STRUCTURAL CHARACTERIZATION OF $[Fe(\eta^6\text{-}C_6H_{6\text{-}n}Me_n)_2]^{2+}$ DICATIONS

A. Lančok[1*]***, B. Štíbr***[2]***, L. Volfová***[1]***, T. Kmječ***[3]***, M. Bakardijev***[1]

[1]*Institute of Physics CAS, v. v. i., Na Slovance 2, 182 21 Prague, Czech Republic,* [2] *Institute of Inorganic Chemistry AS CR, v. v. i., 250 68 Husinec-Řež 1001, Czech Republic,*
[3]*Department of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University in Prague, V Holešovičkách 2, 180 00 Prague, Czech Republic*

E-mail: alancok@fzu.cz

Received 07 May 2016; accepted 16 May 2016

1. Introduction

Iron is one of the most abundant elements on the Earth and also in Mössbauer research. The present study is a part of our search for novel iron compounds that now play an important role in the development of specific areas of metaloorganic and metallocarborane chemistry of iron [1].

As a part of the chemistry these complexes, a short review on the synthesis of bis-(arene) iron complexes and reactions associated with direct and indirect replacement of arene ligands in these complexes is presented. These reactions lead to a broad variety of novel iron sandwich compounds that now play an important role in the development of specific areas of metaloorganic and metallacarborane chemistry of iron. The review comprises recent synthetic routes and approaches to iron sandwich complexes, of which the most significant have been arene and cyclohexadienyl ferradicarba- and ferratricarba-boranes, together with new types of piano-stool structured compounds. The reader will also find references to methods of structural characterization of individual compounds in this area ofchemistry.

2. Experimental Details

The $[FeAr_2]^{2+}$dications were isolated for the first time by E. O.Fischer and R. Bőtcher in 1956, via treatment of arenes with $FeBr_2$ in the presence of $AlCl_3$[2]. The method was later improved by Hellingand Braitsch, who reported syntheses by the reaction between mesitylene (mes) and anhydrous $FeCl_2$ in the presence of $AlCl_3$ inboiling cyclohexane [3].

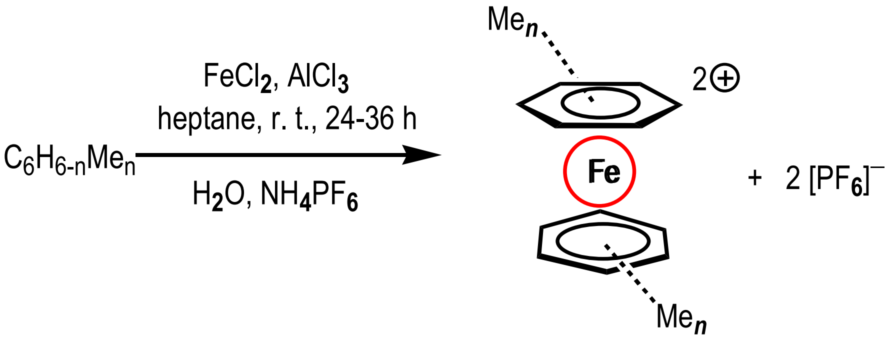
At the room temperature reaction between polymethylatedarenes $C_6H_{6\text{-}n}Me_n$ (Me = CH_3) and $FeCl_2$ is shown in Scheme 1.The presence of $AlCl_3$ in heptane for 24-36 hours proceeded with the formation of the samples. The formation of series of the $[Fe(\eta^6\text{-}C_6H_{6\text{-}n}Me_n)_2]^{2+}$dications (isolated as PF_6^- salts) in yields of 48-71% see on Scheme 2.Scheme 1 (path b) also demonstrates that the reaction between $[FeAr_2](PF_6)_2$ (Ar=1,3,5-$Me_3C_6H_3$ and Me_5C_6H) and $Tl_2[7,9\text{-}C_2B_9H_{11}]$ in refluxing dichloroethane for 6 h can generatemoderate yields (the yields are 30 and 15%, respectively) ofisomeric complexes of structure [1-Ar-*closo*-1,2,4-$FeC_2B_9H_{11}$]. The same complexes are also formed, together with two more cageisomers, [1-Ar-*closo*-1,2,7-$FeC_2B_9H_{11}$] and [1-Ar-*closo*-1,2,8-$FeC_2B_9H_{11}$], by heating of the [1-Ar-*closo*-1,2,3-$FeC_2B_9H_{11}$]isomers in the temperature range 350-500 ^{o}C. Individualisomers have been separated by multiple TLC chromatography onsilica-gel [4].

