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Easy Two-Step Synthesis of New Tris(perfluoroalkylphenyl)phosphites

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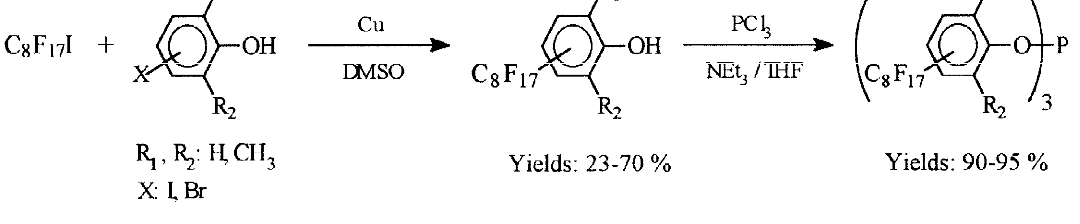
Abstract: A general route for the synthesis of tris(perfluoroalkylphenyl)phosphites from halophenol derivatives and 1-iodoperfluorooctane is described. The stability and the solubility of these new compounds are reported.

Keywords: fluorocarbons, perfluoroalkylated phosphites, copper.

Since the report in 1994 by Horvarth of a new immobilization technique based on the thermally controlled miscibility of perfluorinated hydrocarbons and organic liquids, the interest of the scientific community in this smart concept does not stop growing [1]. In the case of transition-metal catalyzed reactions, the success of this approach relies essentially on the synthesis of ligands which enable to immobilize the catalysts in the fluorocarbon layer [2]. A recent communication describing the synthesis of phosphines containing perfluorinated groups and specially one phosphite, the tris(4-tridecafluorohexylphenyl) phosphite, prompts us to report our own initial efforts in the synthesis of new fluorinated analogues of $P(OPh)_3$, one of the most used ligands in homogeneous catalysis [3]. The general route developed for the synthesis of these compounds is based on the copper mediated coupling reaction of 1-iodoperfluorooctane with various halophenol derivatives, followed by the reaction of the corresponding phenol with phosphorus trichloride.



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The perfluoroalkylphenols were prepared by a modified literature method using an excess of copper bronze in dimethylsulfoxide [4] and were obtained in 23-70 % yields after chromatographic purification and sublimation. Under comparable conditions, the perfluoroalkylation of 3- or 4-iodophenol occured at a faster rate and provided a much cleaner reaction mixture than the 4-iodo-2-methyl or 4-bromo-2,6-dimethylphenol. All phenols were very hygroscopic and required carefull drying by azeotropic distillation before addition of phosphorus trichloride. This precaution allowed to achieve the synthesis of new perfluorooctylphenyl phosphite derivatives in high yields (90-95 %). These phosphites proved to be air-stable. For example, when tris(4-perfluorooctylphenyl)phosphite was dissolved in $C_8F_{17}Br$ and heated at 80 °C for 2 hours under an oxygen atmosphere, no appreciable decomposition or oxidation was detected. As observed by ^1H and ^{31}P NMR experiments, these ligands are subject to hydrolyse slowly in water. The decomposition of tris(4-perfluorooctylphenyl)phosphite into H_3PO_3 and the corresponding phenol derivative reached 30 % after 6 hours and was complete after 24 hours at 20 °C in a water-tetrahydrofuran mixture (50/50; v/v). It is worth mentioning that this decomposition proceeded at a very high rate in the presence of traces of acid (< 5 min.). These compounds are, at room temperature, highly soluble in fluorocarbons ($C_8F_{17}Br$, $CClF_2CCl_2F$, C_6F_{11}-CF_3); soluble in tetrahydrofuran and ether; very slightly soluble in hexane, chloroform, toluene, and insoluble in dimethylsulfoxide and higher hydrocarbons such as decane, undecane and pentadecane.

In conclusion, these new phosphites fulfill the major requirements of the fluorocarbon/hydrocarbon biphasic catalysis, namely high affinities for fluorocarbon media and very poor solubility in common organic solvents. Some fruitful applications of these ligands in transtion metal catalyzed reactions should emerge in a next future.

