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1,4-Difluoro-2,5-dimethyl-3,6-bis(diphenylphosphoryl)benzene: regioselective synthesis and coordination with Mn^{2+} cation

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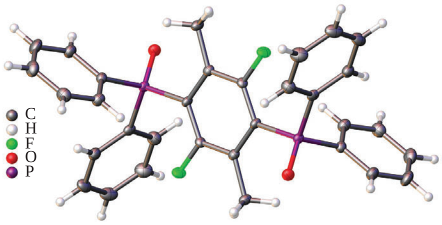
Regioselective synthesis of 1,4-difluoro-2,5-dimethyl-3,6-bis(diphenylphosphoryl)benzene from 1,2,4,5-tetraflouro-3,6-dimethylbenzene and preparation of its coordination polymer with Mn^{2+} have been developed. The structures of the ligand and the complex have been determined by X-ray diffraction.



Keywords: 1,4-difluoro-2,5-dimethyl-3,6-bis(diphenylphosphoryl)benzene, phosphines, phosphine oxides, manganese(II) complexes, organofluorine compounds, organophosphorus compounds, X-ray diffraction analysis, NMR spectroscopy.

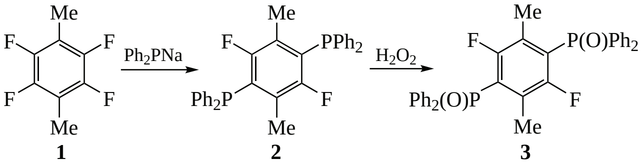
This article is dedicated to Academician M. P. Egorov on his 70th birthday.

Phosphine oxides find application for designing materials with prescribed properties.[1–4] The preparation of metal complexes of poly(phosphine oxides) with aromatic and heteroaromatic scaffolds is the most promising trend in this field.[5–13] It was shown recently[14] that the reaction of 1,2,4,5-tetrafluorobenzene with sodium diphenylphosphide led to 1,2,4,5-tetrakis(diphenylphosphino)benzene whose oxidation resulted in quantitative yield of poorly studied ligand, 1,2,4,5-tetrakis(diphenylphosphinyl)benzene.[14] Complexes of this compound with Mn,[14] Re,[15] Eu and Tb salts[16] proved to be promising light-emitting materials.

With the aim to synthesize new ligands, we reacted 1,2,4,5-tetrafluoro-3,6-dimethylbenzene **1** with sodium diphenylphosphide (Scheme 1).[†] Analysis of the obtained products showed that, in contrast to the case of 1,2,4,5-tetrafluorobenzene, the reaction of its homologue **1** proceeded regioselectively with displacement of only two fluorine atoms. The obtained 1,4-difluoro-2,5-dimethyl-3,6-bis(diphenylphosphino)benzene **2** was oxidized with hydrogen peroxide in a standard way[14] into the corresponding bis(phosphine oxide) **3**.

The NMR spectra of compounds **2** and **3** provide no unambiguous answer on their substitution pattern. The X-ray diffraction study of compound **3** revealed that the phosphorus substituents were *para* located [Figure 1(*a*)].[‡]

Additional confirmation of structure of bis(phosphine oxide) **3** was obtained by the study of its coordination properties with



Scheme 1

[†] *1,4-Difluoro-2,5-dimethyl-3,6-bis(diphenylphosphino)benzene* **2**. Sodium foil (0.62 g, 26.98 mmol) was added to a solution of diphenylphosphine (5.02 g, 26.98 mmol) in anhydrous THF (100 ml), and the mixture was stirred for 4 h until complete dissolution of the metal. 1,2,4,5-Tetrafluoro-3,6-dimethylbenzene **1** (2.0 g, 11.24 mmol) was added to the resultant yellow–brown solution cooled to –20 °C, and the mixture was stirred at –20 °C for 2 h and at 20 °C for 24 h. The mixture was then stirred at 60 °C for 4 h and cooled to 20 °C, methanol (5 ml) was added to quench excess sodium diphenylphosphide, with which the brown colour immediately disappeared. Water (50 ml) was added to the obtained light yellow solution, and THF was removed under reduced pressure. The residue was diluted with water (50 ml), the resultant precipitate was collected by filtration and washed with water (50 ml) and methanol (30 ml). After recrystallization from ethanol–$CHCl_3$ mixture (10 : 1, 200 ml), the substance was vacuum dried to afford 5.22 g (91%) of yellow crystals, mp 198–199 °C.

