# The Pioneering Mark E. Vol'pin: Toward Small Molecule Activation

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***Abstract*—This article summarizes the life and work of an eminent Russian scientist Mark Vol′pin. He pioneered small molecule activation chemistry by transition metal complexes including fixing atmospheric dinitrogen molecule under mild conditions. The life and work of Vol′pin in erstwhile Soviet Union is discussed.**

***Keywords*—Small Molecule, Nitrogen; Activation, Metal Complex**

## I. INTRODUCTION

Nitrogen is an essential ingredients in all different life forms. Amino acid, proteins, DNA and RNA contain nitrogen. Nitrogen is present in fertilizer and explosives. The source of nitrogen is dinitrogen gas in the air. The triple bond between two nitrogen atoms makes dinitrogen inert and hence difficult to be assimilated. Nitrogen fixation is an important process. Naturally,lightening causes nitrogen fixation from air. Biological nitrogen fixation is carried out by enzymes named nitrogenase. Haber process is used for industrial synthesis of ammonia from nitrogen and hydrogen using Fe based catalyst. However, it requires high temperature and gas pressure. Vol′pin was the first to show that nitrogen could be activated under ambient conditions by metal complexes. His work initiated the small molecule activation chemistry which has assumed great significance in recent years for alternative energy. This short review described the life and work of Mark Vol′pin [1].

## II. LIFE AND WORK OF MARK VOL′PIN

Mark Vol′pin was born in Sympheropol (Crimea, Ukraine) on May 23, 1923, in the family of a medical doctor. At age 17, he entered the Chemistry Department of Moscow State University, but his education was interrupted by the war. In 1941, he joined the Red Army. But, he was soon released from active war duty because of ill health and subsequently posted at armament factories in the Ural region. At the Ural plant, he started as a laboratory assistant and worked his way up to become deputy head of the laboratory. Here he developed new methods for metal analysis including a technique for quick determination of tin in bronze. After the war, Vol′pin resumes his education at Moscow State University (1945).

Vol′pin worked under the supervision of Professor A. F. Plate´ at Moscow University for his Ph.D. thesis (1952) entitled “Interaction of olefins with ammonia in the presence of oxide catalysts: Synthesis of Acetonitrile”. After a brief spell in Section of Theoretical Organic Chemistry at All-Union Institute of Scientific and Technical Information, he joined Institute of Organ element Compounds (INEOS) at Moscow in the laboratory of Professor D. N. Kursanov. In 1964, he became the head of the laboratory for the study of organometallic catalysts, and 1988 he became the director of the Institute. In this institute he performed his most outstanding work and created several new fields of research.

Vol′pin started his independent career as an organic chemist, moved to organ metallic chemistry, and then to biological chemistry. In his initial days, Vol′pin was interested in non-benzenoid aromatic system and conducted fundamental research on tropylium and cyclopropenyliumcations [2].The tropylium ion (Figure 1) has molecular formula $[C_7H_7]^+$; it is aromatic and isolated as a salt. Tropyliumtetrafluoroborate is synthesized from Tropilidene(cycloheptatriene) by reacting with $PCl_5$ in carbon tetrachloride solvent and subsequent treatment with 50% aqueous fluoboric acid affords the salt. This is a modification of the original method published by Vol'pin. He also reported an interesting inter-conversion between two aromatic systems - tropylium to benzene on treatment with $H_2O_2$ and the reverse reaction upon the addition of a monohalocarbene to benzene.

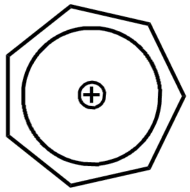


Fig. 1 Schematic drawing of tropylium ion.

The tropylium ion is frequently encountered in mass spectrometry for aromatic compounds containing a benzyl unit exhibiting a signal at m/z = 91. Upon ionization, the benzyl fragment is cleaved off as a cation ($PhCH_2^+$), which rearranges to the stable tropyliumcation ($C_7H_7^+$).

