Mark Efimovich Vol'pin: the path to science

I. S. Akhrem

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: cmoc@ineos.ac.ru

Mark Efimovich Vol'pin was born on May 23, 1923, in Simferopol into the family of doctors. The family often moved to new places, and Mark Efimovich learned Ukrainian and Turkmenian. From his early years, he showed interest in chemistry. In 1938, Vol'pins came in Moscow. At that time, a technical educational center for children was organized at the Polytechnic Museum; and young Vol'pin enthusiastically started to study at the section of chemistry of this center. In 1939, he became a winner of the first All-Union Olympiad for young chemists and was admitted to the Department of Chemistry of the Moscow State University without entrance exams. He successfully completed the first year, but then his education was interrupted by the war.

In 1941, M. E. Vol'pin volunteered in the Army, but soon he was released because of health. During the three subsequent years he worked at the central chemical laboratory of the Ural tank construction plant in Miass (Chelyabinsk Region). These were hard and lean years; he had to work for 12—16 hours under conditions of almost no accident prevention. His lungs, injured during these years, told on him till the end of his life. At the Ural plant, M. E. Vol'pin worked his way up from a laboratory assistant to deputy head of the laboratory, and introduced many new methods into analytical practice. The method for quick determination of tin in bronzes developed by Mark Efimovich was presented at the All-Union competition organized by the Ministry of Nonferrous Metallurgy, and was among the three best works. Only in 1945 did Vol'pin return to the University. At that time, a students' scientific society was organized at the Department of Chemistry. A. F. Platé, who was one of the guides of this society, became a teacher and a friend of Mark Efimovich for many years. A. F. Platé was the supervisor of M. E. Vol'pin's Ph.D. Thesis, entitled "Reactions of alkenes with ammonia in the presence of oxide catalysts; synthesis of acetonitrile" (1952).

In 1953, M. E. Vol'pin started to work in the Section of Theoretical Organic Chemistry at the All-Union Institute of Scientific and Technical Information (VINITI). The Head of the Section, Dmitrii Nikolaevich Kursanov, highly appreciated Vol'pin and invited him to carry out experimental research at his laboratory at the Institute of Organoelement Compounds of the USSR Academy of Sciences (INEOS). In 1958, Vol'pin joined the staff of this Institute. Owing to his work with D. N. Kursanov, who was a prominent scientist and a very cultured person of encyclopedic learning, in a company of people enthusiastic about chemistry, Mark Efimovich quickly showed his talent, and very soon he obtained important scientific results. The subsequent scientific activity of Vol'pin was entirely associated with the Institute of Organoelement Compounds. At this Institute, he accomplished his prominent works, which are recognized all over the world.

The first studies of M. E. Vol'pin were devoted to nonbenzenoid aromatic compounds. He had been interested in the problem of aromaticity back in his student years. Vol'pin's fundamental works dealing with the chemistry of tropylium and cyclopropenylium cations are widely known.[1] He showed that the properties of the tropylium cation are determined, on the one hand, by the fact that it is a carbocation and, on the other hand, by the fact that it is an aromatic system.[2] As a carbenium ion, tropylium reacts with a wide range of nucleophiles,[3] whereas its aromatic nature accounts for its fairly high stability. Indeed, cycloheptatrienylium cations are the most stable carbocations, able to exist in aqueous solutions. Since rotation of the seven-membered ring in the crystal precluded direct X-ray diffraction analysis of tropylium salts,[4] Vol'pin proved the equivalence of all the C—C bonds in the tropylium cation using a ^{14}C isotope label.[5] Since the formation of an aromatic system is favorable, the $C_7H_7^+$ cation is extremely easily generated upon cleavage of the C—H, C—O, and C—C

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 767—770, May, 1998.