The pure compounds were characterised by ^{1}H NMR spectroscopy and Electrospray ionization mass spectrometry, and the structures of $[Fe(m\text{-}xylene)_2][PF_6]_2$ and $[Fe(durene)_2][PF_6]_2$ were established by single-crystal X-ray diffraction analyses [5].

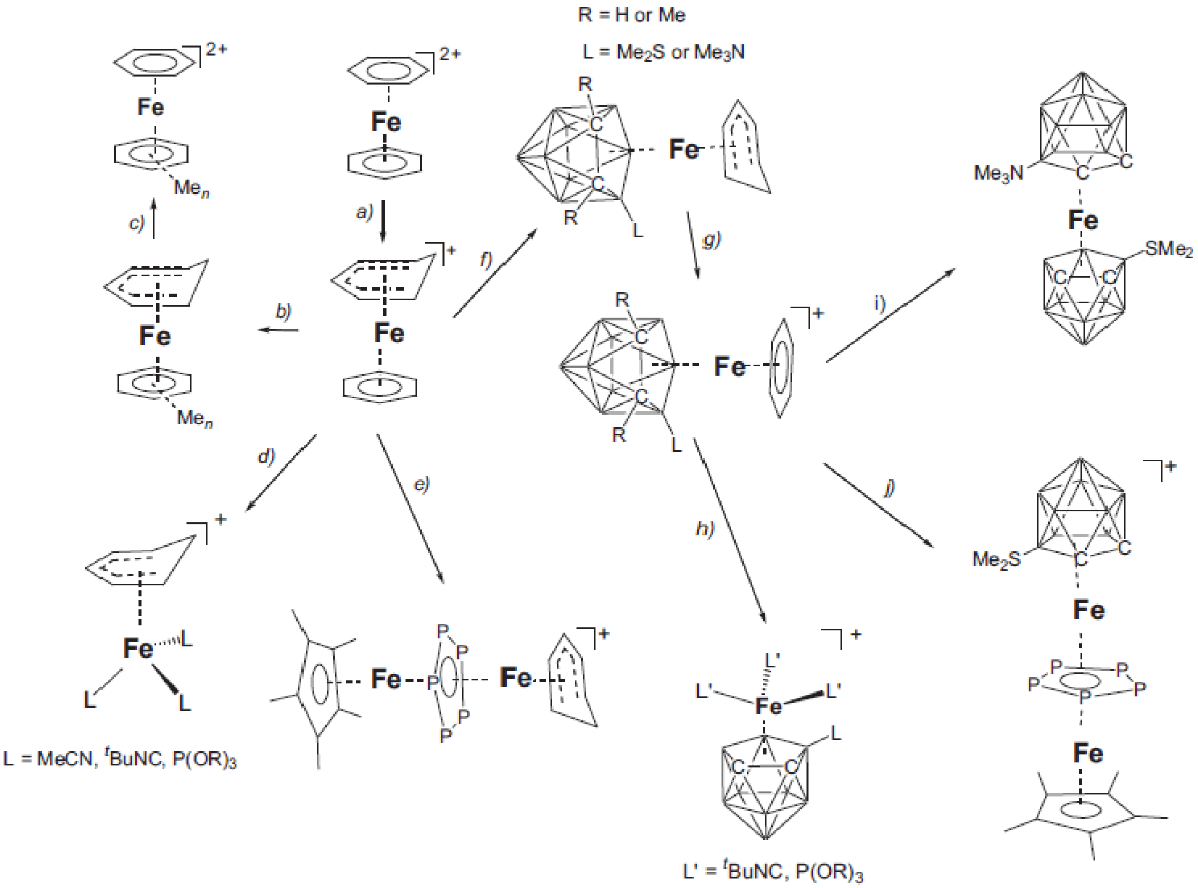
To characterize the thermal behavior and compositional/structural evolution at thermal treatments we used the Mössbauer spestroscopy, XRD and SEM techniques. The structure and phase composition of the powders were inspected using the PANanalyticalX'pert XRD diffractometer at CoK$_\alpha$ radiation with a small addition of CoK$_\beta$. The resulting spectra were recalculated into CuK$_\alpha$ and compared with those for standard. The values of the lattice constants were deduced using an internal standard.

