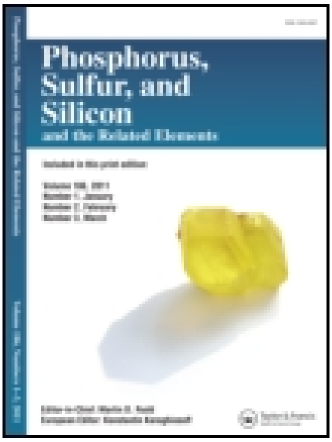

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Synthesis and Spectroscopic Characterization of Novel Aryl-Dithiofluorophosphonate Derivatives and X-Ray Studies of [(4-$CH_3OC_6H_4$)(F)P(S)S^-][PH_4P^+]

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To cite this article: Ertuğrul Gazi Sağlam, Ömer Çelik, Hamza Yılmaz & Nurcan Acar (2012) Synthesis and Spectroscopic Characterization of Novel Aryl-Dithiofluorophosphonate Derivatives and X-Ray Studies of [(4-$CH_3OC_6H_4$)(F)P(S)S^-][PH_4P^+], Phosphorus, Sulfur, and Silicon and the Related Elements, 187:11, 1339-1346, DOI: 10.1080/10426507.2012.685667

To link to this article: http://dx.doi.org/10.1080/10426507.2012.685667

Phosphorus, Sulfur, and Silicon, 187:1339–1346, 2012

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2012.685667

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF NOVEL ARYL-DITHIOFLUOROPHOSPHONATE DERIVATIVES AND X-RAY STUDIES OF [(4-$CH_3OC_6H_4$)(F)P(S)S^-][PH_4P^+]

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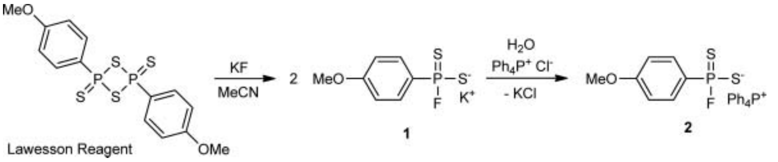
GRAPHICAL ABSTRACT



Abstract *Potassium and tetraphenylphosphonium salts of novel aryldithiofluorophosphonic acids were synthesized. Lawesson's Reagent was allowed to react with KF in acetonitrile to yield the potassium salt of p-methoxyphenyldithiofluorophosphonic acid. Treatment of the latter with tetraphenylphosphonium chloride resulted in the formation of the tetraphenylphosphonium salt. The structures of the compounds were elucidated by FTIR, ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy as well as by ESI-mass spectrometry. The molecular and crystal structure of the tetraphenylphosphonium salt, determined by single crystal X-ray diffraction, is also presented.*

Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.*

Keywords Dithiophosphonic acid; phosphonodithioic acid; dithiofluorophosphonic acid; dithiofluorophosphonate; Lawesson's reagent; X-ray structure determination

INTRODUCTION

Perthiophosphonic anhydrides[1] like the Lawesson's Reagent (LR) are well known to react with alcohols,[2,3] amines,[4,5] Grignard Reagents,[6] and anhydrous alkaline metal fluorides.[7] The products are reported to be promising to find future uses in fields like agricultural pest control,[8] chemotheraphy,[9] synthesis of novel antibiotics,[10] and metal extraction.[11,12]

Received 5 January 2012; accepted 1 April 2012.

The authors gratefully acknowledge the financial assistance of Technical Research Council of Turkey (grant number TBAG 110T016, TUBITAK) and Ankara University Research and Development Fund.

