# Trends and Opportunities for Organometallic Chemistry in Industry

George W. Parshall[1]

*Central Research & Development Department, E. I. du Pont de Nemours & Company, Inc., Experimental Station, Wilmington, Delaware 19898*

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Since 1950, organometallic chemistry has grown to become a significant industrial discipline because of its importance as the underlying science for homogeneous catalysis and the coordination polymerization of olefins. Changes in the chemical industry in the 1975–1985 period, however, have reduced the business emphasis on large scale polymers and commodity chemical products. As a result, much less effort is being applied to research on catalytic processes for these materials. The shift in business interest to fine chemicals, specialty polymers, and electronic materials has opened many new opportunities for organometallic chemistry. Organometallic methods for organic synthesis can have impact in processes for pharmaceuticals, agrichemicals, specialty monomers, and flavors and fragrances. Similarly organometallic reagents are valuable for synthesis of semiconductor compounds and ceramic precursors (preceramic polymers). A major opportunity exists in exploration of the physical properties of organometallic compounds in the solid state. This area of science has been neglected and has the potential to yield materials with valuable new properties.

Organometallic chemistry in industry underwent major change and growth in the 1950s. Before 1950, industrial applications of organometallics dealt largely with stoichiometric uses of main-group compounds. Tetraethyllead was well-established as a gasoline additive, tin compounds were used as stabilizers for polyvinyl chloride, and arsenic derivatives were used in medical and agricultural applications. There was some use of transition-metal carbonyls in catalytic reactions of CO, but soluble catalysts played only a minor role in industry.

Organo-transition-metal chemistry began to emerge as a significant discipline in the American chemical industry in the 1950s. The discipline flourished as the industry grew, primarily because it laid the basis for superior homogeneous catalytic processes for production of polymer intermediates. In recent years, the chemical industry has shown many of the problems associated with maturity. Growth has slowed, and several American companies have taken severe measures to control costs. Organometallic chemistry has been affected in that hiring of new organometallic chemists has slowed at most major chemical companies. While one could be gloomy about the future

of organometallic chemistry in industry, such an outlook would be unjustified. The discipline is in the midst of a transition to a much broader role with impact in the fast-growing electronics and health care industries that will more than compensate for the changes in the traditional chemical industry.

In this paper, I examine the trends that brought us to the situation that exists today and look ahead to the opportunities for organometallic chemistry in industry in the 1990s. The future does not appear to be a simple extrapolation of the past. Major changes are taking place in industry worldwide. Organometallic chemists can profit from these changes if they are adaptable and are willing to seek new outlets for their research.

## Past Trends

The past 35 years have seen enormous growth in transition-metal organometallic chemistry, both as a scientific discipline and as a subject for research in industry. In 1950, organometallic chemistry was a minor component of organic synthesis research and an even smaller component of inorganic chemistry. In industry, it was almost unrecognized and its potential in homogeneous catalysis was certainly not apparent. By 1980, organo-transition-metal chemistry had overshadowed the more traditional areas of inorganic chemistry. Industrial processes based on organometallic chemistry and homogeneous catalysis contributed almost 23 billion dollars to the U.S. economy

in 1980.[2]   In the past 5 years, however, this growth in production based on organometallic technology has slowed. The level of innovation has also decreased, at least in the American chemical industry.

Each decade since 1950 has had its own character in terms of both science and technology. These characteristics are examined decade by decade in the following sections.

**The 1950s: A Decade of Discovery.** The growth of organometallic chemistry, both as a science and as an industrial discipline, erupted in the early 1950s. The discovery of ferrocene and the subsequent seminal discoveries in organo-transition-metal chemistry by Wilkinson, Fischer, and Chatt transformed the science. Extensive synthesis programs, both in universities and in industry, broadened the scope of organometallic chemistry immensely. Previously, compounds containing transition metal-to-carbon bonds had been isolated curiosities. By 1960, there were dozens of such compounds with a wide range of structural characteristics. The evolution of molecular orbital theory began to contribute to the understanding of structure in the new compounds.