He showed that tropyliumion reacts with a wide range of nucleophiles in accordance with its carbenium character, whereas its aromatic (6π electron) character is responsible for its stability. Vol'pin was the first to synthesize diphenylcyclopropenone, a three-membered analogue of tropone that represented an aromatic system involving two π-electrons. Building on this concept, he further synthesized several heteroanalogs of cyclopropene.

The discovery of molecular $N_2$ fixation under mild conditions is undoubtedly the most significant work of Vol′pin [3-4].The present day demand of chemically accessible nitrogen has surpassed the nature's capacity to fix atmospheric nitrogen to ammonia. The Haber-Bosch process is the primary synthetic means to access ammonia by high-pressure reaction of nitrogen and hydrogen over a heterogeneous Fe catalyst at high temperature[5]. It has been estimated that this energy-demanding process provides half of the total nitrogen required for agriculture and consume 1% of the world's energy supply. Nitrogenase enzymes convert atmospheric nitrogen to ammonia at ambient conditions. Nitrogenase binds dinitrogen, and utilizes the metal electrons to reduce nitrogen, allows protonation and then releases fixed nitrogen asammonia. The most common nitrogenise enzyme consists of a Fe-Mo-S cluster (Figure 2) as the active catalytic centre. Nitrogenase enzymes also contain different metal cofactor, containing Fe and Mo or V depending on the bio-availability [6-7].

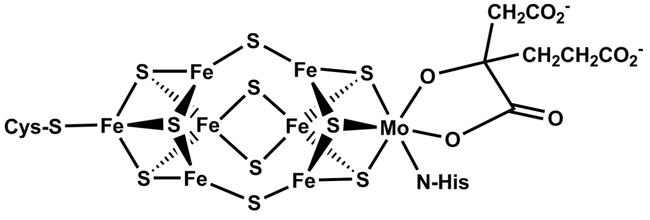
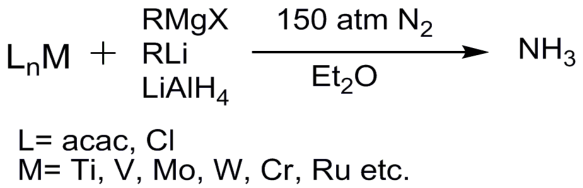


Fig. 2. Schematic drawing of Fe-Mo-S cluster

Vol'pin was the first (1964) to accomplish transformation of dinitrogen to ammonia under mild conditions by transition metal compounds (Equation 1). Subsequently, catalytic systems were also developed. The 1996 *Nature* paper by Vol'pin stimulated a serious research on metal-nitrogen complexes. Subsequent research has led to a large number of metal-nitrogen complexes containing both transition metal and lanthanides. The first stable dinitrogen complex $[Ru(NH_3)_5(N_2)]^{2+}$ was synthesized from an aqueous solution of hydrazine with ruthenium trichloride (1965) [8]. Earlier work on zero-valent Mo and W soon established a catalytic nitrogen fixation cycle (Chatt cycle) that involves several key intermediates including $M(N_2)$, M–N=NH, M=N–$NH_2$, M≡N, M=NH, M–$NH_2$ and $M(NH_3)$ species [9].



$$L_nM + \begin{matrix} RMgX \\ RLi \\ LiAlH_4 \end{matrix} \xrightarrow[Et_2O]{150\ atm\ N_2} NH_3 \tag{1}$$

L= acac, Cl
M= Ti, V, Mo, W, Cr, Ru etc.

Several reaction intermediates have been isolated along the reaction pathway to ammonia production till date. These intermediates provide valuable mechanistic insight and identification of complexes possibly relevant for the generation of organo-nitrogen compounds. It is now well recognized that protonation occur first at the terminal nitrogen of the complexes. Many molybdenum and tungsten hydrazido complexes with various ligand systems have been isolated. The metal-hydrazido intermediate appears to be common to many nitrogen fixation systems. Notably, Schrock's Mo-HIPT system (Figure 3) has provided significant information on the ammonia production [10-11].