General procedure for the synthesis of perfluoroalkylphenols.

Halophenol (11.36 mmol), $C_8F_{17}I$ (11.36 mmol) and copper (28.33 mmol) were dissolved in anhydrous DMSO, and heated to 125-130°C under nitrogen for 18 h. After cooling to room temperature, water (50 ml) and dichloromethane or ether (50 ml) were added to the reaction mixture. The orange solid was filtered and washed with CH_2Cl_2 (50 ml). The organic layer was separated and washed with water (3 x 50 ml), dried over Na_2SO_4 and evaporated in vacuo. The crude product was purified by column chromatography on silica gel with CH_2Cl_2 or CH_2Cl_2/pentane. The resulting solid was further purified by sublimation in vacuo at its melting point temperature.

4-perfluorooctylphenol Yield: 70% of a white solid, Mp: 74°C, ($R_f = 0.53$; CH_2Cl_2). ^1H NMR ($CDCl_3$) δ 7.46 (2H, d, J = 8.6, 2,6-ArH), 6.92 (2H, d, J = 8.6, 3,5-ArH), 5.36 (1H, s, -OH) ^{19}F NMR ($CDCl_3$) δ -81.11 (3F, t, $^3J_{FF} = 9.5$, -CF_3), -110.06 (2F, t, $^3J_{FF} = 14.2$, -CF_2-), -121.60 (2F, um, -CF_2-), -122.23 (6F, um, 3 x -CF_2-), -123.04 (2F, um, -CF_2-), -126.45 (2F, um, -CF_2-) ^{13}C NMR ($CDCl_3$) δ 158.58 (s, 1-C arom), 128.88 (t, $^3J_{CF} = 6.3$, 3,5-CH arom), 121.35 (t, $^2J_{CF} = 24.8$, 4-C arom), 115.61 (s, 2,6-CH arom) + complex signals of -CF_2- and -CF_3 (105-120) MS (EI) m/z: 512 (M^+, 4.3 %), 493 (M^+ - F, 3.5 %), 174 (M^+ - F - C_6F_{13}, 4.2 %), 143 (M^+ - C_7F_{15}, 100 %), 114 ($[C_5H_4\text{-}CF_2]^+$, 2.2 %), 69

(CF_3^+, 8.2 %) Anal. Calcd for $C_{14}H_5F_{17}O$: C, 32.84; H, 0.97; F, 63.09 Found: C, 32.72; H, 1.05; F, 62.58 IRFT (KBr) ν (cm^{-1}): 3380 (s), 1302 (s), 1229 (s), 1200 (vs), 1146 (vs).

3-perfluorooctylphenol Yield: 69% of a white solid, Mp: 45°C, (R*f* = 0.60; CH_2Cl_2) ^1H NMR ($CDCl_3$) δ 7.37 (1H, t, J = 7.8, 5-ArH), 7.16 (1H, d, J = 7.8, 4-ArH), 7.04 (1H, s, 2-ArH), 7.03 (1H, d, J = 7.8, 6-ArH), 5.24 (1H, s, -OH) ^{19}F NMR ($CDCl_3$) δ -81.02 (3F, t, $^3J_{FF}$ = 9.6, $-CF_3$), -110.91 (2F, t, $^3J_{FF}$ =14.0, $-CF_2-$), -121.55 (2F, um, $-CF_2-$), -122.12 (6F, um, 3 x $-CF_2-$), -122.97 (2F, um, $-CF_2-$), -126.37 (2F, um, $-CF_2-$) ^{13}C NMR ($CDCl_3$) δ 155.76 (s, 1-C arom), 130.64 (t, $^2J_{CF}$ = 24.2, 3-C arom), 130.18 (s, 5-CH arom), 119.41 (t, $^3J_{CF}$ = 6.6, 4-CH arom), 119.16 (s, 6-CH arom), 114.02 (t, $^3J_{CF}$ = 6.6, 2-CH arom) + complex signals of $-CF_2-$ and $-CF_3$ (105-120) MS (EI) m/z: 512 (M^+, 22.3 %), 493 (M^+ - F, 7.3 %), 174 (M^+ - F - C_6F_{13}, 2.3 %), 143 (M^+ - C_7F_{15}, 100 %), 114 ($[C_5H_4-CF_2]^+$, 2.5 %), 69 (CF_3^+, 4.4 %) IRFT (KBr) ν (cm^{-1}): 1459 (s), 1307 (s), 1258 (vs), 1208 (vs), 1145 (vs), 1114 (s), 878 (s), 684 (s).