At the same time that the science blossomed, empirical discoveries in industrial laboratories laid the basis for the practical application of organometallic science. Stoichiometric uses included (methylcyclopentadienyl)tricarbonylmanganese as an antiknock for gasoline and ferrocene as a combustion enhancer for heating oil. Applications in catalysis were numerous, for example, olefin metathesis,[3] the Wacker process for oxidation of ethylene to acetaldehyde,[4] and the coordination polymerization of olefins. The latter two discoveries were especially important because they met practical needs of industry.

The commercialization of the Wacker process was a major step in the evolution of homogeneous catalysis. Previously, soluble catalysts had been used primarily for reactions of acetylene with HX molecules (X = Cl, CN, AcO, OH) to give vinyl monomers or acetaldehyde. These products were valuable in developing the chemical industry of 1920–1955, but the market was limited by cost because acetylene was an expensive starting material. The development of the Wacker process to produce acetaldehyde from inexpensive ethylene marked the beginning of the end for acetylene as a major chemical feedstock. It also made homogeneous catalysis more attractive to engineers responsible for the design of commercial processes.

The discovery of the Ziegler–Natta[5] and Phillips[6] catalysts for the polymerization of ethylene, propylene, and other olefins was even more influential. These discoveries led not just to new processes but to entirely new products such as linear polyethylene and isotactic polypropylene. The products produced by this technology in the U.S. in 1980 were valued at 8.7 billion dollars.[2] The Ziegler–Natta catalysts provided a great stimulus to organometallic research through demonstration of the powerful catalytic effects accessible through the M–C bond.

While the discoveries listed above provided "technology push" for development of organometallic chemistry and homogeneous catalysis in industry, a second major factor in the growth of the technology was "market pull". The development of synthetic polymers for fibers, plastics, films, elastomers, and adhesives required many new organic chemicals as intermediates. For example, nylon required caprolactam or adipic acid and hexamethylenediamine. Polyester brought a need for terephthalic acid and ethylene glycol. The polymer intermediates needed to be very pure, well above 99%. The demand for purity put a premium on processes that produced one product selectively. This emphasis on purity was a major stimulant for introduction of soluble catalysts that operate under mild, well-controlled conditions that favor selectivity. Applied homogeneous catalysis rapidly became the major rationale for organometallic research in industry.[7]

**The 1960s: A Time of Excitement.** The scientific and technological discoveries of the 1950s laid the groundwork for one of the most exciting decades in the history of chemistry, a time when anything seemed possible. Organometallic chemistry made possible the capture of exotic species such as cyclobutadiene, carbenes, and trimethylenemethane. These were molecules that the organic chemists could only speculate about previously. Development of instrumental techniques, especially NMR and X-ray crystallography, revolutionized the study of structure and reactivity.

The wealth of new scientific information laid the basis for new technology. While much of the new process development in industry began with empirical discovery, the scientific understanding of the new processes became firmer. Studies of cobalt-catalyzed hydroformylation by Heck[8] and of rhodium-catalyzed olefin dimerization by Cramer[9] pioneered the understanding of mechanisms of homogeneous catalytic processes. Although these studies were crude by current standards, they established many of the basic principles of catalysis that we use today.

Probably the discovery that had the greatest impact in technology was recognition of the catalytic merit of rhodium complexes. One of the first practical applications was the $RhCl_3$-catalyzed reaction of butadiene with ethylene to produce *trans*-1,4-hexadiene,[10] which was commercialized by Du Pont in the 1960s. A better known manifestation was the development of the Wilkinson catalyst[11] for the hydrogenation of olefins. This complex, $RhCl(PPh_3)_3$, and the related Schrock–Osborn catalysts,[12] $[RhL_2(PR_3)_2]^+$, demonstrated the power of phosphine ligands to stabilize catalytically active rhodium species. Both gave rise to catalysts that found industrial application in the 1970s. Wilkinson's work, done in parallel with research in several industrial laboratories, showed that rhodium complexes are outstandingly effective in hydroformylation and other reactions of carbon monoxide.[13] This work had broad commercial impact in the 1970s.