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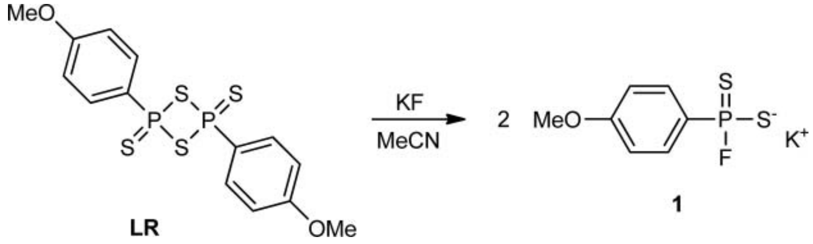
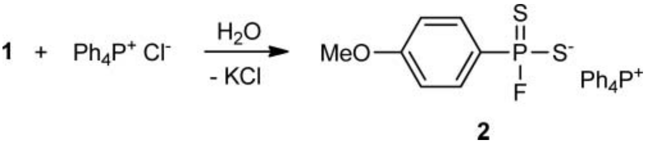
Among the compounds containing a S=P—S group, those which are fluoro-substituted on phosphorus[13,14] and those with fluorinated alkyl or aryl groups[15,16] appear to have attracted little attention. Especially, the last 10 years have become rather infertile in terms of the phosphonyl fluorides.[17]

Here we report on the reaction of LR with dry KF (Scheme 1) to yield the potassium salt of *p*-methoxyphenyl dithiofluorophosphonic acid **1**.



Scheme 1

The product was further allowed to react with tetraphenylphosphonium chloride to give the corresponding tetraphenylphosphonium salt **2** (Scheme 2).



Scheme 2

The compositions of the compounds were studied by elemental analysis and their structures were derived from IR, ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectriscopic and ESI-MS studies. The structure of **2** was confirmed for the solid state by X-ray crystallography.

RESULTS AND DISCUSSION

Mass Spectra

The mass spectra obtained by an ESI source does not display discrete signals attributable to the whole salts, as expected. The anion, observed in the anion mode, appears to remain unchanged in the ionization step with m/z value of 221.4 (calculated for $C_7H_7FOPS_2$, 221.2). The cation of compound **2** was observed in the cation mode and appears at m/z = 339.1 (calculated for $C_{24}H_{20}P$, 339.4).

Infrared Spectra

The prominent characteristic IR-bands of the two compounds are given in the Experimental section. The characteristic asymmetric (as) and symmetric (s) $\nu_{P=S}$ bands are observed at 689–698 cm^{-1} and 658–689 cm^{-1}, respectively. Characteristic ν_{P-F} bands are observed at 737 cm^{-1} and 721 cm^{-1} for **1** and **2**, respectively. The data support the structures suggested in Schemes 1 and 2.

Table 1 ^{19}F, ^{31}P, ^{1}H and ^{13}C NMR data for the anion in compounds **1** and **2**′

	1	2
δ^{19}F	−29.4	−25.9
$^{1}J_{PF}$	1027.2	1028.3
δ^{31}P	129.8	127.5
$^{3}J_{PH}$	14.8	13.8
δ^{1}H *o*-H	7.83	[a]
m-H	6.82	6.85
N	8.72	8.80
OMe	3.63	3.78
δ^{13}C C-*i*	133.5	135.6
$^{1}J_{PC}$	117.3	115.8
$^{2}J_{PF}$	25.4	26.2
C-*o*	131.2	131.4
$^{2}J_{PC}$	14.6	14.5
C-*m*	113.8	112.5
$^{3}J_{PC}$	14.0	15.3
C-*p*	161.5	161.5
$^{4}J_{PC}$	3.0	[b]
OMe	53.7	54.6

[a] $\delta^{31}P = 24.2$ (Ph_4P^+). [b] Signal overlaps with that of Ph_4P^+ protons.

NMR Spectra

NMR spectroscopic data (^{19}F, ^{31}P, ^{1}H, and ^{13}C) and signal patterns are given in Table 1. Due to the solubility properties, the NMR spectra for **1** were recorded in D_2O and those for **2** in CD_3OD. The data observed and in particular the direct P-F coupling constant are in agreement with those reported in the literature.[18–20] In the ^{1}H NMR spectrum of **2,** the multiplet at 7–8 ppm corresponds to the protons of the Ph_4P^+ group. The signals for the aromatic protons of the anion are superimposed with this multiplet. In the ^{13}C NMR spectrum of **1,** the two-bond coupling between the carbon and fluorine and also the direct C-P coupling constant compare well with the reported values for similar structures.[21,22]

Molecular and Crystal Structure of Compound 2

The structures of the cation and the anion in the crystal of compound **2** are shown in Figure 1.