SEM/EDX measurements were performed with TESCAN FERA 3 scanning electron microscope equipped with EDAX Octane 60 mm^2 detector.

Mössbauer spestroscopy has been chosen as a further tool of structural characterization. Mössbauer effect experiments were performed with a constant acceleration spectrometer using a ^{57}Co/Rh source. Calibration was done using a thin (12.5 μm) α-Fe foil at room temperature. Evaluation of the spectra was accomplished by the Confit software [6].



Scheme 1. *Formula of preparation* $[Fe(\eta^6\text{-}C_6H_{6-n}Me_n)_2]^{2+}$ *dications*



Scheme 2.*Formation of the* $[Fe(\eta^6\text{-}C_6H_{6-n}Me_n)_2]$ *dications*

3. Results and discussions

The X-ray diffraction data for orangecrystals of [**1c**][PF_6]$_2$ and [**1f**][PF_6]$_2$ were obtained at 150 K, on a NoniusKappaCCD diffractometer using an Oxford Cryostream low-temperature device, and with Mo-Kα radiation (λ = 0.71073A˚), a graphite monochromator, and the f and c scan mode. Datareductions were performed with DENZO-SMN [7]. The absorptionwas corrected by integration methods [8]. Structures were solvedby direct methods (Sir92)^{12} and refined by full-matrix least-squarebased on F^2 (SHELXL97).13 Hydrogen atoms were mostlylocalized on a difference Fourier map, but to ensure uniformity ofcrystal treatment, all hydrogen-atom positions were recalculatedinto idealized positions (riding model) and assigned temperature factorsH_{iso}(H) of 1.2Ueq(pivot atom), and of 1.5Ueq for the methylmoieties, with C–H = 0.96 A˚, and 0.93 A˚ for methyl hydrogenatoms and ring hydrogen atoms, respectively.

Crystallographic data for [**1c**][PF_6]$_2$: $C_{16}H_{20}F_{12}P_2Fe$,M= 558.11,monoclinic, *C2/c*, *a* = 15.5808(7), *b* = 9.7552(13), *c* = 13.2471(12)A˚, β = 107.37(3)◦, Z = 4, V = 1921.6(3)A˚, Dc = 1.929 g.cm^{-3}, μ =0.8 mm^{-1}, T_{min}= 0.768, T_{max} = 0.867; 7139 reflections measured(θ_{max} = 27.5◦), 2192 independent (R_{int} = 0.0353), 1833 with $I>2\sigma(I)$, 141 parameters, S = 1.103, R_1(obs. data) = 0.0334, wR_2(all data) = 0.0682; max., min. residual electron density = 0.344, -0.462 e.A$^{\circ-3}$.

Crystallographic data for [**1f**][PF_6]$_2$: $C_{20}H_{28}F_{12}P_2Fe$,M= 614.21,chiral orthorhombic space group $P2_12_12_1$, a = 9.9241(7), b =13.4542(8), c = 17.7747(15)A˚ , Z = 4, V = 2373.3(3)A$^{\circ3}$, D_c = 1.719g.cm^{-3}, m = 0.8 mm^{-1}, T_{min} = 0.875, T_{max} = 0.928; 19066 reflectionsmeasured (θ_{max} = 27.5◦), 5398 independent (R_{int} = 0.0415), 4628with $I>2\sigma(I)$, 316 parameters, S = 1.120, R1(obs. data) = 0.0472,wR_2 (all data) = 0.1001; max., min. residual electron density = 0.549, -0.485 eA$^{\circ-3}$.

Crystallographic data for the structural analyses have beendeposited with the Cambridge Crystallographic Data Centre,CCDC reference numbers 782984 and 782983 for [**1c**][PF_6]$_2$and[**1f**][PF_6]$_2$, respectively.