**The 1970s: A Time of Increased Sophistication.** Both in science and technology, the level of sophistication increased greatly in the 1970s. The experimental rigor applied to studies of structure and reaction mechanism was far greater than that in the previous decade. Theory began to emerge as a partner of experiment in yielding understanding of physical properties. Chemists began serious study of polynuclear transition-metal complexes, both as models of metal surfaces and as catalysts for reactions inaccessible with simple mononuclear complexes.

(2) Parshall, G. W.; Putscher, R. E. *J. Chem. Educ.* **1986**, *63*, 189–191.

(3) Eleuterio, H. S. U.S. Patent 3 074 918, 1963.

(4) Jira, R.; Blau, W.; Grimm, D. *Hydrocarbon Process.* **1976**, March, 97.

(5) Ziegler, K.; Martin, H. *Makromol. Chem.* **1956**, *18/19*, 186–194. Natta, G. *Angew. Chem.* **1956**, *68*, 393–411.

(6) Clark, A. *Catal. Rev.* **1969**, *3*, 145–173.

(7) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980.

(8) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 651–654.

(9) Cramer, R. *J. Am. Chem. Soc.* **1965**, *87*, 4717–4727.

(10) Cramer, R. *J. Am. Chem. Soc.* **1967**, *89*, 1633–1639.

(11) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711–1732.

(12) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397–2407.

(13) Hallman, P. S.; Evans, D.; Osborn, J. A.; Wilkinson, G. *Chem. Commun.* **1967**, *305*–306.

**Table I. Selected Processes Commercialized in the 1970s**

| process | catalyst | company | ref |
|---|---|---|---|
| butadiene $\xrightarrow{HCN}$ adiponitrile | Ni(P(OAr)$_3$)$_4$ | Du Pont | 15 |
| ethylene $\rightarrow$ linear $\alpha$-olefines | Ni(chel)$_2$ | Shell | 16 |
| $\alpha$-olefin $\xrightarrow{H_2/CO}$ linear aldehydes | Rh(H)(CO)(PAr$_3$)$_3$ | Celanese, Union Carbide | 17 |
| methanol $\xrightarrow{CO}$ acetic acid | [Rh(CO)$_2$I$_2$]$^-$ | Monsanto | 18 |
| substituted cinnamic acid $\rightarrow$ chiral $l$-DOPA precursor | [RhL$_2$(PR$_3$)$_2$]$^+$ | Monsanto | 19 |

In industry, the large investment in organometallic research in the 1960s began to yield new commercial processes that were far superior to their predecessors.[14] These processes (Table I) represent a major increase in sophistication because the chemistry involved in each is well-understood. While much of the mechanistic understanding followed commercial application, the basic outlines of the chemistry were apparent at the time of plant start-up and played a significant role in the successful operation of the processes.

The two Monsanto processes, which were brought into production in 1970–1971, were particularly important as prototypes of chemistry that will be important in the future. The acetic acid process[18] is a remarkable success in process integration back to starting materials that should be cheap and abundant for an indefinite period in the future. The methanol comes from synthesis gas, a CO/H$_2$ mixture available from oil, gas, coal, or organic refuse. The feasibility of integration back to coal was demonstrated by Tennessee Eastman. In 1983, they opened a large industrial complex in which acetic anhydride is produced by the sequence

$$\text{coal} \rightarrow \text{MeOH} \xrightarrow{CO} \text{MeOAc} \xrightarrow{CO} \text{Ac}_2\text{O}$$
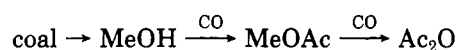
The chemistry of the CO reactions that follow methanol synthesis resembles that of the Monsanto acetic acid process.[20]

A second Monsanto process, the hydrogenation of a prochiral olefin to a specific optical isomer of an $l$-DOPA precursor,[19] appears to be the first example of a catalytic industrial process with enzyme-like chiral specificity. As such, it was the forerunner of many other potential applications in the synthesis of biologically active molecules for the health care industry. Like the other processes in Table I, its development built heavily on the fundamental research of the 1960s. The catalytic metal complex is patterned after the cationic Schrock–Osborn hydrogenation catalysts. The chiral phosphines that impart molecular asymmetry to the catalyst drew on academic research on tertiary phosphines with stable P-centered chirality.

