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Synthesis and Molecular Structure of [2,3,4,5-Tetrafluoro-6-(*p*-methoxyphenylamino)phenyl]diphenylphosphine

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Abstract—The reaction of (pentafluorophenyl)diphenylphosphine with *C*-ethoxycarbonyl- (*p*-methoxyphenyl) nitrile imine was used to synthesize [2,3,4,5-tetrafluoro-6-(*p*-methoxyphenylamino)phenyl]diphenylphosphine oxide whose reduction with trichlorosilane gave [2,3,4,5-tetrafluoro-6-(*p*-methoxyphenylamino)phenyl] diphenylphosphine, the first representative of tertiary *ortho*-arylamino-substituted arylphosphines. According to X-ray diffraction data, the principal steric characteristics of the phosphine are close to those known for triarylphosphines.

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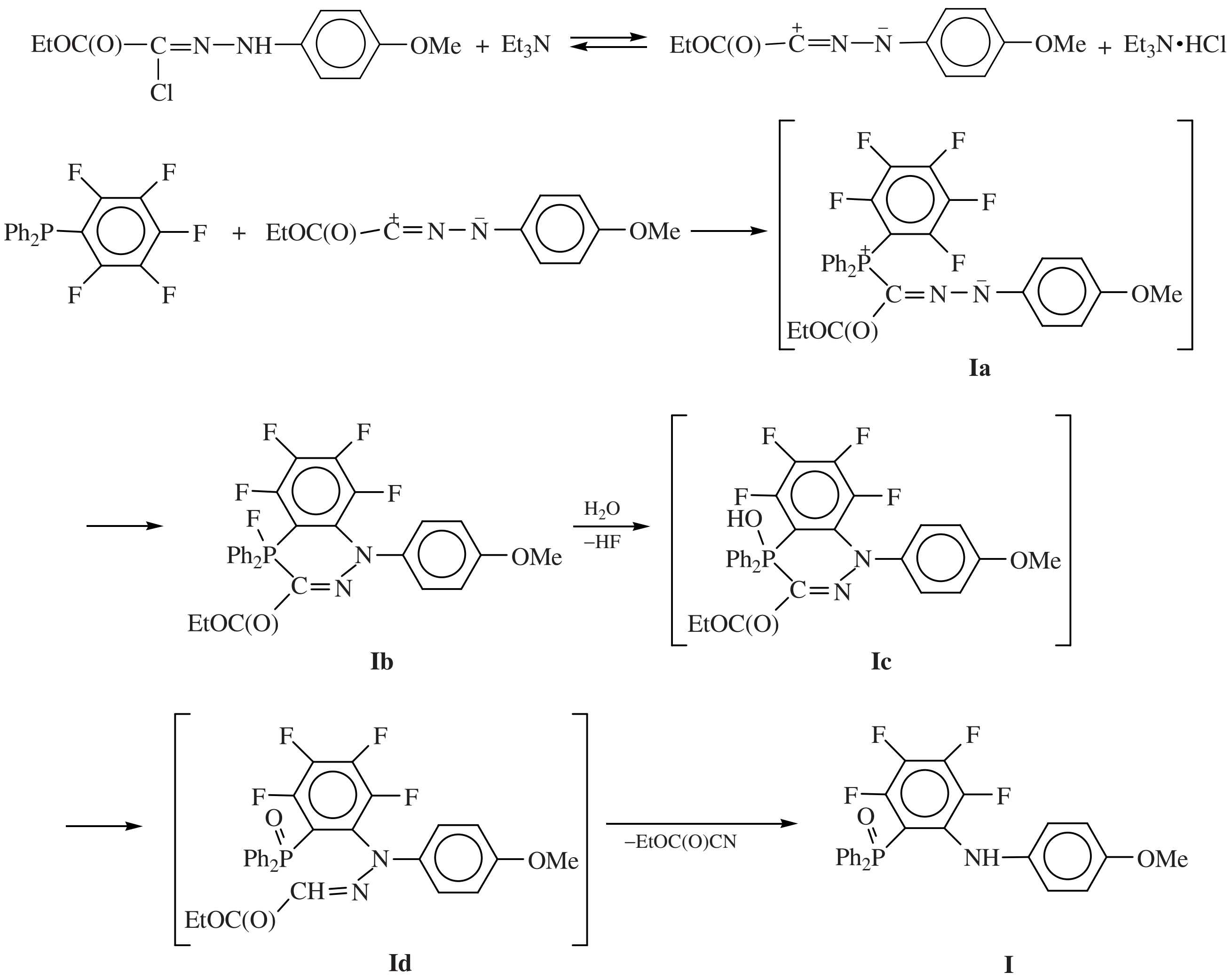
One of the new directions of the search for ligands for metal complex catalysts is associated with the synthesis of phosphorus- and nitrogen-containing compounds which have a P–C–C–N frame [1]. These bidentate ligands containing simultaneously a soft (phosphorus) and a hard (nitrogen) coordination centers hold promise for creation on their basis of unique complexes with platinum, palladium, rhodium and other metals.