Hyperfine parameters including isomer shift, quadrupole splitting, and relative areas revealed differences in the samples with varying amount of methyl groups. At the room temperature MS were fitted by several doublets which corresponded to Fe^{2+} and to Fe^{3+}. The Fig. 1 shows the Mössbauer spectrum of the sample (a) without methyl groups (n=0) and of the sample (b) with six methyl groups (n=6). The typical separation of Mössbauer spectrum is describe in Fig. 2 for the sample with six methyl groups (n=6). This spectrum obtain two doubletscorresponded to Fe^{2+} and to Fe^{3+}.

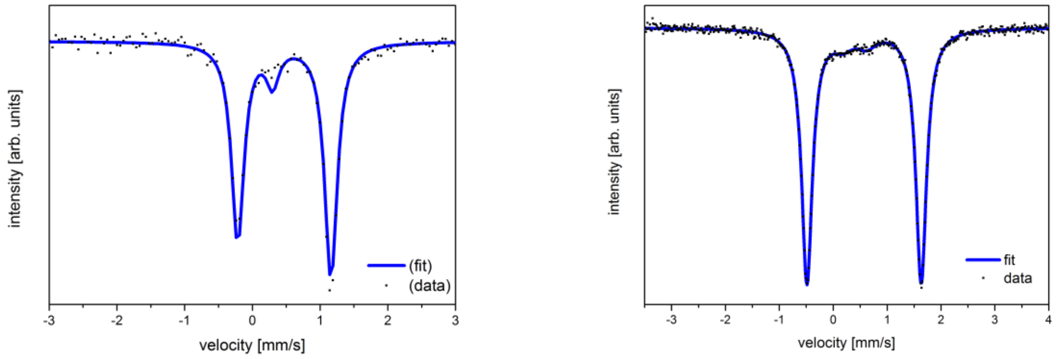


Fig. 1: *The Mössbauer spectrum of the sample (a) without methyl groups (n=0) and(b) with six methyl groups (n=6)*