2-methyl-4-perfluorooctylphenol Yield: 23% of a white solid, Mp: 46°C, (R*f* = 0.68; CH_2Cl_2) ^1H NMR ($CDCl_3$) δ 7.33 (1H, s, 3-ArH), 7.30 (1H, dd, J = 9.4, J' = 2.1, 5-ArH), 6.85 (1H, d, J = 8.3, 6-ArH), 5.12 (1H, s, -OH), 2.29 (3H, s, $-CH_3$) ^{19}F NMR ($CDCl_3$) δ -81.08 (3F, t, $^3J_{FF}$ = 9.8, $-CF_3$), -109.90 (2F, t, $^3J_{FF}$ = 14.5, $-CF_2-$), -121.66 (2F, um, $-CF_2-$), -122.13 (6F, um, 3 x $-CF_2-$), -122.97 (2F, um, $-CF_2-$), -126.41 (2F, um, $-CF_2-$) ^{13}C NMR ($CDCl_3$) δ 156.86 (s, 1-C arom), 129.77 (t, $^3J_{CF}$ = 6.3, 3-CH arom), 126.29 (t, $^3J_{CF}$ = 6.5, 5-CH arom), 124.51 (s, 2-C arom) 121.22 (t, $^2J_{CF}$ = 24.4, 4-C arom), 115.00 (s, 6-CH arom), 15.75 (s, $-CH_3$) + complex signals of $-CF_2-$ and $-CF_3$ (105-120) MS (EI) m/z: 526 (M^+, 4.8 %), 507 (M^+ - F, 3.8 %), 188 (M^+ - F - C_6F_{13}, 2.4 %), 157 (M^+ - C_7F_{15}, 100 %), 127 ($[H_2C{=}C_5H_3-CF_2]^+$, 4.1 %), 69 (CF_3^+, 7.0 %) IRFT (KBr) ν (cm^{-1}): 1310 (s), 1232 (s), 1199 (vs), 1147 (vs).

2,6-dimethyl-4-perfluorooctylphenol Yield: 30% of a white solid, Mp: 46°C, (R*f* = 0.87; CH_2Cl_2/pentane (1/1) v/v) ^1H NMR($CDCl_3$) δ 7.19 (2H, s, 3,5-ArH), 4.95 (1H, s, -OH), 2.28 (6H, s, $-CH_3$) ^{19}F NMR ($CDCl_3$) δ -81.12 (3F, t, $^3J_{FF}$ = 9.6, $-CF_3$), -109.85 (2F, t, $^3J_{FF}$ = 14.5, $-CF_2-$), -121.59 (2F, um, $-CF_2-$), -122.11 (6F, um, 3 x $-CF_2-$), -123.01 (2F, um, $-CF_2-$), -126.44 (2F, um, $-CF_2-$) ^{13}C NMR ($CDCl_3$) δ 155.26 (s, 1-C arom), 127.35 (t, $^3J_{CF}$ = 6.3, 3,5-CH arom), 123.44 (s, 2,6-C arom) 120.52 (t, $^2J_{CF}$ = 24.4, 4-C arom), 15.90 (s, $-CH_3$) + complex signals of $-CF_2-$ and $-CF_3$ (105-120) MS (EI) m/z: 540 (M^+, 5.6 %), 521 (M^+ - F, 4.8 %), 202 (M^+ - F - C_6F_{13}, 1.6 %), 171 (M^+ - C_7F_{15}, 100 %), 141 ($[H_2C{=}C_5H_2(-CH_3)-CF_2]^+$, 2.6 %), 69 ($CF_3^+$, 7.5 %) IRFT (KBr) ν ($cm^{-1}$): 1242 (s), 1210 (vs), 1199 (vs), 1146 (vs), 1130 (s).