In this work we obtained [2,3,4,5-tetrafluoro-6-(*p*-methoxyphenylamino)phenyl]diphenylphosphine oxide (**I**) on the basis of our recently discovered reaction of (pentafluorophenyl)diphenylphosphine with nitrile imines. Compound **I** was reduced with trichlorosilane to synthesize [2,3,4,5-tetrafluoro-6-(*p*-methoxyphenylamino)phenyl]diphenylphosphine (**II**), the first representative of tertiary *ortho*-arylamino-substituted arylphosphines.

The reaction of (pentafluorophenyl)diphenylphosphine with *C*-ethoxycarbonyl-*N*-*p*-methoxyphenylnitrile imine, leading to phosphine oxide **I,** is a multistep process. It is probably begins with the nucleophilic attack of the phosphine phosphorus on the nitrile imine carbenium carbon, which gives rise to a dipolar ion **Ia**. Further on intramolecular nucleophilic aromatic substitution of the fluorine atom in the *ortho* position to the phosphonium group, followed by heteroring close, take place. Therewith, the expelled fluoride attaches to the phosphorus atom to form fluorinated phosphorane **Ib** as a brown oily, gradually hardening substance. It is stable enough at 20°C in the absence of air moisture. The ^{31}P NMR spectrum of compound **Ib** shows a typical doublet at δ_P –96.4 ppm ($^1J_{PF}$ 655.0 Hz). Under the action of water, phosphorane **Ib** undergoes facile hydrolysis, releasing hydrogen fluoride and forming as intermediates first hydroxyphosphorane **Ic** and then phosphine oxide **Id** which contains a hydrazo group bound with a fluorinated benzene ring. Finally, the hydrazo group cleaves with liberation of ethyl cyanoformate and formation the final phosphorus-containing product, [2,3,4,5-tetrafluoro-6-(*p*-methoxyphenylamino)phenyl]diphenylphosphine oxide (**I**).

The formation of ethyl cyanoformate is established by the presence in the IR spectrum of the reaction mixture of an absorption band at 2250 cm^{-1} ($\nu_{C\equiv N}$). Earlier we mentioned [2] that N–N bond cleavage in intermediates like **Id** is, in essence, a new example of the amino–nitrile rearrangement well known in hydrazones [3]. Phosphine oxide **I** is a colorless crystalline substance stable for a long time on storage



in usual conditions. It is readily soluble in chloroform, acetone, benzene, and tetrahydrofuran, moderately soluble in diethyl ether, and poorly soluble in hexane. The signal in the ^{31}P NMR spectrum appears at δ_P 32.3 ppm, which is characteristic of triarylphosphine oxides [4]. The ^{1}H NMR spectrum shows amino (δ 9.52 ppm), methoxy (δ 3.69 ppm), and aromatic (δ 6.62–7.76 ppm) proton signals. The presence of NH and P=O groups is proved by IR spectral data (ν_{NH} 3175 cm^{-1}, ν_{PO} 1242 cm^{-1}).

Phosphine oxide **I** was reduced into phosphine **II** by the action of trichlorosilane in the presence of triethylamine in benzene under prolong heating (100° C) in a sealed ampule. After separation of triethylamine hydrochloride and treatment of the reaction mixture with aqueous sodium hydroxide, phosphine **II** was isolated in 47 % yield as light yellow crystals. Unlike triphenylphosphine, compound **II** is gradually oxidized in air; therefore, it was stored under argon.