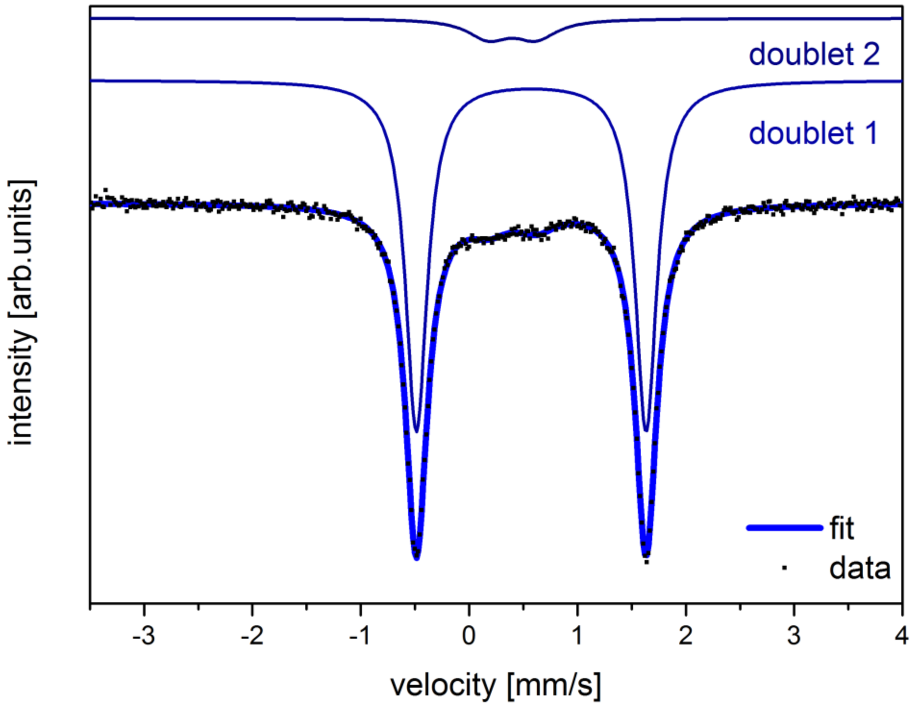


Fig. 2: *The separation of Mössbauer spectrum with six methyl groups (n=6)*

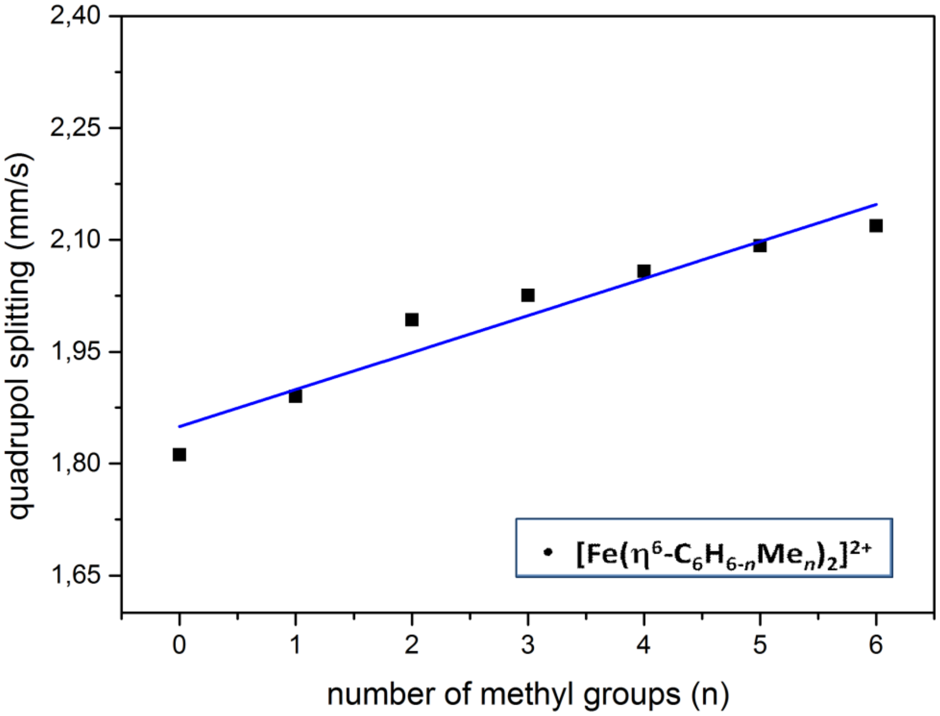


Fig. 3: *The dependence of quadrupole splitting to number of methyl groups*

It can be concluded that the effects of the Me-substituents (Fe) on the arene ligands are transmitted via the arene ring onto the iron centre. The effect can be employed for useful inter-comparisons among iron environments that differ in the number of substituents.