1,4-Difluoro-2,5-dimethyl-3,6-bis(diphenylphosphoryl)benzene **3**. Hydrogen peroxide (30% aq., 3 ml, 26.5 mmol) was added to a solution of bis-posphine **2** (5.22 g, 10.2 mmol) in chloroform (100 ml) over 20 min, on so doing, the solution temperature rose to 45 °C. The mixture was stirred for 2 h without cooling, washed with water (50 ml), the organic layer was separated, and chloroform was removed under reduced pressure to dryness. The residue was vacuum dried at 0.1 Torr at 100 °C for 8 h. Yield 5.53 g (100%), white powder, mp 305–306 °C.

[‡] Crystals of compounds $\mathbf{3}\cdot 2\,CHCl_3$ and $\mathbf{4}\cdot 2\,CHCl_3$ were grown from $CHCl_3$ and $CHCl_3$–MeCN (2 : 1) solutions, respectively.

Crystal data for $\mathbf{3}\cdot 2\,CHCl_3$. $C_{34}H_{28}Cl_6F_2O_2P_2$, M = 781.20, monoclinic, space group $P2_1/c$, 100.0(2) K, a = 12.3481(4), b = 8.6017(3) and c = 16.7090(5) Å, β = 106.364(2)°, Z = 2, V = 1702.85(10) Å^3, d_{calc} = 1.524 g cm^{-3}, $F(000)$ = 796. Colourless prism-shaped single crystal with dimensions 0.27 × 0.19 × 0.12 mm was selected, and intensities of 25108 reflections were measured using a Bruker Apex 2 CCD diffractometer (ω scans, sealed tube, $\lambda[\mathrm{MoK}_\alpha]$ = 0.71073 Å, μ = 0.642 mm^{-1}, $2\theta_{\max}$ = 61.37°). After merging of equivalents and absorption correction, 5258 independent reflections (R_{int} = 0.1198) were used for the structure solution and refinement. Final R factors: R_1 = 0.0541 [3304 reflections with $I > 2\sigma(I)$], wR_2 = 0.1254 (all reflections), GOF = 1.044.

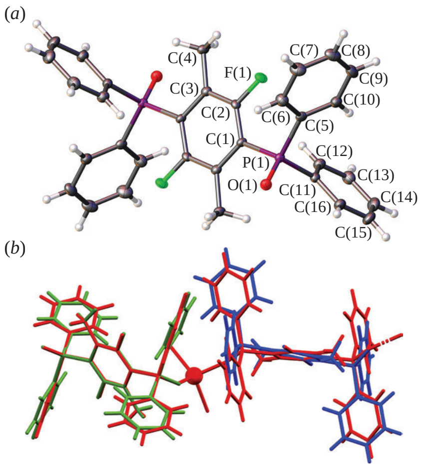


Figure 1 (*a*) Molecular view of **3** in representation of atoms with thermal ellipsoids (p = 50%). Only symmetrically independent atoms are labelled. Selected bond distances (Å): P(1)=O(1) 1.491(2), C(2)–F(1) 1.358(3), P(1)–C(1) 1.827(2), P–Ph 1.803(2)–1.804(2). (*b*) Conformations of the bis(phosphine oxide) in solid $\mathbf{3}\cdot 2\,CHCl_3$ (green and blue) and $\mathbf{4}\cdot 2\,CHCl_3$ (red). Overlaid atoms are oxygen and fluorine.