Selected atom distances and bond angles are listed in Table 2. The distances of the phosphorus atom P1 to the directly bonded carbon atoms C1, C7, C13, and C19 are 1.788(10), 1.783(10), 1.805(12), and 1.824(11) Å, respectively. These data are in good agreement with previous findings.[23] For the phosphorus atom in the anion P2, the corresponding distances to the directly bonded atoms P2-C25, P2-F and P2-S1, and P2-S2 are 1.791(13), 1.671(7), 1.929(5), and 1.848(7) Å, respectively.

The puckering amplitudes of the centroids of the rings, namely Cg1, Cg2, Cg3, Cg4, and Cg5, were found to be 2.9, 2.2, 2.5, 3.5, and 4.2 Å, respectively.[24] The shortest intramolecular distance and dihedral angle between the centroids Cg1–Cg5(x, y, z) are 4.923(7) Å and 62.06°, respectively. The corresponding values for Cg2–Cg5 (1−x, 1/2+y,

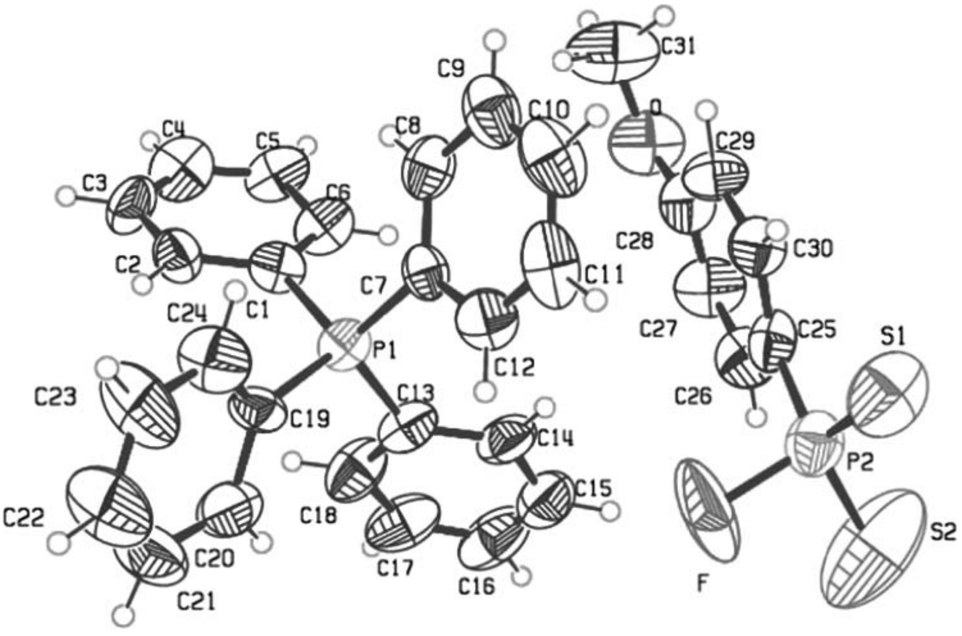


Figure 1 ORTEP view of the molecular structure of cation and anion in compound **2** with atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

1/2-z) are 4.132(7) Å and 34.87°. The data relating to similar distances and dihedral angles are given in Table 2.

Two intra- and intermolecular C-H· · ·S type hydrogen bonds become evident and the relevant parameters are listed in Table 2. The donor-acceptor distances for C26-H26· · ·S2, C30-H30· · ·S1, C27-H27· · ·S1, and C22-H22· · ·S2 are 3.408(16), 3.283(13), 3.464(15), and 3.401(21) Å, respectively. The π-electron clouds of the various rings seem also to be involved in the hydrogen bonding interactions. Assuming the centroids (Cg(n)) of the rings as imaginary atoms, six different C-H· · ·Cg(n) bonds, two intramolecular, and four intermolecular, can be located and the respective parameters are given in Table 2.

The dihedral angles between the five planar phenyl rings R1, R2, R3, R4, and R5 are given in Table 3. The rings are labeled as indicated in Figure 1.

EXPERIMENTAL

Analytical grade LR, potassium fluoride, and tetraphenylphosphonium chloride were purchased from Acros (Geel, Belgium) and used directly without further purification. Acetonitrile, diethyl ether, and methanol, were purchased from Merck (Darmstadt, Germany). Acetonitrile was distilled and dried before use.