1066-5285/98/4705-0735 $20.00

bonds in cycloheptatriene derivatives, induced even by relatively weak electrophilic systems.[6] Vol'pin discovered a very interesting interconversion of two aromatic systems, namely, transformation of tropylium into benzene on treatment with H_2O_2 and transformation of benzene into tropylium upon the addition of a monohalocarbene.[7] Using the addition of a dihalocarbene to tolan, Vol'pin synthesized for the first time a novel compound that represented an aromatic system involving two p-electrons, namely, diphenylcyclopropenone, which is the three-membered analog of tropone.[8] This work marked an important stage in the research carried out by Vol'pin: from carbenes, he proceeded to the idea of possible existence of carbene heteroanalogs that could be used to synthesize heteroanalogs of cyclopropenylium.[8] Despite the fact that the addition of GeI_2 and $SiMe_2$, prepared *in situ*, to acetylene derivatives yielded only six-membered heterocyclic compounds,[10] the idea of the possible existence of unsaturated three-membered heterocycles proved to be fruitful; later, heteroanalogs of cyclopropene, containing various atoms such as Si,[11] Ge,[12] B,[13] Sn,[14] SO_2,[15] and P,[16] have been prepared. Thus, the prediction that these derivatives could be stable proved to be correct. For the works dealing with non-benzene aromatic compounds, M. E. Vol'pin and D. N. Kursanov were awarded the Lenin Prize.

The discovery of molecular nitrogen fixation under mild conditions was the most sensational among Vol'pin's works. In 1964, M. E. Vol'pin and V. B. Shur accomplished the first transformation of dinitrogen into ammonia under mild conditions under the action of transition metal compounds.[17,18] Later, systems able to serve as catalysts for this process have been found.[19] The synthesis of aniline and its derivatives from dinitrogen was fundamentally important.[20] The paper by Vol'pin and Shur published in *Nature* in 1966[18] aroused wide interest in the world and initiated studies on nitrogen fixation in the USA, Japan, Great Britain, Italy, The Netherlands, Germany, Poland, Switzerland, and other countries. For the series of work dealing with nitrogen fixation, M. E. Vol'pin and his coworkers were awarded the USSR State Prize.

At present, a large number of systems capable of transforming dinitrogen into ammonia, hydrazine, and amines are known;[21,22] various dinitrogen complexes have been synthesized, and examples of their convertion into various nitrogen-containing compounds on treatment with certain reagents have been found.[21–24] A. E. Shilov and coworkers discovered nitrogen fixation in protic media and developed a method for the synthesis of hydrazine from N_2.[22] Perhaps, even more efficient nitrogen-fixing systems, permitting dinitrogen to be used as a conventional chemical reagent, can be found in the future.

M. E. Vol'pin and I. S. Kolomnikov hold the priority in discovering the metal-complex activation of CO_2. Similarly to nitrogen, carbon dioxide is present in the atmosphere; therefore synthesis of organic compounds based on CO_2 is of prime importance. In 1967, Vol'pin and Kolomnikov discovered[25] that many transition metal compounds form complexes with carbon dioxide; they demonstrated that CO_2 is capable of being inserted into M—H and M—R bonds (where M is a transition metal).[26–28] The metal-complex activation of carbon dioxide is now a vigorously developing field of catalysis. In a recent review,[29] it was claimed that transformation of CO_2 into valuable products will be associated with the use of metal-complex catalysis. Undoubtedly, the research along this line has been stimulated by Vol'pin's works.

Of the numerous studies carried out by M. E. Vol'pin in the field of organometallic chemistry, we will consider two series of work. M. E. Vol'pin and I. Ya. Levitin performed elegant experiments in which they were able for the first time to stabilize a metal in a high oxidation state; more precisely, they obtained Co and Rh with an oxidation number of +4 stabilized in chelate complexes containing metal—carbon bonds. It was shown that the M—C bond in these complexes can undergo not only homolytic cleavage (this had been a known fact) but also heterolytic cleavage.[30–32]

The idea of another work related to organometallic chemistry was outlined in the report presented by M. E. Vol'pin at the Presidium of the Academy of Sciences. It read: "If we look at graphite from the viewpoint of nonclassical concepts of the modern chemistry of transition metals, we can imagine possible formation of new types of organometallic compounds from it. It can be expected that, by analogy with sandwich compounds like dibenzenechromium, we could obtain a sort of "puff-pastry" in which metal atoms, located between the graphite layers, form π-bonds with the aromatic networks of graphite." Proceeding from this idea, M. E. Vol'pin and Yu. N. Novikov synthesized compounds of transition metals with graphite. In these studies, they discovered diverse types of bonding between metal atoms and graphite networks. Graphite compounds with molybdenum were built as bis-arene complexes, whereas those with iron were half-sandwiches; nickel formed a planar hexagonal network, and the compound with cobalt consisted of corrugated layers of metal atoms arranged between the graphite networks. Some of the complexes exhibited interesting catalytic properties.[33–37] Vol'pin's works dealing with graphite compounds have been awarded the A. N. Nesmeyanov Gold Medal.