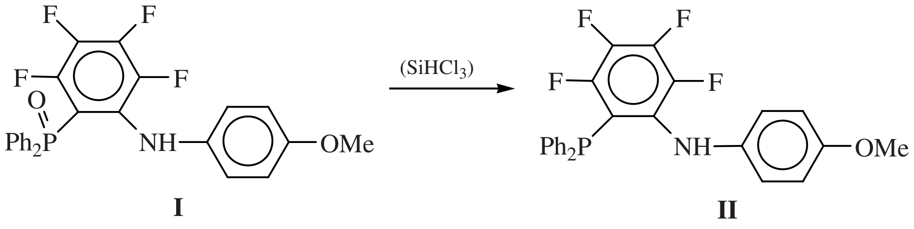


Table 1. Bond lengths in the molecule of diphenyl(2,3,4,5-tetrafluoro-6-*p*-methoxyphenylaminophenyl)phosphine **II**

Bond	*d*, Å	Bond	*d*, Å
$P–C^{19}$	1.821(2)	$C^7–C^8$	1.385(3)
$P–C^{13}$	1.835(2)	$C^8–C^9$	1.380(3)
$P–C^1$	1.839(2)	$C^9–C^{10}$	1.370(3)
$F^1–C^3$	1.349(2)	$C^{10}–C^{11}$	1.378(3)
$F^2–C^4$	1.340(2)	$C^{11}–C^{12}$	1.382(3)
$F^3–C^5$	1.332(2)	$C^{13}–C^{14}$	1.383(3)
$F^4–C^6$	1.348(2)	$C^{13}–C^{18}$	1.392(3)
$O–C^{10}$	1.377(3)	$C^{14}–C^{15}$	1.384(3)
$O–C^{25}$	1.411(3)	$C^{15}–C^{16}$	1.369(4)
$N–C^2$	1.392(3)	$C^{16}–C^{17}$	1.362(4)
$N–C^7$	1.427(3)	$C^{17}–C^{18}$	1.391(4)
$C^1–C^6$	1.383(3)	$C^{19}–C^{20}$	1.377(3)
$C^1–C^2$	1.414(3)	$C^{19}–C^{24}$	1.388(3)
$C^2–C^3$	1.390(3)	$C^{20}–C^{21}$	1.382(3)
$C^3–C^4$	1.364(3)	$C^{21}–C^{22}$	1.369(4)
$C^4–C^5$	1.380(3)	$C^{22}–C^{23}$	1.367(4)
$C^5–C^6$	1.372(3)	$C^{23}–C^{24}$	1.385(4)
$C^7–C^{12}$	1.372(3)		

Table 2. Valence angles in the molecule of diphenyl(2,3,4,5-tetrafluoro-6-*p*-methoxyphenylaminophenyl)phosphine **II**

Angle	ω, deg	Angle	ω, deg
$C^{19}PC^{13}$	104.70(9)	C^8C^7N	123.45(19)
$C^{19}PC^1$	105.63(9)	$C^9C^8C^7$	121.0(2)
$C^{13}PC^1$	100.80(9)	$C^{10}C^9C^8$	120.5(2)
$C^{10}OC^{25}$	117.8(2)	$C^9C^{10}O$	116.04(19)
C^2NC^7	121.75(19)	$C^9C^{10}C^{11}$	119.2(2)
$C^6C^1C^2$	117.67(18)	$OC^{10}C^{11}$	124.7(2)
C^6C^1P	124.31(14)	$C^{10}C^{11}C^{12}$	119.9(2)
C^2C^1P	117.65(15)	$C^7C^{12}C^{11}$	121.5(2)
C^3C^2N	119.43(19)	$C^{14}C^{13}C^{18}$	118.5(2)
$C^3C^2C^1$	118.1(2)	$C^{14}C^{13}P$	125.50(16)
NC^2C^1	122.41(19)	$C^{18}C^{13}P$	115.97(18)
$F^1C^3C^4$	117.9(2)	$C^{13}C^{14}C^{15}$	120.3(2)
$F^1C^3C^2$	119.6(2)	$C^{16}C^{15}C^{14}$	120.9(3)
$C^4C^3C^2$	122.46(19)	$C^{17}C^{16}C^{15}$	119.4(3)
$F^2C^4C^3$	120.7(2)	$C^{16}C^{17}C^{18}$	120.8(3)
$F^2C^4C^5$	119.5(2)	$C^{13}C^{18}C^{17}$	120.0(3)
$C^3C^4C^5$	119.85(19)	$C^{20}C^{19}C^{24}$	117.6(2)
$F^3C^5C^6$	121.4(2)	$C^{20}C^{19}P$	123.86(17)
$F^3C^5C^4$	120.08(19)	$C^{24}C^{19}P$	118.07(17)
$C^6C^5C^4$	118.5(2)	$C^{19}C^{20}C^{21}$	121.5(2)
$F^4C^6C^5$	116.90(18)	$C^{22}C^{21}C^{20}$	120.2(3)
$F^4C^6C^1$	119.69(17)	$C^{21}C^{22}C^{23}$	119.4(2)
$C^5C^6C^1$	123.39(18)	$C^{22}C^{23}C^{24}$	120.5(3)
$C^{12}C^7C^8$	117.9(2)	$C^{23}C^{24}C^{19}$	120.8(2)
$C^{12}C^7N$	118.60(19)		