## Current Trends

**The 1980s: A Time of Transition.** In the mid-1970s distressing signs of maturity began to appear in the American chemical industry. Growth rates and profitability declined for the major chemical companies, although the trend was obscured by the cyclical nature of American business and the unusual economic stresses that resulted from the 1973 and 1979 oil crises.

An even more disturbing trend for the industrial organometallic chemist was a decline in the number of opportunities for innovation, at least in the accepted area of homogeneous catalysis research. Most of the processes commercialized in the 1970s were very successful, both technically and economically, and are unlikely to be replaced by new processes. Even more seriously, the number of new products being commercialized dropped substantially. Major new products of the magnitude of polyester fiber did not appear, and, as a consequence, there was little call for major new processes for new intermediates.

Most major chemical companies went through a period of reassessment of their businesses about 1980. The consensus was that their traditional areas of business, polymers and bulk chemicals, offered little opportunity for improvement of earnings. As a consequence, diversification into other areas of business seemed desirable. The consensus was that the best opportunities for growth and profitability lay in fine chemicals, specialty polymers, and products for the electronics and health care industries. The consequence of this decision was a major restructuring of industrial research organizations to create and to support the businesses of the future. Many new disciplines (such as molecular genetics and nonlinear optics) have been brought into corporate research departments, and traditional research groups are being redirected.

The restructuring of research is well-advanced at most American chemical companies, and the outlines of the future of organometallic chemistry in industry seem apparent. The following section is a personal perspective on where the opportunities for our discipline lie.

## Future Trends

**1986–2000: New Horizons Emerge.** As the chemical industry diversifies, its boundaries with the electronics and pharmaceutical industries will become indistinct. The more enterprising organometallic chemists will find rewarding opportunities to contribute in these areas. Several pharmaceutical companies already have small organometallic groups to aid in design of new radiopharmaceuticals and metallopharmaceuticals as well as to contribute to the development of new synthesis procedures. The electronics industry makes extensive use of organometallics in vapor deposition of semiconductor materials. Research in this area is often done in empirical fashion by physicists and electronic engineers.

Within the definable chemical industry, substantial research in homogeneous catalysis will continue, but the level of effort will be much lower than in the past. Three rationales will support this activity: improvement of existing processes; development of processes for new products characterized by small volume and high value, such as those discussed in succeeding sections; long-range research on processes based on cheap, abundant feedstocks.

The third area merits discussion. Although the world is currently enjoying cheap energy and abundant petroleum-based feedstocks, it seems likely that future crises in the supply of petroleum and natural gas will occur. Political crises in the Middle East could bring shortages early in the 1990s. The long-term depletion of fossil fuel reservoirs make energy shortages inevitable in the future regardless of political aspects. If policy makers were far-sighted, research to produce the staples of American industry from abundant carbon sources such as coal and

(14) Parshall, G. W.; Nugent, W. A.; Chan, D. M.-T.; Tam, W. *Pure Appl. Chem.* **1985**, *57*, 1809–1818.
(15) Tolman, C. A.; McKinney, R. J.; Seidel, W. C.; Druliner, J. D.; Stevens, W. R. *Adv. Catal.* **1985**, *33*, 1.
(16) Lutz, E. F. *J. Chem. Educ.* **1986**, *63*, 202–203.
(17) Pruett, R. L. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 239–248.
(18) Roth, J. F.; Craddock, J. F.; Hershman, A.; Paulik, F. E. *Chem. Tech.* **1971**, *1*, 600–605.
(19) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106–112.
(20) Polichnowski, S. W. *J. Chem. Educ.* **1986**, *63*, 206–209.

biowaste would be under way today. Synthesis gas can provide a large number of the needed intermediates, but much research remains to be done to make processes like the Union Carbide syn gas based ethylene glycol synthesis[17] economically attractive.

**Organometallics in Organic Synthesis.** Organometallic methods have found wide acceptance in the organic synthesis laboratory, both in universities and in industry. For many organic transformations, an organometallic reagent or a homogeneous catalytic reaction can replace several steps with conventional synthesis methods. Even better, metal reagents or catalysts can serve as templates for stereoselective transformations that would be difficult to achieve by other methods. These virtues have made organometallic methods increasingly acceptable for industrial use in the synthesis of biologically active compounds for use as pharmaceuticals and crop protection chemicals. In these applications, the value of the product is high. Complex structures and involved syntheses can be tolerated if the desired biological activity is obtained.