Synthesis of new types of compounds and activation of inert molecules have always been the focus of attention of M. E. Vol'pin. His approach to various tasks has been distinguished by interest in fundamental problems and search for simple solutions. M. E. Vol'pin and his coworkers were the first to carry out works on nucleophilic activation of Hg,[38] cleavage of inert Si—C bonds in silaparaffins by transition metal compounds,[39] and cleavage of Si—H bonds in trialkylsilanes under the action of fluoride ions.[40] Later, the activation of organosilicon compounds by transition metal compounds and ionic fluorides has become a routine method in organosilicon synthesis. These studies have stimulated M. E. Vol'pin's work on the activation of δ-bonds in alkanes.

In the late 1960s, vigorous development of the chemistry of alkanes began. Leading scientific groups in various countries became engaged in this research. Nevertheless, M. E. Vol'pin and I. S. Akhrem were able to find original approaches to this problem. They discovered new efficient catalysts for hydrocracking of alkanes based on Ziegler type complexes and small osmium clusters stabilized by carbon-containing ligands.[41–43] However, the most impressive of Vol'pin's achievement along this line is certainly the development of new types of superelectrophiles, whose reactivity toward alkanes substantially exceeds the reactivities of all the known electrophilic systems including the strongest protic superacids.[44] Under the action of the novel superelectrophilic complexes, alkanes and cycloalkanes have been involved in a broad range of transformations, including direct functionalization, many of which are selective and give products in high yields. Study of the nature of the active systems revealed the large diversity of the types of superelectrophiles.[46] The discovery of the new type of superelectrophiles was a step forward to the direct synthesis of organic compounds from alkanes and cycloalkanes.

In recent years, M. E. Vol'pin made a contribution to the field of fullerenes. He suggested that if a biologically active hydrophobic group is attached to the bulky fullerene group, the resulting fullerene derivatives would exhibit unusual biological activities. Together with Z. N. Parnes,[45] he synthesized a number of water-soluble monosubstituted amino-acid and dipeptide derivatives. The first results showed that these compounds increase the activity of immunoactivating agents by several orders of magnitude, *i.e.*, they exhibit adjuvant capacity.

Being a broad-minded scientist, M. E. Vol'pin took great interest in the chemical aspects of life and was constantly trying to apply his chemical knowledge to biology and medicine. He was indubitably among the pioneers in bioinorganic chemistry. Vol'pin suggested that transition metal complexes with chelating macrocyclic ligands, which catalyze oxidation of natural substrates by oxygen, should be active in biological systems.

Since the late 1960s, M. E. Vol'pin and G. N. Novodarova have studied the ability of transition metal compounds to "shunt" the enzymatic reactions that determine the vitally important processes of respiration, photosynthesis, *etc.*[46] A significant result obtained in these studies is the proof of formation of active forms of oxygen from O_2 molecules upon the action of a natural reducing agent, ascorbic acid, in the presence of cobalt and iron complexes in chemical and biochemical systems.[47,48] The active forms of oxygen affect the key cell targets, DNA and RNA, and normally induce nonselective rupture of their chains. However, if an addressing oligonucleotide is grafted to the metal complex, then this complementary chain will be fixed near the DNA target in such a way that each nitrogen base of the nucleotide is bound to the corresponding nitrogen base of the DNA target. In this case, rupture of the DNA target will be selective. This idea was realized.[49] It is clear that this approach opens up the way for specified structural transformations of the genetic cell apparatus.

