the team at Takasago Perfume Company where the process was commercialized. Here we can see a good example of cooperation between academic and industrial chemists.

As far as asymmetric synthesis is concerned there are many other active groups in Japan. Makoto Kumada had a particularly strong influence in the development of chiral ligands based on ferrocenylphosphines, with his coworkers Tamio Hayashi, now at Hokkaido University, and Keiji Yamamoto, now at Tokyo Institute of Technology. Hayashi has continued to produce interesting results in asymmetric synthesis including asymmetric synthesis through π-allylpalladium intermediates and his recent success, together with F. Ozawa, in accomplishing Heck-type arylation of olefins.

One may sometimes wonder why asymmetric synthesis using transition metal complexes is so intensely pursued in Japan. Besides the basic reason, the unquestioned importance of asymmetric synthesis for producing biologically active compounds, this might be connected with the Japanese attitude as shown in the manufacture of high-tech products. Once the target is set, they will not stop working hard and racking their brains until the goal is reached.

In general, contributions from industry in the form of papers related to fundamental research in chemistry have not been conspicuous except for the contributions of Tsuji when he worked for industry before he moved to university. However, Japanese industry did accomplish commercialization of some novel processes based on organometallic chemistry. In addition to the large scale production of polyolefins and the asymmetric processes previously mentioned, the following middle to small scale processes have been successfully commercialized in Japan among others [19]. The Ube process converts carbon monoxide and alkyl nitrite into oxalic esters with palladium catalyst; Kuraray succeeded in production of vinyl acetate by acetoxylation of ethylene as well as in hydrative dimerization of butadiene to octanol; hydrogenation of NBR and palladium catalyst-based production of Jasmonate were commercialized by Nippon Zeon; while a few hydroformylation processes using rhodium catalysts have been developed by Mitsubishi Kasei.

5. Development of studies on fundamental aspects of organotransition metal chemistry

Besides the organic synthesis-oriented chemists there are some schools interested in the fundamental aspects of organotransition metal chemistry. Among the organometallic chemists invited to contribute to the reviews published in every hundredth issue of the *Journal of Organometallic Chemistry*, one finds some Japanese in the field of fundamental organotransition metal chemistry. S. Otsuka [20] describes his work on the chemistry of zero valent Group 10 transition metal complexes having bulky tertiary phosphines. A Yamamoto discusses mainly transition metal alkyls [21], whereas A. Nakamura deals with the chemistry of the Group 4 metal complexes coordinated with dienes [22]. Their former coworkers and organometallic chemists from other schools such as H. Kurosawa of Osaka University and Y. Wakatsuki of the Institute of the Physical and Chemical Research are active in various research institutions with fundamental aspects of organotransition metal complexes. From these rising generations more are expected to make their contribution in this way.

As they are also topics related to organotransition metal chemistry, nitrogen and carbon dioxide fixation merit mentioning here. One of the first N_2-binding complexes, triphenylphosphine-coordinated cobalt complex, was prepared by A. Yamamoto [23]. Tertiary phosphine-coordinated ruthenium and molybdenum as well as tungsten complexes were added later as N_2-binding examples [24]. Although the initial fever for discovering a new catalytic system to fix molecular nitrogen has waned, the transformation of the metal-bound dinitrogen into organonitrogen compounds is still pursued tenaciously in M. Hidai's group at Tokyo University and attempts to utilize molecular nitrogen directly as the nitrogen source have been reported by M. Mori and her group [25].

Japanese workers were among the first who coped with the problem of utilization of carbon dioxide with metal complexes [26]. Prominent success in the utilization of CO_2 has come from the work of S. Inoue at Tokyo University with aluminium porphyrin complexes. Copolymerization of carbon dioxide and propylene oxide has been achieved to produce polycarbonates [27]. The concept of immortal polymerization emerged from the study. Catalytic incorporations of CO_2 with dienes and with dialkynes have been pursued by Y. Inoue at Tohoku University and by T. Tsuda at Kyoto University.

In the field related to bioinorganic chemistry, Y. Murakami is producing interesting results on the activity of vitamin B_{12}. Z. Yoshida, Y. Ogoshi, and Y. Aoyama have explored the reactivities of metal porphyrin analogues. Kitazume and Moro-oka recently developed interesting O_2 binding models involving copper complexes.

In contrast to the situation elsewhere, however, the chemistry of metal clusters has received rather limited attention from Japanese organometallic chemists. This may have been partly caused by a lack of automatic X-ray diffractometers due to inadequate funding of university research in Japan (those who may be surprised by the poor support given by the government are referred to the article published in *Nature* [28]).

The other possible reason for the relative lack of activity in metal cluster chemistry may again be found in the somewhat pragmatic nature of Japanese chemists that I have already touched upon. Among the few organometallic chemists interested in metal clusters are Hiroshi Yamazaki and his group at the Institute of Physical and Chemical Research and Taro Saito's group presently at Tokyo University. It is noted that even in their work there may be found the intention to relate the properties of the metal clusters with catalysis. This attitude seems to me somewhat different from that of metal cluster chemists in Europe who seem to be enjoying synthesizing a variety of metal clusters for the sake of pure chemistry or for the sheer pleasure of making metal clusters that are pleasing to the eye. One interesting recent development with the prospect of future expansion is found in the work of H. Suzuki at Tokyo Institute of Technology on dinuclear and trinuclear ruthenium complexes that exhibit remarkable properties achievable only with polynuclear complexes.

As time passes, the older generations leave and younger generations emerge. The future of Japanese organometallic chemistry is in the hands of these younger generations. I had better stop my account of achievements of Japanese organometallic chemists here since the works of younger generations are still difficult to put in their historical perspective.