Mass spectra were recorded with a Waters 2695 Allonce micromass spectrometer with APCI/ESI ionizing attachment. Melting points were measured with a Gallenkamp apparatus using a capillary tube. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded with a 400 MHz Varian Mercury 400 High Performance Digital FT-NMR spectrometer in D_2O (**1**) or CD_3OD (**2**). $SiMe_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P) were used as internal and external standard, respectively. ^{19}F chemical shifts are given with respect to trifluoroacetic acid as

Table 2 Diffraction data relating to some important geometrical features of compound **2**

Selected distances (Å) and bond angles (°)				Hydrogen bonding and Cg … π geometry (Å, °)*				Distances between the centroid of the rings (Cg)(Å)**	
Bond lengths		Bond angles		D – H … A	D … A (Å)	H … A (Å)	D – H … A (°)	Cg-Cg*	Cg-Cg (Å)
S1-P2	1.929 (5)	C7-P1-C1	110.0 (5)	C26-H26 … S2 ^{i}	3.408 (16)	2.986 (7)	109.29 (85)	Cg (1) - Cg (3)^{i}	4.994(8)
S2-P2	1.848 (7)	C7-P1-C13	113.2 (6)	C30-H30 … S1 ^{i}	3.283 (13)	2.801 (4)	113.39 (76)	Cg (1) - Cg (5)^{i}	4.923(7)
P1-C7	1.783 (10)	C13-P1-C19	112.1 (5)	C27-H27 … S1 ^{ii}	3.464 (15)	2.748 (4)	134.57 (88)	Cg (2) - Cg (4)^{i}	5.027(8)
P1-C1	1.788 (10)	F -P2-C25	103.9 (5)	C22-H22 … S2 ^{iii}	3.401 (21)	2.763 (8)	126.69 (99)	Cg (1) - Cg (4)^{ii}	5.297(8)
P1-C13	1.805 (12)	F -P2-S2	91.8 (5)					Cg (2) - Cg (3)^{ii}	4.968(9)
P1-C19	1.824 (11)	C25-P2-S2	115.5 (5)	C29-H29 … Cg (1)^{i}	3.714 (12)	2.9518	140.10	Cg (1) - Cg (2)^{iii}	5.905(8)
P2-C25	1.791 (13)	F -P2-S1	114.9 (5)	C8-H8 … Cg (5)^{i}	4.033 (12)	3.3328	133.82	Cg (3) - Cg (5)^{iii}	5.155(8)
F-P2	1.671 (7)	C25-P2-S1	111.0 (5)	C5-H5 … Cg (2)^{ii}	3.879 (14)	3.3515	118.24	Cg (2) - Cg (1)^{iv}	4.950(7)
		S2 -P2-S1	117.5 (3)	C11-H11 … Cg (3)^{iv}	3.901 (18)	3.3172	122.90	Cg (3) - Cg (4)^{iv}	5.415(10)
				C14-H14 … Cg (5)^{v}	3.945 (13)	3.1998	138.42	Cg (2) - Cg (5)^{v}	4.132(7)
				C16-H16 … Cg (3)^{vi}	4.04 (2)	3.2500	144.17		

*Symmetry codes: (i) x,y,z, (ii) x-1,+y,+z, (iii) x+1/2,-y-1/2,-z, (iv) 1+x,y,z, (v) 1-x,1/2+y,1/2-z, (vi)-1/2+x,3/2-y,-z.

**Symmetry codes for Cg which is the centroid of the ring: (i) x,y,z, (ii) −1+x,y,z, (iii) 1-x, −1/2+y,1/2-z, (iv) 1+x,y,z, (v) 1-x,1/2+y,1/2-z.