Mn^{2+}. Its treatment with $MnBr_2$ in MeCN–$CHCl_3$ solution afforded crystalline complex **4** of 1 : 1 composition.[§] Complex **4** is a coordination polymer; it was characterized by elemental analysis, IR and Raman spectroscopy data as well as X-ray diffraction study (Figure 2).[‡] The compound crystallizes from chloroform as a disolvate. Asymmetric unit contains one manganese atom, two bromine atoms coordinated as terminal ligands, two halves of bis(phosphine oxide) **3** and two solvent molecules. The ligand acts as a bridge ligand towards the cation, so that infinite chain of the complex **4** parallel with crystallographic axis *b* is observed. Coordination polyhedra MnN_2Br_2 adopt the distorted tetrahedral geometry. Lengths of all bonds in the ligand remain nearly unchanged upon coordination. Moreover, conformations of two independent ligands in complex **4** are very close to that for solid **3**; only phenyl groups underwent some rotation along P–C(Ph) bonds [see Figure 1(*b*)].

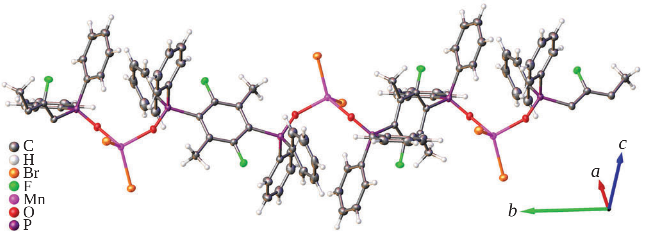


Figure 2 Fragment of **4** chains. Selected bond distances (Å): Mn–Br 2.4840(9)–2.4770(7), Mn–O 2.034(2)–2.045(2), P=O 1.499(2)–1.508(2), P–Ar 1.822(3), P–Ph 1.787(3)–1.795(3), Mn···Mn 9.592(2); angle Mn···Mn···Mn 154.15(2)°.

In summary, regioselective method for the synthesis of 1,4-difluoro-2,5-dimethyl-3,6-bis(diphenylphosphoryl)benzene, a new ligand for design of coordination polymers with Mn^{2+} salts, has been developed.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.10.009.

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Crystal data for $\mathbf{4}\cdot 2\,CHCl_3$. $C_{34}H_{28}Br_2Cl_6F_2MnO_2P_2$, $M = 995.96$, monoclinic, space group $P2_1/c$, 100.0(2) K, $a = 9.6380(19)$, $b = 20.953(4)$ and $c = 19.839(4)$ Å, $\beta = 102.54(3)°$, $Z = 4$, $V = 3910.8(14)$ Å^3, $d_{calc} = 1.692$ g cm^{-3}, $F(000) = 1972$. White hexagonal-shaped single crystal with dimensions 0.13 × 0.10 × 0.03 mm was selected, and intensities of 36145 reflections were measured using a 'Belok/XSA' beamline of NIC 'Kurchatov Institute' [φ scans, Si(111) monochromator, $\lambda = 0.7527$ Å, $\mu = 3.379$ mm^{-1}, $2\theta_{max} = 61.79°$]. After merging of equivalents and absorption correction with XDS software,[17] 10170 independent reflections ($R_{int} = 0.0311$) were used for the structure solution and refinement. Final R factors: $R_1 = 0.0411$ [8794 reflections with $I > 2\sigma(I)$], $wR_2 = 0.1026$ (all reflections), GOF = 1.005.

The structures were solved by direct method and refined by full-matrix technique against F^2 in anisotropic approximation. The positions of hydrogen atoms were calculated geometrically and refined in rigid body approximation. All calculations were carried out with SHELXL[18] (structure solution and refinement) and OLEX2[19] (refinement and molecular graphics) programs.

CCDC 2282911 and 2282912 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

[§] *Complex* **4**. A solution of $MnBr_2\cdot 4\,H_2O$ (0.1 mmol) in MeCN (2 ml) was added dropwise with stirring to a solution of ligand **3** (0.1 mmol) in $CHCl_3$ (3 ml). The mixture was stirred at room temperature for 3 h and allowed to stand overnight. Transparent almost colourless crystals were separated by decantation, washed with MeCN and dried at 62 °C in a vacuum (0.1 Torr). Yield 70%, mp (decomp.) > 360 °C.