The ^{31}P NMR spectrum phosphine **I** contains a signal at δ_P –27.1 ppm, which is typical for triarylphosphines [4]. In ^{1}H NMR spectrum, the proton signal of the amino group is shifted upfield (δ 6.44 ppm) from that of starting compound **I**, implying absence of the intramolecular NH···OP hydrogen bond inherent in phosphine oxide **I**. We previously found such bond in a structurally similar [2,3,4,5-tetrafluoro-6-(phenylamino)phenyl]phosphine oxide [2].

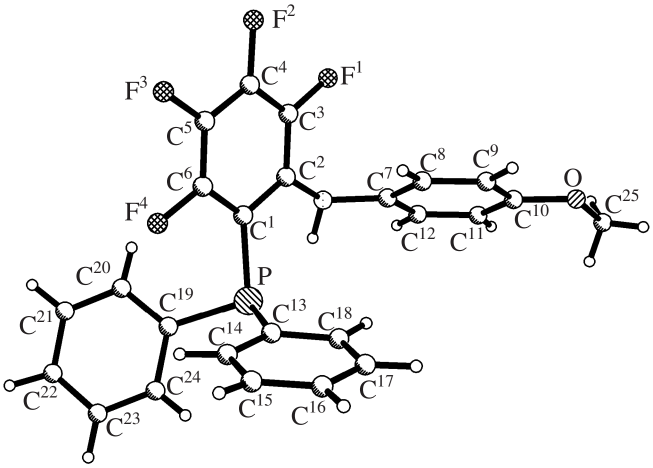


Fig. 1. Molecular structure of diphenyl(2,3,4,5-tetrafluoro-6-*p*-methoxyphenylaminophenyl)phosphine **II**.

The molecular structure of phosphine **II** was studied by X-ray diffraction (Figs. 1 and 2; Tables 1 and 2) to find that its principal geometric parameters correspond to those in known triarylphosphines [5]. Thus, the P–C bond lengths with an unsubstituted benzene ring are 1.821 Å ($P–C^{19}$) and 1.835 Å ($P–C^{13}$), and with fluorinated, 1.839 Å ($P–C^1$). The bond angles at the pyramidal phosphorus atom are 100.8–105.6°. The torsion angles between the rings are as follows, deg: $C^1–C^6$ and $C^7–C^{12}$ 67.9; $C^1–C^6$ and $C^{13}–C^{18}$ 92.6; $C^1–C^6$ and $C^{19}–C^{24}$ 63.0; and $C^{13}–C^{18}$ and $C^{19}–C^{24}$ 63.3.

EXPERIMENTAL

The IR spectra were recorded on an IKS-29 spectrophotometer (KBr). The ^{1}H NMR spectra of compounds **I** and **II** were obtained on a Bruker AC-200 spectrometer (200.1 MHz) operated in the ^{2}H internal stabilization mode. The ^{31}P spectra were measured on the same device at 81.4 MHz, solvent $CDCl_3$, reference 85 % H_3PO_4.

The X-ray structural analysis of crystals of [2,3,4,5-tetrafluoro-6-(*p*-methoxyphenylamino)phenyl]diphenylphosphine (**II**) was performed on a CAD-4 diffractometer (MoK_a radiation, W/2Q scanning). Crystals are monoclinic: $C_{24}H_{16}F_4NOP$; *a* 9.256(2), *b* 21.169(4), *c* 11.060(2) Å, b 94.00(3)°, *V* 2161.8 (7) Å; space group $P2_1/n$, *Z* 4, d_{calc} 1.399 g/cm^3. The structure was solved by the direct method; *R* 0.0204 and R_W 0.0875 [4122 reflections with $I > 2\sigma(I)$]. The bond lengths and bond angles are given in Tables 1 and 2. The atomic coordinates and equivalent isotropic thermal factors are available in the Cambridge Structural Database (registration number CCDC 668615).