General procedure for the synthesis of tris(perfluoroalkylphenyl)phosphites.

The perfluoroalkylphenol (1.87 mmol) was azeotropically distilled with toluene (30 ml, distilled over sodium under N_2) and dissolved in THF (10 ml, distilled over sodium under N_2). Triethylamine (1.87 mmol, dried over CaH_2 under N_2) was added to this solution. Phosphorus trichloride (0.80 mmol) dissolved in 5 ml of THF was added dropwise at 0°C for 0.5 h under N_2 to the stirred solution of perfluoroalkylphenol. Subsequently the reaction mixture was stirred for 2 h at room temperature. The amine salts formed were removed by filtration over dried silica gel under N_2 with further 40 ml of THF. The solvent was removed in vacuo to afford the pure phosphite.

Tris(4-perfluorooctylphenyl)phosphite Yield: 95% of a white solid, Mp: 47°C, ^{31}P-{^{1}H} NMR ($CDCl_3$) δ: +125.99 ^{1}H NMR ($CDCl_3$) δ 7.56 (6H, d, J = 8.3, 3,5-ArH), 7.22 (6H, d, J = 8.3, 2,6-ArH) ^{19}F NMR ($CDCl_3$) δ -81.25 (9F, t, $^{3}J_{FF}$ = 8.9, -CF_3), -110.69 (6F, t, $^{3}J_{FF}$ = 13.5, -CF_2-), -121.63 (6F, um, -CF_2-), -122.26 (18F, um, -CF_2-), -123.13 (6F, um, -CF_2-), -126.56 (6F, um, -CF_2-) ^{13}C NMR ($CDCl_3$) δ 154.18 (s, 1-C arom), 128.98 (t, $^{3}J_{CF}$ = 6.2, 3,5-CH arom), 125.42 (t, $^{2}J_{CF}$ = 24.5, 4-C arom), 120.78 (d, $^{3}J_{CP}$ = 7.1, 2,6-CH arom) + complex signals of -CF_2- and -CF_3 (105-120) MS (EI) m/z: 1564 (M^+, 7 %), 1545 (M^+ - F, 2 %), 1195 (M^+ - C_7F_{15}, 2.5 %), 1091 (1.5 %), 1072 (8 %), 1053 (M^+ - (O-C_6H_4-C_8F_{17}), 100 %), 703 (42 %), 413 (13 %), 211 (10 %) Anal. Calcd for $C_{42}H_{12}F_{51}O_3P$: C, 32.25; H, 0.77; F, 61.93 Found: C, 31.99; H, 0.82; F, 60.74 IRFT (KBr) ν (cm^{-1}): 1213 (vs), 1202 (vs), 1171 (s), 1147 (vs).

Tris(3-perfluorooctylphenyl)phosphite Yield: 90% of a white solid, Mp: 53°C, ^{31}P-{^{1}H} NMR ($CDCl_3$) δ +126.03 ^{1}H NMR ($CDCl_3$) δ 7.46 (3H, t, J = 7.8, 5-ArH), 7.38 (3H, d, J = 7.8, 4-ArH), 7.31 (3H, d, J = 7.8, 6-ArH), 7.29 (3H, s, 3-ArH) ^{19}F NMR ($CDCl_3$) δ -81.41 (9F, t, $^{3}J_{FF}$ = 10.0, -CF_3), -111.31 (6F, t, $^{3}J_{FF}$ = 14.5, -CF_2-), -121.78 (6F, um, -CF_2-), -122.31 (18F, um, -CF_2-), -123.37 (6F, um, -CF_2-), -126.69 (6F, um, -CF_2-) ^{13}C NMR ($CDCl_3$) δ 151.29 (s, 1-C arom), 131.01 (t, $^{2}J_{CF}$ = 24.5, 3-C arom), 130.36 (s, 5-CH arom), 124.17 (d, $^{3}J_{CP}$ = 6.8, 6-CH arom), 123.18 (t, $^{3}J_{CF}$ = 6.1, 4-CH arom), 119.42 (q, J = 6.4, 2-CH arom) + complex signals of -CF_2- and -CF_3 (105-120) MS (EI) m/z: 1564 (M^+, 24 %), 1545 (M^+ - F, 6 %), 1072 (24 %), 1053 (M^+ - (O-C_6H_4-C_8F_{17}), 100 %), 1033 (3.5 %), 719 (7 %), 703 (20 %), 561 (14 %), 512 (37 %), 493 (20 %) IRFT (KBr) ν (cm^{-1}): 1248 (vs), 1203 (vs).