In the last several years, M. E. Vol'pin directed much effort toward development of anticancer preparations. The foundations for this research were laid by his earlier studies dealing with the synthesis and chemical properties of transition metal chelates including their behavior in biochemical systems. According to the approach used by M. E. Vol'pin, transition metal complexes acting as sources of free radicals have been employed as selective antitumor preparations. Two types of compounds were especially interesting. The first type included complexes that generate active forms of oxygen. The selectivity of their action is due to the specific affinity of polydentate ligands (for example, porphyrins) for tumor tissue. The second type comprised tridentate cobalt chelates with Schiff bases containing Co—C bonds and behaving as pH-dependent sources of carbon-centered free radicals.[31,32] Since a tumor cell is characterized by increased acidity, it has been expected that it is in this cell that free radicals would be formed. The first papers,[50,51] reports at conferences,[52] and materials for patenting appeared in 1996, which was the last year of Mark Efimovich's life.

M. E. Vol'pin's studies in organometallic chemistry have received wide recognition all over the world. In 1979, he was elected a Corresponding Member of the USSR Academy of Sciences, and in 1987, he became a Full Member of the Academy. In 1991, M. E. Vol'pin was elected a member of the European Academy (*Academia Europea*).

M. E. Vol'pin possessed great talent and remarkable scientific intuition; he passed on his creative energy to people around him. Vol'pin's contribution to science cannot be evaluated merely by the number of published papers, trained pupils, and honorary rewards. The main thing he gave to science can be expressed by the following words: he gave food for thought. His ideas, heard and taken up by other people, will be influencing the development of science for many years to come and will thus continue his legacy.

References

1. (a) A. N. Nesmeyanov and N. A. Nesmeyanov, *Nachala organicheskoi khimii* [*Fundamentals of Organic Chemistry*], Khimiya, Moscow, 1974, **I**, 536 (in Russian); (b) A. N. Nesmeyanov and N. A. Nesmeyanov, *Nachala organicheskoi khimii* [*Fundamentals of Organic Chemistry*], Khimiya, Moscow, 1974, **II**, 462 (in Russian).
2. D. N. Kursanov and M. E. Vol'pin, *Dokl. Akad. Nauk SSSR* [*Comm. USSR Akad. Sci.*], 1957, **113**, 339 (in Russian).