Table 3 Dihedral angles between rings for compound **2**

Plane–plane	Dihedral angle (°)
C1-C2-C3-C4-C5-C6 [R1, Cg1] - [R2, Cg2] C7-C8-C9-C10-C11-C12	73.60 (37)
C1-C2-C3-C4-C5-C6 [R1, Cg1] - [R3, Cg3] C13-C14-C15-C16-C17-C18	72.90 (35)
C1-C2-C3-C4-C5-C6 [R1, Cg1] - [R4, Cg4] C19-C20-C21-C22-C23-C24	81.05 (42)
C1-C2-C3-C4-C5-C6 [R1, Cg1] - [R5, Cg5] C25-C26-C27-C28-C29-C30	73.98 (37)
C7-C8-C9-C10-C11-C12 [R2, Cg2] - [R3, Cg3] C13-C14-C15-C16-C17-C18	60.72 (46)
C7-C8-C9-C10-C11-C12 [R2, Cg2] - [R4, Cg4] C19-C20-C21-C22-C23-C24	77.84 (37)
C7-C8-C9-C10-C11-C12 [R2, Cg2] - [R5, Cg5] C25-C26-C27-C28-C29-C30	34.65 (43)
C13-C14-C15-C16-C17-C18 [R3, Cg3] - [R4, Cg4] C19-C20-C21-C22-C23-C24	59.57 (50)
C13-C14-C15-C16-C17-C18 [R3, Cg3] - [R5, Cg5] C25-C26-C27-C28-C29-C30	60.84 (42)
C19-C20-C21-C22-C23-C24 [R4, Cg4] - [R5, Cg5] C25-C26-C27-C28-C29-C30	60.78 (42)

Note: R: ring; Cg: the centroid of the ring.

internal standard. IR spectra were recorded with a Mattson 1000 FTIR spectrophotometer (400–4000 cm^{-1}) in KBr pellets (1% w/w) and are reported in cm^{-1} units. Microanalyses were performed using a LECO CHNS-932 C elemental analyzer. Representative ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra for compounds I and II are found in the online Supplementary Materials (Figures S1–S8).

A single crystal of 0.5 × 0.40 × 0.40 mm size was selected for X-ray diffraction. Unit-cell dimensions were obtained using 25 centered reflections on an Enraf-Nonius CAD4 diffractometer[25] operating with graphite monochoromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å).

The intensity data were collected in $\omega = 2\theta$ scan mode within $4.2° \leq 2\theta \leq 46.0°$ for $-8 \leq h \leq 0, 0 \leq k \leq 14$, and $0 \leq l \leq 31$. Out of 2250 unique reflections, 1185 with I > 2σ(I) were used for structure solution and refinement. Data were corrected for Lorenz and polarization effects. The structure was solved in the orthorhombic space group P2$_1$2$_1$2$_1$ by the combination of direct and Fourier techniques and refined by full-matrix least squares. All of the nonhydrogen atoms were refined anisotropically. WinGX program package was used to solve[26] and refine the structure (SHELXL97), and ORTEP-3 for Windows[27] was used to draw molecular graphics. Details on data collection and structure refinement for compound **2** are given in Table 4.

Synthesis of Compounds 1 and 2

Compound 1: 1.00 g (2.50 mmol) of LR was mixed with 0.29 g (4.90 mmol) of freshly dried (250 °C) and finely ground KF in 50 mL of dry acetonitrile at ambient temperature. After stirring for 10 min, the mixture was refluxed for 1 h. The reaction mixture was cooled, filtered through a black-band filter paper, and the solvent was evaporated with a rotary evaporator. The resulting white solid was washed three times with dry diethylether while etching with a policeman to remove the unreacted ether-solubles and the remaining solid was dried under vacuum. White powder. Yield: 1.80 mmol, 0.50 g, 71%. M.p. 195–197 °C. IR: ν(cm^{-1}) = 689, 658 (P=S)$_{\mathrm{as,s}}$; 737 (P-F); 1593, 1496 (C=C); 3010 (C-H)$_{\mathrm{arom}}$. Anal. Calcd. for $C_7H_7FKOPS_2$ (260.33): C, 32.3; H, 2.71; S, 24.63; Found: C, 31.95; H, 2.64; S, 24.45%. ^{1}H NMR (D$_2$O): $\delta = 3.63$ (s, 3H, OC$\underline{\mathrm{H}}_3$), 6.82 (A-part of AA′MM′X, N = 8.7 Hz, 2H, m-H), 7.83 (M-part of AA′MM′X, $^{3}J_{\mathrm{PH}} = 14.0$ Hz (J_{MX}), N = 8.7 Hz, 2H,