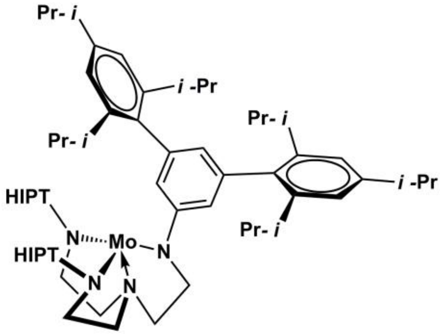


Fig. 3 Schematic drawing of Mo-HIPT system

As indicated above, a large number of metal-$N_2$ complexes have been structurally characterized. Two interesting examples, a linear dinuclear dinitrogen complex of iron supported by sterically demanding anionic diketiminato ligands has been prepared by the reduction of the (diketiminato)iron(II) chloride under $N_2$ (Figure 4). The $[\{(C_5Me_5)_2Sm\}_2(\mu_2\text{-}N_2)]$ exhibits novel planar side-on $N_2$ binding mode (Figure 5) [12].

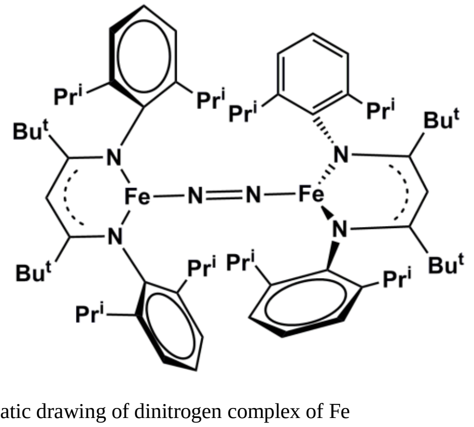


Fig. 4 Schematic drawing of dinitrogen complex of Fe

The relatively large negative charge density on the terminal nitrogen of end-on metal-$N_2$ complexes have been exploited to incorporate organic molecules. Although interesting chemistry is being developed for the incorporation of dinitrogen into organo-nitrogen compounds, these methods are not competitive with traditional methods for introducing nitrogen. Until the realization of a catalytic system, novel transformations with complexes derived from molecular nitrogen will continue to be of the most practical value for the generation of organo-nitrogen compounds.

Vol′pin was also the first one to report the activation of $CO_2$ by transition metal complex. It was demonstrated that $CO_2$ readily inserts into M-H or M-R bonds to form metal-formyl or metal–carboxyl complexes. Utilization of $CO_2$ to value-added products has become an important topic in contemporary organometallic chemistry. The present day activity has origin to Vol′pin's work that was initiated decades earlier [13-14].

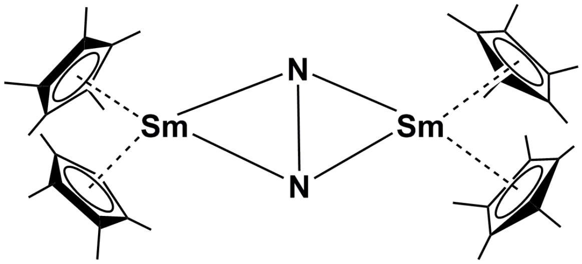


Fig. 5 Schematic drawing of $[\{(C_5Me_5)_2Sm\}_2(\mu_2\text{-}N_2)]$

Vol′pin also embarked on the chemistry of alkanes. His team developed a diverse range of superelectrophiles whose activities surpassed all known electrophilic systems including the strongest proticsuperacids. A broad array of transformations, including direct functionalization of alkanes and cycloalkanes were achieved raising the prospect of direct synthesis of organic compounds from readily available but inert alkanes [15].

Vol′pin's team has the distinction to be the first on several topics. His group synthesised lamellar graphite complexes with zero-valent transition metals and studied their catalytic properties. In his last years, Vol′pin directed his research towards biological chemistry involving inorganic complexes. He synthesized organometallic Co-Schiff base complexes which act as pH-dependent source of carbon-centered free radicals. His work underscored the potential of transition metal complexes for regulating enzymatic redox processes. Vol′pin introduced novel approaches for the chemotherapy of cancer and other serious diseases by metal complexes.