3. (a) M. E. Vol'pin, I. S. Akhrem, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* [*Bull. USSR Acad. Sci., Div. Chem. Sci*], 1957, 1501 (in Russian); (b) M. E. Vol'pin, I. S. Akhrem, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR* [*Comm. USSR Akad. Sci.*], 1958, **120**, 531 (in Russian); (c) M. E. Vol'pin, I. S. Akhrem, and D. N. Kursanov, *Zh. Obshch. Khim.* [*J. Gen. Chem.*], 1959, **29**, 2855; 1960, **30**, 159, 1187 (in Russian); (d) Z. N. Parnes, M. E. Vol'pin, and D. N. Kursanov, *Tetrahedron Lett.*, 1960, **21**, 20.
4. (a) A. I. Kitaigorodskii, Yu. T. Struchkov, T. L. Khotsyanova, M. E. Vol'pin, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* [*Bull. USSR Acad. Sci., Div. Chem. Sci*], 1960, 39 (in Russian); (b) A. I. Kitajgorodsky, T. L. Khocjanova, and Yu. T. Struchkov, *Acta Crystallogr.*, 1957, **10**, 797.
5. M. E. Vol'pin, D. N. Kursanov, M. I. Shemyakin, V. I. Maimind, and L. A. Neyman, *Chem. Ind.*, 1958, **39**, 1261.
6. M. E. Vol'pin, I. S. Akhrem, *Dokl. Akad. Nauk SSSR*, 1965, **161**, 597 [*Dokl. Chem.*, 1965, **161** (Engl. Transl.)].
7. M. E. Vol'pin, D. N. Kursanov, and V. G. Dulova, *Tetrahedron*, 1960, **8**, 33.
8. D. N. Kursanov, M. E. Vol'pin, and Yu. D. Koreshkov, *Zh. Obshch. Khim.*, 1960, **30**, 2877 [*J. Gen. Chem. USSR*, 1960, **30** (Engl. Transl.)].
9. M. E. Vol'pin and D. N. Kursanov, *Zh. Obshch. Khim.*, 1962, **32**, 1137, 1142 [*J. Gen. Chem. USSR*, 1962, **32** (Engl. Transl.)].
10. (a) M. E. Vol'pin, V. G. Dulova, Yu. T. Struchkov, N. G. Bokiy, and D. N. Kursanov, *J. Organomet. Chem.*, 1967, **8**, 67; (b) M. E. Vol'pin, Yu. T. Struchkov, L. V. Vilkov, V. S. Mastryukov, V. G. Dulova, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* [*Bull. USSR Acad. Sci., Div. Chem. Sci*], 1963, 2067 (in Russian).
11. (a) D. Seyferth, D. C. Annarelli, and S. C. Vick, *J. Am. Chem. Soc.*, 1976, **98**, 6382; (b) K. Hirotsu, T. Higuchi, M. Ishikawa, H. Sugisawa, and M. Kumada, *J. Chem. Soc., Chem. Commun.*, 1982, 726.
12. (a) A. Krebs and J. Berndt, *Tetrahedron Lett.*, 1983, **24**, 4083; (b) M. P. Egorov, S. P. Kolesnikov, Yu. T. Struchkov, M. Yu. Antipin, S. V. Sereda, and O. M. Nefedov, *J. Organomet. Chem.*, 1985, **290**, 27.
13. (a) C. Pues and J. Berndt, *Angew. Chem.*, 1984, **96**, 306; (b) K. Krogh—Jespersen, D. Cremer, J. D. Dill, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1987, **103**, 2589.
14. L. R. Sita and R. D. Bickerstaft, *J. Am. Chem. Soc.*, 1988, **110**, 5208.
15. (a) L. A. Carpino and L. V. Mc Adam, III, *J. Chem. Soc., Chem. Commun.*, 1972, **3**, 178; (b) R. H. Rynbrandt and J. W. Sprewak, *J. Am. Chem. Soc.*, 1971, **93**, 476.
16. (a) O. Wagner, M. Ehle, and M. Regitz, *Angew. Chem.*, 1989, **101**, 227; (b) V. Haber, R. Boese, and M. Regitz, *Angew. Chem.*, 1990, **102**, 1523.
17. M. E. Vol'pin and V. B. Shur, *Dokl. Akad. Nauk SSSR*, 1964, **156**, 1102 [*Dokl. Chem.*, 1964, **156** (Engl. Transl.)].
18. M. E. Vol'pin and V. B. Shur, *Nature*, 1966, **209**, 1236.
19. M. E. Vol'pin, M. A. Ilatovskaya, L. V. Kosyakova, and V. B. Shur, *J. Chem. Soc., Chem. Commun.*, 1968, 1074.