The pharmaceutical industry seems an especially attractive field for organometallic methods[21] although the acceptance of organometallic methodology has been limited to date. One conspicuous success was the previously mentioned synthesis of *l*-DOPA, a drug used in treatment of Parkinson's disease. In this instance, only the *l*-isomer exhibits the desired biological activity. Use of an asymmetric catalyst in its synthesis produces the desired optical isomer in greater than 90% enantiomeric excess.[19] This selectivity reduces the requirement for a difficult and costly optical resolution step in the production process. More recently, a rhodium-catalyzed ring closure has been incorporated into a commercial process for production of the antibiotic thienamycin.[22] It effects a transformation difficult to accomplish by conventional synthesis methods. These two examples indicate the potential of organometallic and homogeneous catalytic methods in pharmaceutical synthesis. As the pharmaceutical industry becomes more competitive, it is reasonable to expect that new production methods will be accepted as a way to reduce costs and maintain profits.

The agricultural chemicals industry is undergoing changes that should lead to greater use of metal-based synthesis methods. New generations of crop protection chemicals are emerging in response to environmental concerns and to development of pesticide resistance by many species of insects and weeds. The new products are characterized by higher selectivity and lower application rates than traditional products. For example, Du Pont's new sulfonylurea herbicides have extremely low mammalian toxicity and are applied at rates of a few grams or a few ounces per acre in contrast to the traditional rates of pounds per acre. Many of the synthetic pyrethroid insecticides are similarly selective. These high levels of activity permit consideration of complex chemical structures and organometallic synthesis methods. In fact, a rhodium-catalyzed cyclopropanation[23] has been used to construct the three-membered ring that lies at the center of some synthetic pyrethroid molecules.

New approaches to the control of agricultural pests, for example, the use of pheromones to lure insects, also open opportunities for organometallic methods. The Sharpless asymmetric oxidation methodology has provided a prac-

tical synthesis of Disparlure, an attractant for the gypsy moth.[24] Many of the insect pheromones are olefins that, in principle, are accessible through olefin metathesis. The increasing use of biological methods of control will bring demands for a variety of complex molecules, many of which will contain chiral centers most easily accessible through asymmetric catalysis.

Flavors and fragrances represent another area in which the cost of complex production processes can be justified by achievement of a specific biological activity. The synthesis of some terpene alcohols is carried out on a significant scale by homogeneous catalysis. A rhodium-catalyzed olefin isomerization is used in a major process for production of *l*-menthol.[25] An asymmetric hydrogenation of an enamide, analogous to that in the previously described *l*-DOPA synthesis, is used to make the methyl ester of *l*-phenylalanine.[26] It is presumably used in production of the synthetic sweetener aspartame. Greater understanding of human taste and scent receptors including pheromone receptors should generate new product opportunities that will be interesting challenges to the synthesis chemist.

**Synthesis of Electronic and Optical Materials.** Most of the major chemical companies are developing materials for use by the fast-growing electronics industry as well as in other applications in which a specific function imparts high value to a product. Much current research on polymers deals with materials that have specific electronic, biological, or chemical properties. The synthesis of these functional polymers presents many interesting challenges to the organometallic chemist. Similar opportunities exist in the synthesis of ceramics and semiconductors.

