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Synthesis and structure of ferrocenylphosphinic acids



Ruslan P. Shekurov^a, Vasili A. Miluykov^{a,*}, Daut R. Islamov^b, Dmitry B. Krivolapov^a, Olga N. Kataeva^{a,c}, Tatyana P. Gerasimova^a, Sergey A. Katsyuba^a, Gulnaz R. Nasybullina^a, Vitaliy V. Yanilkin^a, Oleg G. Sinyashin^a

^aA.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, 8 Arbuzov Str., 420088 Kazan, Russia

^bA.M. Butlerov Chemistry Institute, Kazan Federal University, 420008 Kazan, Russia

^cLeibniz-Institute for Solid State and Materials Research IFW Dresden, Dresden, Germany

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ABSTRACT

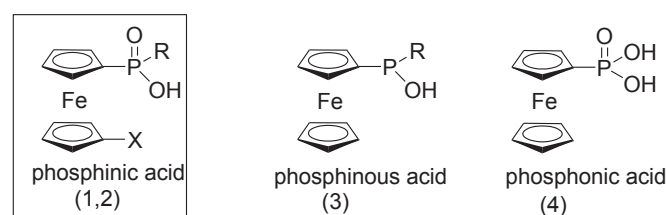
The series of ferrocenylphosphinic acids $\text{Fc}(\text{P}(\text{R})(\text{O})(\text{OH}))$ (**1a–d**) and ferrocene-1,1'-diyl-phosphinic acids $\text{Fc}(\text{P}(\text{R})(\text{O})(\text{OH}))_2$ (**2a–d**) ($\text{R} = \text{H}$ (a), Me (b), Et (c), Ph (d)) have been obtained and studied using X-ray single crystal diffraction, IR-spectroscopy and quantum chemistry. The intermolecular hydrogen bonding in **1a–d** proceeds highly stereoselectively and results in formation of racemic conglomerate of **1d**. The formation of inter- and intra-molecular hydrogen bonds for disubstituted acids **2c–d** depends on substituent at phosphorus atoms.

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Introduction

The arylphosphinic acids $\text{ArP}(\text{R})(\text{O})(\text{OH})$ ($\text{R} = \text{H}$, alkyl, aryl) are widely used for the construction of self-assembled two- and three-dimensional structures or single molecular magnets (SMM) based on p- [1], d- [2] and f- [3] metals, e.g., Ru [4] and Mn [5] complexes. The replacement of the aryl fragment in these acids for the cognate ferrocenyl fragment, containing redox-active iron atom, may result in additional interesting properties like enhanced exchange interactions and give the opportunity to make sensors or switchable devices.

However ferrocenylphosphinic acids (**1,2**) are poorly studied in contrast to other ferrocenyl-containing phosphorus acids. For example, ferrocenylphosphinous acids (**3**) existing as the mixtures of two tautomeric forms have been widely employed as ligands in transition metals catalysis of cross-coupling reactions [6,7], asymmetric hydrogenation [8] etc. Ferrocenylphosphonic acid (**4**) has been considered as redox-active pH-responsive molecule and the redox half-wave potential of ferrocenylphosphonates is sensitive to the bonding mode with metal atoms [9–14].



$\text{R} = \text{H}$: $\text{X} = \text{H}$ (**1a**), $\text{P}(\text{O})(\text{OH})\text{H}$ (**2a**)
 $\text{R} = \text{Me}$: $\text{X} = \text{H}$ (**1b**), $\text{P}(\text{O})(\text{OH})\text{Me}$ (**2b**)
 $\text{R} = \text{Et}$: $\text{X} = \text{H}$ (**1c**), $\text{P}(\text{O})(\text{OH})\text{Et}$ (**2c**)
 $\text{R} = \text{Ph}$: $\text{X} = \text{H}$ (**1d**), $\text{P}(\text{O})(\text{OH})\text{Ph}$ (**2d**)

The data on the synthesis, structure and redox properties of ferrocenylphosphinic acids are scarcely presented, although their first synthesis dates back to 1962: Sollott and Howard found that ferrocene reacts with PCl_3 under Fridel–Crafts reaction conditions in the presence of AlCl_3 to form (**1a**) and (**2a**) with the yield of 3.2% and 4.6% respectively after the hydrolysis [15]. Diferrocenylphosphinic acid was also isolated from this mixture [16]. The yield of (**1a**) was slightly improved to 8.6% using Me_2NPCl_2 as starting reagent instead of PCl_3 [17]. The formation of (**1a**) as a side-product has been also observed in the hydrolysis of diphosphene

* Corresponding author. Tel.: +7 843 273 93 44; fax: +7 843 273 22 53.
 E-mail address: miluykov@iopc.ru (V.A. Miluykov).