[2,3,4,5-Tetrafluoro-6-(phenylamino)phenyl]phosphine oxide (I). A solution of 2.7 g of (pentafluorophenyl)diphenyl phosphine, 2.0 g of ethyl chloro(*p*-methoxyphenylhydrazono)acetate, and 3 ml of triethylamine in 40 ml of absolute benzene was left to stand for 24 h under argon. Triethylamine hydrochloride (95 %) precipitated and was filtered off and washed with benzene. The filtrate was evaporated at reduced pressure. The brown oily was fluorinated phosphorane **Ib,** according to ^{31}P NMR data (δ_P –96.4 ppm, $^1J_{PF}$ 655.0 Hz). It was dissolved in 10 ml of absolute diethyl ether. The solution was decanted from a little undissolved residue, diluted with 0.2 ml of water, and left to stand for 24 h at 20°C. Ether was then removed at atmospheric pressure, and the residue was recrystallized from ethanol. Yield 2.2 g (60.9 %), mp 110–112°C. IR spectrum, ν, cm^{-1} : 3175 (NH), 1242 (P=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm): 3.69 s (3H, OCH_3), 6.62–7.76 m (14H, Ar), 9.52 s (1H, NH). ^{31}P NMR spectrum ($CDCl_3$): δ_P 32.3 ppm. Found, % : C 63.87; H 3.67; N 2.72; P 6.69. $C_{25}H_{18}F_4NO_2P$. Calculated, % : C 63.70; H 3.85; N 2.97; P 6.57.

[2,3,4,5-Tetrafluoro-6-(phenylamino)phenyl]phosphine (II). A solution of 1.1 g of phosphine oxide **I**, 0.3 g of triethylamine, and 4.0 g of trichlorosilane in 10 ml of absolute benzene was boiled in a sealed ampoule at 100ºC for 10 h. After cooling, the precipitate of triethylamine hydrochloride was filtered off and treated with 30 ml of 30% aqueous sodium hydroxide. The organic layer was separated and dried over sodium sulfate. Benzene was removed at reduced pressure. Petroleum ether (40–70°C), 10 ml, was added to the residue. The precipitate was recrystallized from a benzene–hexane mixture (1 : 3). Yield 0.5 g (47.0 %), slightly yellowish crystals, mp 79–80°C. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 3.75 s (3H, OCH_3), 6.62–7.76 m (14H, Ar), 6.44 (1H, NH). ^{31}P NMR spectrum ($CDCl_3$): δ_P –27.1 ppm. Found, % : C 65.75; H 3.78; N 3.19; P 6.95. $C_{25}H_{18}F_4NOP$. Calculated, % : C 65.94; H 3.98; N 3.08; P 6.80.

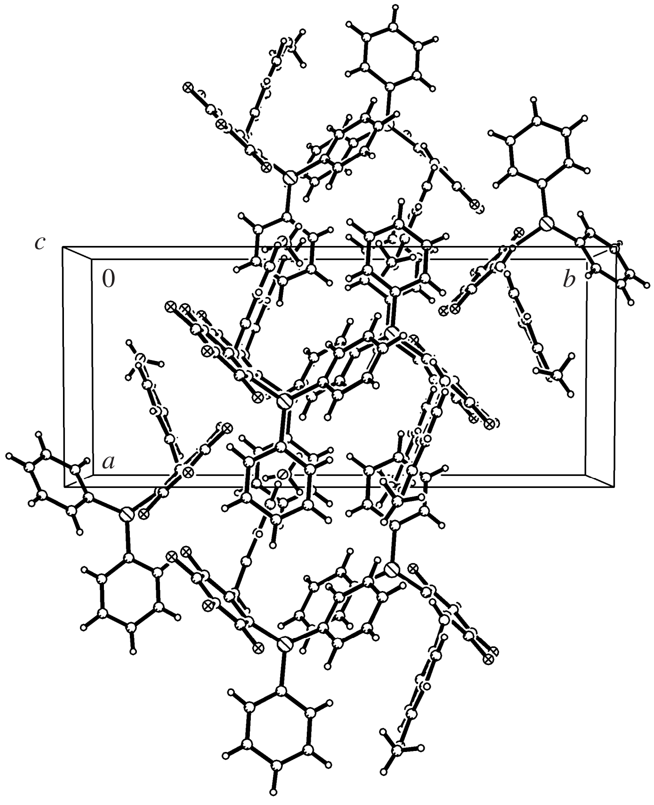


Fig. 2. Crystal cell of diphenyl(2,3,4,5-tetrafluoro-6-*p*-methoxyphenylaminophenyl)phosphine **II**.

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