In the area of specialty polymers, organometallic methods should find application both in synthesis of monomers and in polymerization reactions. An example of monomer synthesis involves a potentially attractive commercial process for 3,3,3-trifluoropropene, which is a precursor to an insulating polymer with desirable physical properties. A key step in the process is addition of a C–Cl bond of $CCl_4$ to ethylene to form $ClCH_2CH_2CCl_3$. This reaction is mediated by $FeCl_2[P(OEt)_3]_4$ that is generated *in situ*[27] or, better, preformed by standard synthesis methods.[28]

Broad scope exists for polymerization of olefins, acetylenes, and acrylate esters to give materials with specific physical, chemical, electronic, and optical properties. Polyacetylene, for example, is a material that is undergoing intensive study as a material for electronic or optical switching as well as for storage of electrical energy.[29] It is likely that practical processes for synthesis of this polymer will employ organometallic polymerization catalysis. Other types of desirable properties are selective permeability and optical transparency. Many of the most promising concepts for electronic sensors for specific chemical species rely on selectivity in allowing the target molecule to reach a microelectrode or the "gate" of a transistor device. The amount of material required for a

(21) Scott, J. W. *Ind. Chem. News* **1986**, *7*(3), 32–35.

(22) King, A. O., Seminar, University of Delaware, March 1985. Ratcliffe, R. W.; Salzmann, T. N.; Christensen, B. G. *Tetrahedron Lett.* **1980**, 31–34.

(23) Holland, D.; Milner, D. J. *J. Chem. Res., Miniprint* **1979**, 3734–3746.

(24) Rossiter, B. E.; Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 464–465.

(25) Tani, K.; Yamagata, K.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208–5217.

(26) Fiorini, M.; Riocci, M.; Giongo, M. Eur. Patent 77 099, 1983; *Chem. Abstr.* **1983**, *99*, 122916.

(27) Sato, T.; Kurita, N.; Kise, H.; Seno, M.; Asahara, T. *Nippon Kagaku Kaishi* **1975**, 398–399; *Chem. Abstr.* **1975**, *83*, 27447.

(28) Dunn, G. F.; Feiring, A. E.; Ittel, S. D.; Parshall, G. W.; Wonchoba, E. R., unpublished results.

(29) Chien, J. C. W. *Polyacetylene*; Academic Press: New York, 1984.

specific application may be minute, but the value-in-use may be extremely high. On a somewhat larger scale, methacrylate polymers (including perdeuteriated poly(methyl methacrylate)) are used in optical fibers for transmission of light over short distances. The recently discovered group transfer polymerization uses organosilicon synthesis methodology to prepare methacrylate polymers with carefully tailored physical properties.[30] This type of polymerization extends the virtues of coordination catalysis to monomers with reactive functional groups. New polymerization methods will also be useful in development of biocompatible polymers, which are tailored for use in prosthetic devices such as cartilage and artery transplants.

Ceramics is another discipline that should benefit from the infusion of organometallic expertise. Ceramics research has received strong impetus from the requirements of the electronics industry for strong, stable materials with specific physical and electronic properties. Silicon chip devices, for example, are customarily "packaged" in an alumina matrix, a material chosen for low dielectric constant and reasonable thermal conductivity. Other materials such as silicon carbide, silicon nitride, and aluminum nitride are potentially superior in various applications but have proven extraordinarily difficult to fabricate. A promising approach to production of shaped objects of these materials is production of "preceramic polymers". These materials, such as polycarbosilanes which contain $[Si(H)-(CH_3)CH_2]_n$ units, can be fabricated by conventional polymer-forming methods but are subsequently pyrolyzed to ceramic objects (e.g., SiC) that retain the shape of the preceramic polymer.[31] In such applications, the organometallic precursors are used stoichiometrically rather than as catalysts.

Similarly, in the synthesis of III–V (13–15[34]) semiconductors such as gallium arsenide, main-group organometallic compounds are used stoichiometrically in synthesis techniques such as MOCVD (metal–organic chemical vapor deposition).[32] The methodology is still underdeveloped because the III–V semiconductors are just entering commercial production. These materials find use in ultrahigh speed microcircuitry in the generation of supercomputers now under development. The III–V materials also provide the basis for light-emitting devices and photon detectors in electrooptic circuitry used in conjunction with fiber optic communications. Gallium arsenide and Al-doped GaAs are the prime materials currently, but indium phosphide appears very promising for optical applications.

In areas such as specialty polymers, ceramics, and semiconductor synthesis, a great deal of empirical organometallic research is currently conducted by persons trained in other disciplines. Organometallic chemists have an outstanding opportunity to contribute to both the science and the technology of these fields.