Table 4 Crystal and experimental data for the compound **2**

Empirical formula	$C_{31}H_{27}FOP_2S_2$
Formula weight	560.59
T(K)	293
Crystal system	Orthorhombic
Space group (No.)	$P\ 2_1\ 2_1\ 2_1$ (19)
Colour/shape	Colorless/Prism
a (Å)	7.6640(10)
b (Å)	12.991(3)
c (Å)	28.404(6)
V (Å^3)	2827.9(9)
Z	4
Radiation	0.71073 (Mo K_α)
μ (mm^{-1})	0.331
F(000)	1168
h, k, l range	$-8 \le h \le 0, 0 \le k \le 14, 0 \le l \le 31$
Crystal size (mm)	0.50 × 0.40 × 0.40
No. of reflections collected	2250
No. of independent reflections	1185
θ range for data collection	2.1–23.5
Data/restraints/parameters	1185/0/335
Goodness-of-fit on F^2	1.012
R indices [I>2s(I)]: R1, wR2	0.066, 0.172
R indices (all data): R1, wR2	0.175, 0.220
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ eÅ^{-3}	0.503, −0.346
Measurement	Enraf-Nonius CAD4
Program system	Enraf-Nonius CAD4 Express
Structure determination	WinGX (SHELXL and SHELXS)
Refinement	Full matrix
CCDC deposit number	828914

o-H). $^{13}C\{^1H\}$ NMR (D_2O): $\delta = 55.7$ (s, $O\underline{C}H_3$), 113.8 (d, $^3J_{PC} = 14.0$ Hz, C-*m*), 131.2 (d, $^2J_{PC} = 14.6$ Hz, C-*o*), 133.5 (dd, $^1J_{PC} = 117.3$ Hz, $^2J_{CF} = 25.4$ Hz, C-*i*), 161.5 (d, $^4J_{PC} = 3.0$ Hz, C-*p*). ^{31}P NMR (D_2O): $\delta = 129.8$ (td, $^3J_{PH} = 14.8$ Hz, $^1J_{PF} = 1030.4$ Hz). ^{19}F NMR (D_2O): $\delta = -29.4$ (d, $^1J_{PF} = 1027.2$ Hz). APCI/ESI MS (anion mode); m/z: 221.4 calculated for the anion of **1**: 221.2, 100%.

Compound 2: 0.50 g (1.20 mmol) of compound **1** was dissolved in 10 mL of water. To this solution, equivalent volume of 5% aqueous tetraphenylphosphonium chloride was added dropwise. The precipitation of compound **2** is almost immediate; the salt can be recrystallized from methanol or water. Colorless crystals. Yield: 1.40 mmol, 0.80 g, 74%. M.p. 150–151 °C. IR: $\nu(\mathrm{cm}^{-1}) = 698, 689\ (P{=}S)_{as,s}$; 721 (P-F); 1590, 1481 (C=C); 3050 $(C\text{-}H)_{arom}$. Anal. Calcd. for $C_{31}H_{27}FOP_2S_2$ (560.62): C, 66.41; H, 4.85; S, 11.44; Found: C, 66.42; H, 4.79; S, 11.51%. ^1H NMR (CD_3OD): $\delta = 3.37$ (s, 3H, $OC\underline{H_3}$), 6.85 (A-part of AA′MM′X, $N = 8.8$ Hz, 2H, *m*-H), 7.70–8.02 (m, 22H, *o*-H, Ph_4P^+). $^{13}C\{^1H\}$ NMR (CD_3OD): $\delta = 54.7$ (s, $O\underline{C}H_3$), 112.5 (d, $^3J_{PC} = 15.3$ Hz, C-*m*), 131.4 (d, $^2J_{PC} = 14.5$ Hz, C-*o*), 135.6 (dd, $^1J_{PC} = 102.7$ Hz, $^2J_{CF} = 26.2$ Hz, C-*i*), 161.5 (s, C-*p*). ^{31}P NMR (CD_3OD): $\delta = 127.5$ (td, $^3J_{PH} = 13.8$ Hz, $^1J_{PF} = 1024.6$ Hz), 24.2 (s, $Ph_4\underline{P}^+$). ^{19}F NMR (CD_3OD): $\delta = -25.9$ (d, $^1J_{PF} = 1028.3$ Hz). APCI/ESI MS (anion mode): m/z: 221.4; Calculated for the anion of **2**: m/z: 221.2; 100%; cation mode: m/z: 339,1; Calculated for the cation of **2**: m/z: 339.4.