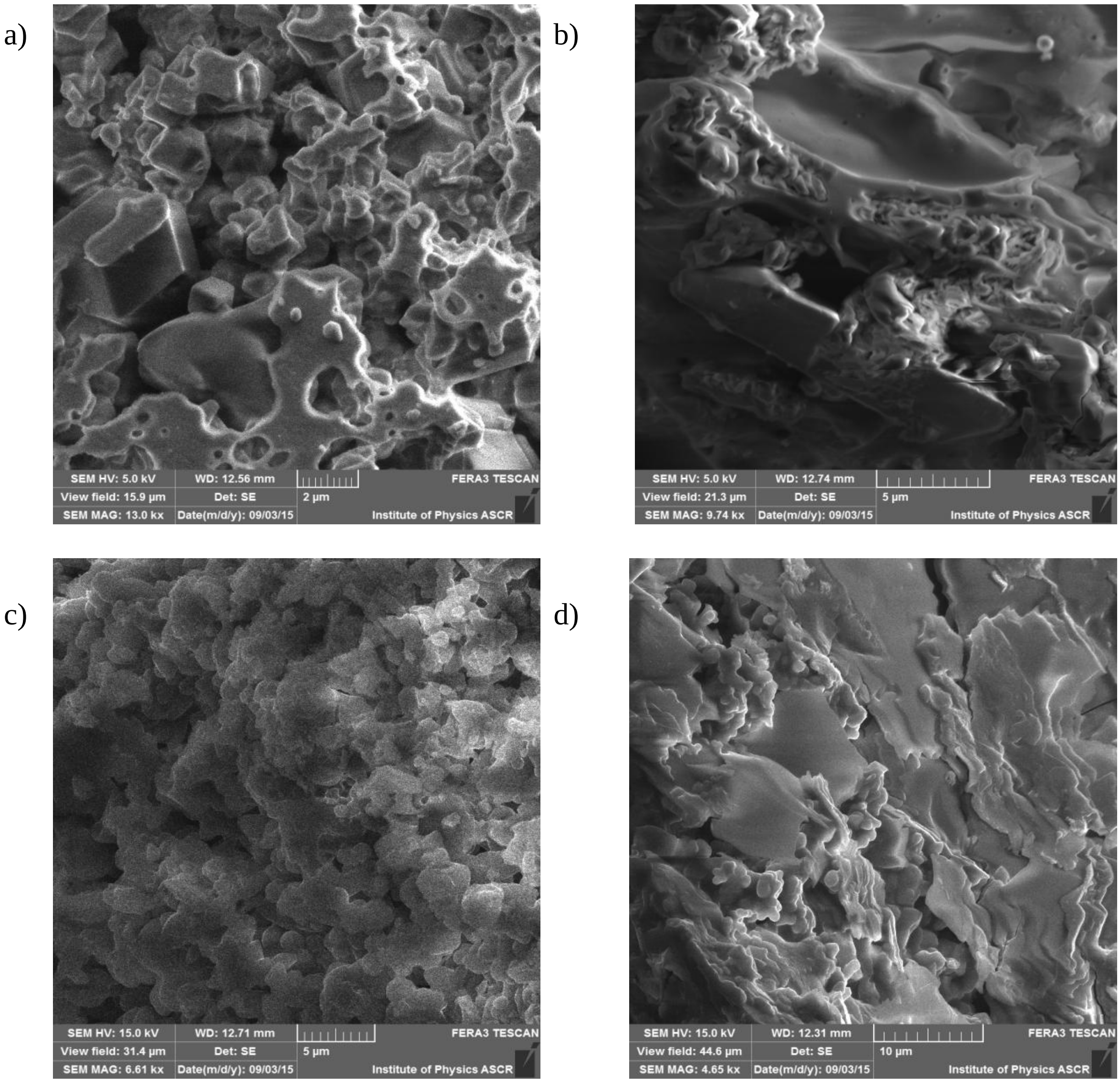


Fig. 4: *Typical SEM pictures of the* $[Fe(\eta^6\text{-}C_6H_{6\text{-}n}Me_n)_2]^{2+}$ *dications with a) magnification 13 kx, b) magnification 9.74 kx, c) magnification 6.61 kx, d)magnification 4.65 kx*

It is also found from Fig. 4 that the product is composed of different microsphere structure, but the assembly method of the circle and squareis different compared with Fig. 4a. The distance between the circle and square is closer and more intensive and the opening of the hole structure were observed in the middle of the microsphere, which greatly increases the specific surface area of the microsphere. The slight difference of the morphologies of the microspheres is mainly because reagents in different solvents have different solubility and diffusion velocity, which can greatly affect the product morphology. The diffusion of ions would speed up and was helpful for the formation of new nucleus before their growth at the surface of a pre-existing nucleus. This process was associated with nanocrystal formation.

4. Conclusions

Outlined are methods recently designed for the synthesis of bis-(arene) iron complexes and reactions associated with direct and indirect replacement of arene ligands in these complexes. It is demonstrated that arene displacement reactions lead to a broadvariety of novel iron sandwich compounds that now play importantrole in the development of specific areas of metaloorganic and metallacarborane chemistry of iron. The review comprises recentsynthetic routes and approaches to iron sandwich complexes, inwhich one of the sandwiching ligands is either η^6-arene or η^5-cyclohexadienyl anion. Among these compounds the most significantrole is played by ferradicarba- and ferratricarba-boranes and new types of piano-stool structured compounds that may sometimesbecome a part of designed syntheses of components ofcatalytic or biologically active systems. The reader will also find references to methods of structural characterization of individualcompounds in this rapidly developing area of iron-sandwichchemistry.It is readily seen that for the doublet ascribed to Fe^{3+} the isomer shift, equal to ~0.5 mm/s, does not change while the quadrupole splitting varies with the number of arene methyl groups (n).It can be concluded that the effects of the Me-substituents (Fe) on the arene ligands are transmitted via the arene ring onto the iron centre. The effect can be employed for useful inter-comparisons among iron environments that differ in the number of substituents.

Acknowledgement

This work was supported by the structural funds EC project FUNBIO: CZ.2.16/3.1.00/21568 MEYS CR for LO1409 and LM2011029 projects.

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