**Solid-State Organometallic Science.** Another area of major scientific opportunity is the study of organometallic compounds in the crystalline or glassy states. The physical properties of organometallic solids have received far less attention than those of pure inorganic compounds or even of organic compounds. In general, most studies of organometallic solids have not gone beyond determination of molecular structure in the crystal. Interesting properties such as conductivity, magnetism, and optical effects have been neglected. Sometimes the neglect has been for good reason; organometallic chemists have concentrated on diamagnetic molecules in order to utilize NMR for characterization. Nevertheless, these underexplored areas can offer fascinating science. Recent studies of crystalline decamethylferrocenium salts of paramagnetic anions have uncovered a variety of magnetic properties that are extremely sensitive to the nature of the anion.[33] The practical ramifications are not clear, but the science is intriguing.

Another area that has not received much study is the optical properties of organometallic compounds. In particular, the nonlinear optical properties, which are dependent on light intensity, are virtually unexplored for both organometallic and coordination complexes. Much of the neglect of this area seems attributable to the fact that organometallic chemists seldom have the tools or the training to measure these properties. Despite the difficulties, however, the study of nonlinear optical properties should be exceptionally rewarding because the field is young and the basic principles are still being elucidated. The variety of electronic properties that can be built into organometallic and coordination complexes make these compounds exceptionally attractive for the design of nonlinear optical effects. Various nonlinear effects are potentially valuable in frequency doubling and in optical switching modulation and memory devices.

One difficulty with work in solid-state organometallic chemistry is that most organometallic chemists lack the skills and background needed for work in the area. We have skills in synthesis, structure determination, and characterization of reactivity that have served well for using organometallics as reagents or catalysts. We need to complement these skills with those needed for determination and interpretation of physical properties. The quickest and most effective remedy is through partnership with physicists, physical chemists, and spectroscopists. They have the necessary physical expertise but often lack the chemical expertise to design and synthesize molecules and solids of interest. Such collaborations require effort, but they can be mutually rewarding and can advance the science most effectively.

**Metals in Medicine.** Organometallic compounds are once again beginning to receive serious consideration as agents for the diagnosis and treatment of disease. At one time, organoarsenic compounds such as Salvarsan were used in treatment of syphilis and organomercurials were sold widely as antiseptics. These relatively toxic products were displaced by natural and synthetic antibiotics. Medicinal studies of organometallics received little attention until the 1970s. Coordination complexes of the transition metals have had some conspicuous successes in this area (e.g., *cis*-platin in treatment of testicular cancer and technetium complexes in radiographic imaging). In contrast, little research was done on organometallic compounds as pharmaceuticals and imaging agents. In principle, organometallics can be tailored to deliver a metal ion to almost any part of the body by proper design of the organic ligand. In practice, this intellectual approach to design of targeted reagents has had only limited use. One

(30) Webster, O. W. In *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 1986.
(31) Wynne, K. J.; Rice, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 297–334.
(32) Moss, R. H. *Chem. Br.* **1983**, 735–737.

(33) Miller, J. S.; Calabrese, J. C.; Epstein, A. J.; Bigelow, R. W.; Zhiang, J. H.; Reiff, W. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1026–1028.
(34) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

problem has been the lack of fundamental information on the molecular biology of the target cells. The basic principles of biology at the molecular level are still not always clear.

Just as in solid-state research, the quickest and most effective way for the organometallic chemist to become effective in this area is to form a partnership with an appropriate biologist (immunologist, radiologist, enzymologist, ...). The collaboration can be very stimulating, but it requires openness on the part of both parties to learn the other's jargon and idiosyncratic thought patterns.

## Summary

The role of the organometallic chemist in industry is changing substantially. While the traditional role of providing expertise for design of organometallic and coordination catalysts will remain important, the objectives will shift to production of smaller volume, higher value products such as pharmaceuticals, agrichemicals, and specialty polymers. Attractive opportunities are emerging in organometallic approaches to preparation of sensors, ceramics, and semiconductors.