6. Grant-awarding system in Japan

For non-Japanese readers it may be of interest to know about the systems supporting research in Japanese universities. In Japan we have three main sources funding university research. One is the fund distributed automatically to each national university through the Ministry of Education, Science and Culture (Monbusho). Private universities generally provide the corresponding fund from the budget of each university. The other important source is the Scientific Research Grant in which applications are granted on a kind of peer review system administered by Monbusho. The rest comes from donations from industries and private foundations. In the Scientific Research Grant administered by Monbusho, the principal funds are general research grants and special grants allocated to programs to achieve a special target or to raise the level of a particular area. In the program previously known as the "Special Project Program" a project related specifically to organometallic chemistry was supported in the period from 1986 to 1989. The program worked to upgrade the level of organometallic chemistry in Japan particularly by encouraging the activity of young chemists. About 70 organometallic chemists were involved in the program. The granting system was somewhat modified later, and from 1993 a new project entitled "Functions and Properties of Reactive Organometallic Molecules" has been supported as the Priority Area Project. Here are involved about 70 people participating in the program receiving about 250 million yen (1 US $ is about 110 yen) annually for the three year period. In addition to this program a project entitled "Activation of inactive small molecules" led by M. Hidai had been supported. Another program now running is the project on "Asymmetric synthesis" in which some organometallic chemists belonging to faculties of Science, Engineering and Pharmacy are participating.

In relation to the support system a few comments are in order on research and the educational system in Japan. In national universities and in research-oriented private universities, many graduates from chemistry-related universities proceed to graduate schools for master's degrees. But the number of students proceeding to the PhD is limited. Thus the type of research work is influenced by the system and sometimes a long term project or one requiring the special expertise of PhD students or post-doctoral fellows is considered difficult to accomplish. To improve the situation more governmental aid to support PhD students is necessary.

In general governmental support for university research has not been adequate. There is evidence that the situation might be somehow improved now that there is recognition of the poor research conditions in Japanese universities. However, it is expected to be a slow process.

7. Conclusion

Organometallic chemistry in Japan has shown considerable growth in past years despite somewhat inadequate support by the government. There are signs of continuing growth in the foreseeable future. It is yet to be seen if outstanding discoveries are made by future generations.

Although I have tried to provide a balanced view in this article regarding the organometallic chemistry of the past and present with a focus on organotransition metal chemistry, it is quite possible that I have failed to refer to some important contributions and events. I would like to apologize for possible omissions which did not arise out of any intention of slighting them.

References

1 The Chemical Society of Japan, *100 Years of the Chemistry in Japan*, Tokyo Kagaku Dojin, Tokyo, 1978.
2 T. Tsumaki, *Bull. Chem. Soc. Jpn.*, *13* (1938) 252.
3 M. Iguchi, *J. Chem. Soc. Jpn. Pure Chem. Sect.* (in Japanese), *63* (1942) 1752.
4 M. Kumada, *J. Organomet. Chem.*, *100* (1975) 127.
5 H. Sakurai, *J. Organomet. Chem.*, *200* (1980) 261.
6 N. Hagihara, *J. Chem. Soc. Jpn. Pure Chem. Sect.* (in Japanese), *73* (1952) 237.
7 H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Jpn.*, *37* (1964) 908.
8 N. Hagihara and H. Yamazaki, *J. Organomet. Chem.*, *7* (1967) 22.
9 P.J. Kim, H. Masai, K. Sonogashira and N. Hagihara, *Nucl. Chem. Lett.*, *6* (1970) 181.
10 K. Tamao, K. Sumitani and M. Kumada, *J. Am. Chem. Soc.*, *94* (1972) 4374.
11 T. Yamamoto and A. Yamamoto, *Chem. Lett.*, (1977) 353.
12 A. Suzuki, *Pure Appl. Chem.*, *57* (1985) 1749.
13 J. Tsuji, *Organic Synthesis with Palladium Compounds*, Springer-Verlag, Berlin, 1980.
14 K. Mori, T. Mizoroki and A. Ozaki, *Bull. Chem. Soc. Jpn.*, *46* (1973) 1505.
15 R. Heck, *Acc. Chem. Res.*, *12* (1979) 146.
16 I. Moritani and Y. Fujiwara, *Tetrahedron Lett.*, *12* (1967) 1119.
17 For example, T. Sakakura and M. Tanaka, *Chem. Lett.*, (1987) 249.
18 T. Jintoku, H. Taniguchi and Y. Fujiwara, *Chem. Lett.*, (1987) 1865.
19 K. Wada, *Shokubai* (in Japanese), *35* (1993) 238.
20 S. Otsuka, *J. Organomet. Chem.*, *200* (1980) 191.
21 A. Yamamoto, *J. Organomet. Chem.*, *300* (1986) 347.
22 A. Nakamura, *J. Organomet. Chem.*, *400* (1990) 35.
23 A. Yamamoto, S. Kitazume, L.S. Pu and S. Ikeda; *J. Chem. Soc., Chem. Commun.*, (1967) 79.
24 T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida and M. Hidai, *J. Am. Chem. Soc.*, *102* (1980) 7461.
25 Y. Uozumi, N. Kawasaki, E. Mori, M. Mori and M. Shibasaki, *J. Am. Chem. Soc.*, *111* (1989) 3725.
26 S. Inoue and N. Yamazaki (eds.), *Organic and Bio-Organic Chemistry of Carbon Dioxide*, Kodansha, Tokyo, 1981.
27 S. Inoue, H. Koinuma and T. Tsuruta, *Polym. Lett.*, *7* (1969) 287.
28 A. Yamamoto, *Nature*, *239* (1989) 575.