REFERENCES

1. Foreman, M. St. J.; Slawin, A. M. Z.; Woollins, J. D. *Heteroat. Chem.* **1999,** 10, 651-657.
2. Karakuş, M.; Yılmaz, H.; Bulak, E. *Rus. J. Coord. Chem.* **2005,** 31, 316-321.
3. Van Zyl, W. E. *Comments Inorg. Chem.* **2010,** 31, 13-45.
4. Aragoni, M. C.; Arca, M.; Demartin, F.; Devillanova, F. A.; Graiff, C.; Isaia, F.; Lippolis, V.; Tiripicchio, A.; Verani, G. *Eur. J. Inorg. Chem.* **2000,** 2239-2244.
5. Przychodzen, W.; Chojnacki, J. *Heteroat. Chem.* **2008,** 19, 271-282.
6. Diemert, K.; Kuchen, W. *Phosphorus, Sulfur Silicon Relat. Elem.* **1977,** 3, 131-136.
7. Hoffmann, H.; Schumacher, G. *Tetrahedron Lett.* **1967,** 31, 2963-2966.
8. Chavdarian, C. G. US Patent *4483225*, **1987**.
9. Bara, A. C.; Silvestru, C.; Haiduc, I. *Anticancer Res.* **1991,** 11, 1651-1656.
10. Dürckheimer, W.; Bormann, D.; Ehlers, E.; Schrinner, E.; Heymes, R. U.S. Patent *5710146*, **1998**.
11. Klaehn, J. R.; Harrup, M. S.; Law, J. D.; Peterman, D. R. US Patent *7704468 B1*, **2010**.
12. Klaehn, J. R.; Peterman, D. R.; Harrup, M. S.; Tillotson, R.; Luther, T. A.; Law, J. D.; Daniels, L. M. *Inorg. Chim. Acta* **2008,** 361, 2522-2532.
13. Roesky, H. W. *Chem. Ber.* **1968,** 101, 3679-3687.
14. Roesky, H. W. *Angew. Chem. Int. Ed.* **1968,** 7, 814-815.
15. Cavell, R. G.; Doty, L. F. *Inorg. Chem.* **1978,** 17, 3086-3093.
16. Leavitt, C. M.; Gresham, G. L.; Benson, M. T.; Gaumet, J. J.; Peterman, D. R.; Klaehn, J. R.; Moser, M.; Aubriet, F.; Stipdonk, M. J. V.; Groenewold, G. S. *Inorg. Chem.* **2008,** 47, 3056-3064.
17. Tworowska, I.; Dabkowski, W. *Chem. Commun.* **1998**, 2611-2612.
18. Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; London: Harper & Row Publishers: 1976; p. 87.
19. Roesky, H. W. *Z. Naturforsch.* **1967,** 22b, 716-718.
20. Roesky, H. W.; Tebbe, F. N.; Muetterties, E. L. *Inorg. Chem.* **1970,** 9, 831-836.
21. Silverstein, R. M.; Webster, F. X.; Kiemle, D. J. *Spectrometric Identification of Organic Compounds*, Vol. 4, 7th ed.; Hoboken, NJ: Wiley: 2005; pp. 204-245.
22. Klaehn, J. R.; Peterman, D. R.; Harrup, M. S.; Luther, T. A.; Daniels, L. M. *Inorg. Chim. Acta* **2011,** 370, 519-522.
23. Sağlam, E. G.; Çelik, O.; Yılmaz, H.; Ide, S. *Transition Met. Chem.* **2010,** 35, 399-405.
24. Cremer, D.; Pople, J. A. *J. Am.Chem. Soc.* **1975,** 97, 1354-1358.
25. Enraf-Nonius, D. *CAD4 Express Software*; Enraf-Nonius, Delft: The Netherlands, 1994.
26. Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found Crystallogr.* **2008,** 64, 112-122.
27. Farrugia, L. *J. Appl. Crystallogr.* **1997,** 30, 565-566.