As the American chemical industry moves toward businesses in health care products and electronic and optical materials, opportunities arise in some relatively unexplored areas of organometallic science. Although the chemical properties of organometallics are well-explored, much less research has been done on the biological and physical properties (e.g., conductivity, magnetism, optical). Work in these new areas will be multidisciplinary in nature. It will require initiative on the part of the organometallic chemist to work effectively with ceramists, physicists, and molecular biologists. In general, the effort required to establish such collaborations will be rewarded with new opportunities in both fundamental science and applied technology.

It is clear that the future of organometallic chemistry in industry is not a simple extrapolation of past trends. The chemical industry is changing character rapidly, and organometallic chemistry is strongly affected. The future appears bright for those willing to grasp the opportunities presented by these changes.

# Photolysis of Acylpolysilanes Containing α-Hydrogens. Formation of Linear Head-to-Head Silene Dimers

Kim M. Baines and A. G. Brook*

*Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, Toronto M5S 1A1, Canada*
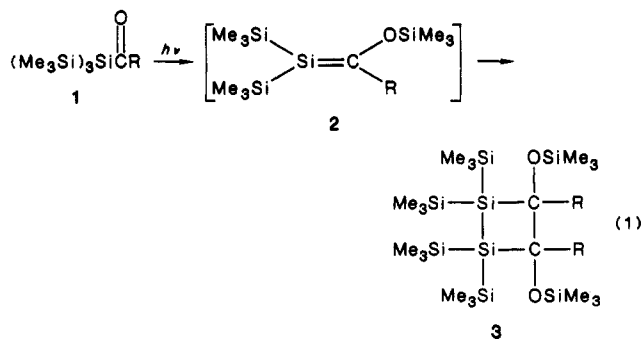
The photolysis of a series of acylpolysilanes, $(Me_3Si)_3SiCOR$ (R = $CH_2CH_3$, $CH(CH_3)_2$, $CH_2Ph$ (1b–d)), containing α-hydrogens has been investigated. The photoproducts, linear (4b–d) and cyclic (3c,d) head-to-head dimers of the intermediate silenes $(Me_3Si)_2Si$=$C(OSiMe_3)R$, were fully characterized by IR and $^1H$, $^{13}C$, and $^{29}Si$ NMR spectroscopy and mass spectrometry.

## Introduction

The chemistry of silenes has been a very active area of research over the last 20 years;[1] however, only recently has the isolation and characterizations of solid, stable silenes been accomplished.[2] Most often, the existence of silenes as reactive intermediates has been proven by the isolation and characterization of their trapping products. Alcohols (e.g. methanol) or dienes (e.g. 2,3-dimethylbutadiene) trap silenes cleanly and in high yield and thus have been used frequently for this purpose.[1] In the absence of trapping reagents, the common fate of these reactive species is head-to-tail dimerization to give 1,3-disilacyclobutanes. Again, this reaction proceeds cleanly and in high yield and thus has also been used as proof of an intermediate silene.[1]

Silenes, derived from the photolysis of acyltris(trimethylsilyl)silanes, are unusual since they consistently undergo head-to-head dimerization in the absence of a trapping reagent to give 1,2-disilacyclobutanes (eq 1).[3]



A second type of head-to-head dimer has been observed when the intermediate silene contains α-hydrogens in the R group. Thus, when acetyltris(trimethylsilyl)silane (1a, R = Me) was photolyzed in inert solvent, a linear

(1) For recent reviews see: (a) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* 1986, *25*, 1. (b) Raabe, G.; Michl, J. *Chem. Rev.* 1985, *85*, 419. (c) Wiberg, N. *J. Organomet. Chem.* 1984, *273*, 141.

(2) (a) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* 1982, *104*, 5667. (b) Nyburg, S. C.; Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Wong-Ng, W. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 1985, *C41*, 1632. (c) Wiberg, N.; Wagner, G.; Muller, G. *Angew. Chem., Int. Ed. Engl.* 1985, *24*, 229. (d) Wiberg, N.; Wagner, G. *Chem. Ber.* 1986, *119*, 1455. (e) Wiberg, N.; Wagner, G. *Chem. Ber.* 1986, *119*, 1467.

(3) (a) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* 1979, *101*, 83. (b) Brook, A. G.; Kallury, R. K. M. R.; Poon, Y. C. *Organometallics* 1982, *1*, 987.