20. (a) M. E. Vol'pin, V. B. Shur, R. V. Kudryavtsev, and L. A. Prodayko, *J. Chem. Soc., Chem. Commun.*, 1968, 1038; (b) M. E. Vol'pin, A. A. Belyi, V. B. Shur, N. A. Katkov, L. M. Nekayena, and R. V. Kudryavtsev, *J. Chem. Soc., Chem. Commun.*, 1971, 246; (c) V. B. Shur, E. G. Berkovich, S. M. Yunusov, Sh. N. Mamedov, I. L. Nizker, and M. E. Vol'pin, *Izv. Akad. Naul SSSR, Ser. Khim.*, 1977, 2841 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26** (Engl. Transl.)]; (d) E. G. Berkovich, V. B. Shur, M. E. Vol'pin, R. Lorenz, S. Rummel, and M. Wahren, *Chem. Ber.*, 1980, 113, 70.
21. M. E. Vol'pin and V. B. Shur, *New Trends in the Chemistry of Nitrogen Fixation*, Eds. L. M. da Camara Pina and R. L. Richards, Acad. Press, London, 1980, 67.
22. T. A. Bazhenova and A. E. Shilov, *Coord. Chem. Rev.*, 1995, **144**, 69.
23. A. D. Allen and C. V. Senoff, *J. Chem. Soc., Chem. Commun.*, 1965, 621.
24. H. Hidai and Y. Mizole, *Chem. Revs.*, 1995, **95**, 1115.
25. M. E. Vol'pin, I. S. Kolomnikov, and T. S. Lobeeva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* [*Bull. USSR Acad. Sci., Div. Chem. Sci*], 1969, 2084 (in Russian).
26. I. S. Kolomnikov, T. S. Lobeeva, V. V. Gorbachevskaya, G. G. Aleksandrov, Yu. T. Struchkov, and M. E. Vol'pin, *J. Chem. Soc., Chem. Commun.*, 1971, 972.
27. I. S. Kolomnikov, A. O. Gusev, T. S. Belopotapova, M. Kh. Grigoryan, T. V. Lysyak, Yu. T. Struchkov, and M. E. Vol'pin, *J. Organomet. Chem.*, 1974, **69**, 10.
28. M. E. Vol'pin and I. S. Kolomnikov, *The Reactions of Organometallic Compounds with Carbon Dioxide*, in *Organometallic Reactions*, Eds. E. I. Becker and M. Tsutsui, J. Wiley, New York, 1975, 5, 313.
29. D. Gibson, *Chem. Rev.*, 1996, 2063.
30. M. E. Vol'pin, I. Ya. Levitin, A. L. Sigan, and A. T. Nikitaev, *J. Organomet. Chem.*, 1985, **279**, 263.
31. I. Ya. Levitin, A. N. Kitaigorodskii, A. T. Nikitaev, V. I. Bakhmutov, A. L. Sigan, and M. E. Vol'pin, *Inorg. Chem. Acta*, 1985, **100**, 65.
32. I. Ya. Levitin, M. V. Tsikalova, V. I. Bakhmutov, A. I. Yanovsky, Yu. T. Struchkov, and M. E. Vol'pin, *J. Organomet. Chem.*, 1987, **330**, 161.
33. M. E. Vol'pin, Yu. N. Novikov, Yu. T. Struchkov, and V. A. Semion, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 2608 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1970, **19**, 2452 (Engl. Transl.)].
34. M. E. Vol'pin, Yu. T. Novikov, N. D. Lapkina, V. I. Kasatochkin, Yu. T. Struchkov, M. E. Kazakov, R. A. Sukan, and V. A. Povitskii, *J. Am. Chem. Soc.*, 1975, **97**, 3366.
35. Yu. N. Novikov and M. E. Vol'pin, *Physica*, 1981, **105B**, 471.
36. V. Tremel, R. Hoffmann, M. E. Vol'pin, and Yu. N. Novikov, *Metalloorg. Chem.*, 1988, **1**, 1370 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].
37. (a) M. E. Vol'pin and Yu. N. Novikov, *Coordination Chemistry of Graphite, Pure and Appl. Chem.*, 1988, **60**, 1133; (b) M. E. Vol'pin, *Graphite as an Aromatic Ligand*, in *Topics in Nonbenzenoid Aromatic Chemistry*, Tokyo, 1973, **1**, 269.
38. (a) M. E. Vol'pin, E. Ch. Tevdoradze, and K. P. Butin, *Zh. Obshch. Khim.*, 1970, **50**, 315 [*J. Gen. Chem. USSR*, 1970, **50** (Engl. Transl.)]; (b) M. E. Vol'pin and E. Ch. Tevdoradze, *Zh. Obshch. Khim.*, 1970, **50**, 1655 [*J. Gen. Chem. USSR*, 1970, **50** (Engl. Transl.)].
39. (a) I. S. Akhrem, N. M. Chistovalova, and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 2130 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1972, **21**, 2078 (Engl. Transl.)]; (b) I. S. Akhrem, D. V. Avetisyan, R. S. Vartanyan, and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 253 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26** (Engl. Transl.)]; (c) I. S. Akhrem, N. M. Chistovalova,