Vol′pin was a rational non-political intellectual who had his share of trouble with the communist regime in Soviet Union. There are many stories that remind us of the plight of open-minded academician in Soviet era. Vol′pin had a Jewish origin, but it was the general intolerance and dogmatic approach of the communist regime toward free thinking individual that resulted in his tribulation. In 1984, Vol′pin left the banquet of the International Symposium on Homogeneous Catalysis in Leningrad on his way to a conference in France. He never got there, but when he resurfaced in Moscow after few days he would not comment on exactly what happened in-between. In 1979, the Portuguese Academy invited Vol′pin to attend a major conference on nitrogen fixation. The officer of USSR Academy of Sciences did not bother to process his travel application. On hearing this, the President of the Portuguese Academy, an influential retired general, sent a strong message to the USSR Academy through its embassy in Moscow. Travel documents were issued immediately and Vol′pin could join the conference in the right time to address the congress. Next year he could attend the Royal Society of Chemistry meeting as Centenary Lecturer without much incident [16-17].

Vol′pin's outstanding contributions to chemistry are greatly appreciated by the scientific community. He was a member of the Soviet and then Russian Academy of Sciences and the Academia Europaea. He received highest national scientific awards, the Lenin Prize and the USSR State Prizes.

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## REFERENCES

[1] I. S. Akhrem, "Mark EfimovichVol′pin: The path to science", Russian Chemical Bulletin, vol. 47, pp. 735, 1998.

[2] D. N. Kursanov and M. E. Vol′pin, DokladyAkad. Nauk SSSR, vol.113, pp. 339, 1957.

[3] M. E. Vol′pin, V. B. Shur, "Nitrogen Fixation by Transition Metal Complexes", Nature, vol. 209, pp. 1236, 1966.

[4] M. E. Vol′pin, M.A. Ilatovskaya, L. V. ,Kosyakova, V. B. Shur , "Catalytic Fixation of Nitrogen", Chemical Communications, pp. 1074-1075, 1968.

[5] F. Haber, "BemerkungzuvorstehenderNotiz", Naturwissenschaften, vol. 11, pp. 339–340, 1923.

[6] P. A. McLean, D. A. Wink, S. K. Chapman, A. B. Hickman, D. M. McKillop, W. H. Orme-Johnson, Biochemistry, vol. 28, pp. 9402, 1989.

[7] J. Kim, D. C. Rees, Science, vol. 360, pp. 563, 1992.

[8] A. D. Allen, C. V. Senoff, "Nitrogenopentammineruthenium(II) complexes", J. Chem. Soc., Chem.Commun., vol. 24, pp. 621–622. 1965.

[9] J. Chatt, A. J. Pearman, R. L. Richards, J. Chem. Soc., Dalton Trans. pp. 1852. 1977.

[10] D. V. Yandulov, R. R. Schrock, Science, vol. 301, pp. 76, 2003.

[11] D. V. Yandulov, R.R. Schrock, J. Am. Chem. Soc., vol. 124, pp. 6252-6253, 2002.

[12] W. J. Evans, D. K. Drummond, L. R. Chamberlain, R. J. Doedens, S. G. Bott, H. Zhang, J. L. Atwood, "Synthetic, structural, and reactivity studies of the reduction and CO derivatization of azobenzene mediated by divalent lanthanide complexes", J. Am. Chem. Soc., vol. 110, pp. 4983–4994, 1988.

[13] M. E. Vol'pin, Pure Appl. Chem., vol. 30, pp. 607, 1972.

[14] M. E. Vol'pin, I. S. Kolomnikov, T. S. Loboeva, Izv. Akad.Nauk SSSR, Ser. Khim.,pp. 2084, 1969.

[15] [15] I. S. Akhrem, A. V. Orlinkov,M. E. Vol′pin "Alkane and Cycloalkane Transformations in Superelectrophilic Liquids", NATO Science SeriesVol. 92, pp 483-497, 2002.

[16] Yu. N. Bubnov, "Mark E. Vol′pin, 1923-1996 - In Memoriam", Inorganic Chemistry, vol. 36, pp. 749 – 750, 1997.

[17] P. Maitlis, "Obituaries: Mark EfimovichVol′pin", The Independent, 25 October 1996.