Tris(2-methyl-4-perfluoroctylphenyl)phosphite Yield: 92% of a colorless oil, ^{31}P-{^{3}H} NMR ($CDCl_3$) δ +128.30 ^{1}H NMR ($CDCl_3$) δ 7.42 (3H, s, 3-ArH), 7.36 (3H, dd, J = 8.6, J' =1.9 Hz, 5-ArH), 7.24 (3H, d, J = 9.1, 6-ArH), 2.18 (9H, s, -CH_3) ^{19}F NMR ($CDCl_3$) δ -81.35 (9F, t, $^{3}J_{FF}$ = 9.9, -CF_3), -110.74 (6F, t, $^{3}J_{FF}$ = 14.2, -CF_2-), -121.69 (6F, um, -CF_2-), -122.32 (18F, um, -CF_2-), -123.19 (6F, um, -CF_2-), -126.64 (6F, um, -CF_2-) ^{13}C NMR ($CDCl_3$) δ 152.88 (s, 1-C arom), 130.72 (d, $^{3}J_{CP}$ = 1.8, 2-C arom), 130.18 (t, $^{3}J_{CF}$ = 6.0, 3-CH arom), 126.02 (t, $^{3}J_{CF}$ = 6.3, 5-CH arom), 125.13 (t, $^{2}J_{CF}$ = 24.6, 4-C arom), 120.05 (d, $^{3}J_{CP}$ = 11.3, 6-CH arom), 16.49 (s, -CH_3) + complex signals of -CF_2- and -CF_3 (105-120) MS (MALDI) m/z: 1606 (M^+) IRFT (deposited on KBr support) ν (cm^{-1}): 1237 (vs), 1203 (vs), 1176 (vs).)

Tris(2,6-dimethyl-4-perfluoroctylphenyl)phosphite Yield: 92% of a white solid, Mp: 77°C ^{31}P-{^{1}H} NMR ($CDCl_3$) δ + 141.76 ^{1}H NMR ($CDCl_3$) δ 7.25 (6H, s, 3,5-ArH), 2.28 (18H, s, -CH_3) ^{19}F NMR ($CDCl_3$) δ -81.29 (9F, t, $^{3}J_{FF}$ = 9.7, -CF_3), -110.76 (6F, t, $^{3}J_{FF}$ = 13.8, -CF_2-), -121.66 (6F, um, -CF_2-), -122.24 (18F, um, -CF_2-), -123.14 (6F, um, -CF_2-), -126.58 (6F, um, -CF_2-) ^{13}C NMR ($CDCl_3$) δ 151.47 (s, 1-C arom), 131.29 (d, $^{3}J_{CP}$ = 2.2, 2,6-C arom), 127.73 (t, $^{3}J_{CF}$ = 5.8, 3,5-CH arom), 125.21 (t, $^{2}J_{CF}$ = 24.2, 4-C arom), 17.79 (d, $^{4}J_{CP}$ = 5.7, -CH_3) + complex signals of -CF_2- and -CF_3 (105-120) MS (MALDI) m/z: 1648 (M^+) IRFT (KBr) ν (cm^{-1}): 1334 (s), 1324 (s), 1245 (vs), 1208 (vs), 1153 (vs).

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