M. I. Mysov, and M. E. Vol'pin, *J. Organomet. Chem.*, 1974, **72**, 163; (d) I. S. Akhrem, N. M. Chistovalova, H. N. Safoyan, M. E. Vol'pin, and I. I. Moiseev, *J. Organomet. Chem.*, 1979, **178**, 23; (e) I. S. Akhrem, N. M. Chistovalova, A. V. Malysheva, and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2696 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 2417 (Engl. Transl.)].

40. (a) I. S. Akhrem, M. Deneux, and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 932 [*Bull. Acad. Sci. USSR*, 1973, **22** (Engl. Transl.)]; (b) M. Deneux, I. S. Akrem, D. V. Avetissian, E. I. Mysoff, and M. E. Vol'pin, *Bull. Soc. Chim. Fr.*, 1973, **9**, 2638.

41. M. E. Vol'pin, I. S. Akhrem, S. V. Reznichenko, and V. V. Grushin, *J. Organomet. Chem.*, 1987, **334**, 109.

42. I. S. Akhrem and M. E. Vol'pin, *Usp. Khim.*, 1990, **59**, 1906 [*Russ. Chem. Rev.*, 1990, **59**, 1118 (Engl. Transl.)].

43. I. S. Akhrem, S. V. Reznichenko, N. M. Chistovalova, V. V. Grushin, and M. E. Vol'pin, *Catal. Lett.*, 1993, **20**, 275.

44. I. S. Akhrem and A. V. Orlinkov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 771 [*Russ. Chem. Bull.*, 1998, **47**, 735 (Engl. Transl.)] (see also references therein).

45. M. E. Vol'pin, Z. N. Parnes, and V. S. Romanova, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1050 [*Russ. Chem. Bull.*, 1998, **47**, 1021 (Engl. Transl.)] (see also references therein).

46. M. E. Vol'pin, G. N. Novodarova, E. M. Kolosova, N. N. Gushova, A. N. Kononenko, and Yu. N. Leiken, *Inorg. Chim. Acta*, 1981, **50**, 21.

47. M. E. Vol'pin and G. N. Novodarova, *Catal. Lett.*, 1990, 265.

48. M. E. Vol'pin and G. N. Novodarova, *J. Mol. Catal.*, 1992, **74**, 153.

49. V. M. Belkov, N. F. Krynetskaya, E. M. Volkov, Z. A. Shabarova, N. Yu. Krainova, and G. N. Novodarova, *Bioorg. Khim.*, 1995, **21**, 446 [*Russ. J. Bioorg. Chem.*, 1995, **21** (Engl. Transl.)].

50. (a) M. E. Vol'pin, I. Ya. Levitin, and S. Osinsky, *Angew. Chem, Int. Ed. Engl.*, 1996, **35**, 2395; (b) I. Ya. Levitin, V. M. Belkov, G. N. Novodarova, Z. N. Shabarova, and M. E. Vol'pin, *Mendeleev. Commun.*, 1996, **4**, 153; (b) S. Osinsky, I. Levitin, L. Bubnovskaya, N. Komuta, I. Ganusevich, M. Tsikalova, and M. Vol'pin, *Med. Biol. Environ.*, 1997, **25** (1), 75; (d) S. Osinsky, I. Levitin, L. Bubnovskaya, I. Ganusevich, M. Tsikalova, E. Zhavrid, Yu. Istomin, and M. Vol'pin, *Anticancer Res.*, 1997, **17**, 35a, 3457.

51. M. E. Vol'pin, N. Yu. Krainova, I. V. Moskaleva, G. N. Novodarova, G. N. Vorozhtsov, M. G. Gal'pern, O. Ya. Kaliya, E. A. Luk'anets, and S. A. Mikhalenko, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2105 [*Russ. Chem. Bull.*, 1996, **45**, 2000 (Engl. Transl.)]; (b) V. M. Belkov, N. F. Krynetskaya, Z. A. Shabarova, G. N. Novodarova, and M. E. Vol'pin *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2112 [*Russ. Chem. Bull.*, 1996, **45**, 2008 (Engl. Transl.)].

52. (a) M. E. Vol'pin, I. Ya. Levitin, and S. P. Osinsky, *Proc. 3rd European Conference on Bioinorganic Chemistry*, Noordwijkerhout (The Netherlands), 1996, P2; (b) G. N. Novodarova, V. M. Belkov, M. E. Vol'pin, and Z. A. Shabarova, *6th International Symposium on the Activation of Dioxygen and Homogeneous Catalytic Oxidation, Posters, Program and Abstracts*, Noordwijkerhout (The Netherlands), 1996, 216.

Received February 19, 1998