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P-Bis(trifluoromethyl) Ylides: Synthesis and Reactions

Uwe Dieckbreder,[1] Gerd-Volker Röschenthaler,[1]
and Alexander A. Kolomeitsev[2]

[1]*Institute für Anorganische & Physikalische Chemie, Universität Bremen, Leobener Strasse, D-28334 Bremen, Germany*

[2]*Institute of Organic Chemistry, Ukrainian Academy of Sciences, Murmanskaya 5, 02094 Kiev, Ukraine*

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ABSTRACT: *Bis(trifluoromethyl)phosphines RP(CF$_3$)$_2$ (R = Me, NEt$_2$) were methylated by MeOSO$_2$CF$_3$, yielding the respective phosphonium salts [RP(CF$_3$)$_2$Me]$^+$ and CF$_3$SO$_3$$^-$. Deprotonation using MeN=P(NEt$_2$)$_3$ led to the phosphorus ylides RP(CF$_3$)$_2$=CH$_2$, stable in solution at ambient temperature, which could be converted into 1,2$\lambda^5\sigma^5$-oxaphosphetanes by adding hexafluoroacetone.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:650–653, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10061

INTRODUCTION

Phosphorus ylides are versatile reactants in organic chemistry, e.g. in the synthesis of naturally ocurring compounds [1]. There are only a few ylides containing fluorine or perfluoroalkyl groups in the alkylidene moiety [2] and not many *P*-halogeno derivatives [3]. Recently, we synthesized the first *P*-trifluoromethyl ylides, having one CF$_3$ group bonded to phosphorus [4]. Because the phosphines RP(CF$_3$)$_2$ (R = Me, NEt$_2$) are easily accessible by using "Ruppert's reagent" [5] [CF$_3$Br/P(NEt$_2$)$_3$], methylation followed by deprotonation should yield the desired ylides.

RESULTS AND DISCUSSION

The Ruppert-system CF$_3$Br/(Et$_2$N)$_3$P [5] proved to be a useful system to synthesize the bis(trifluoromethyl)phosphines **2a–c** as oxygen-sensitive liquids (**2a** being pyrophoric) from the respective dichlorophosphines **1a–c** (Scheme 1) in good yields. Compounds **2a** and **2c** have already been obtained by other methods [6,7].

While **2b** and **2c** could be obtained in dichloromethane, in the case of **2a** (R = Me), triglyme had to be used as a solvent because of its higher boiling point, necessary to isolate **2a** (bp 30°C). Methylation was possible only using methyl triflate at 100°C without a solvent to give the first bis-trifluoromethyl phosphonium salts **3a** and **3c**, moisture sensitive compounds, in good yields. In the case of **2b**, decomposition was observed during this procedure. Compounds **3a** and **3c** decomposed rapidly in diethyl ether and THF. The phosphonium triflates **3a** and **3c** could be deprotonated using as a neutral base a weak nucleophile *N*-methyliminotris(diethylamino) phosphine imide **4** [pK_s = 28] [8], yielding the desired ylides **5a** and **5c** (Scheme 2) which were stable in solution at room temperature, whereas CF$_3$Me$_2$P=CH$_2$ decomposed at

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Correspondence to: Gerd-Volker Röschenthaler or Alexander Kolomeitsev; e-mail: gvr@chemie.uni-bremen.de; alex@chemie.uni-bremen.de.

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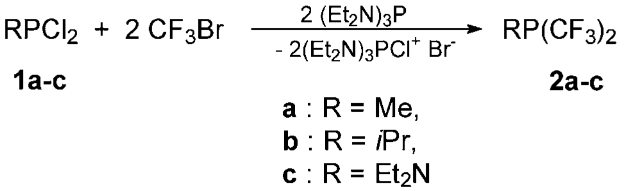


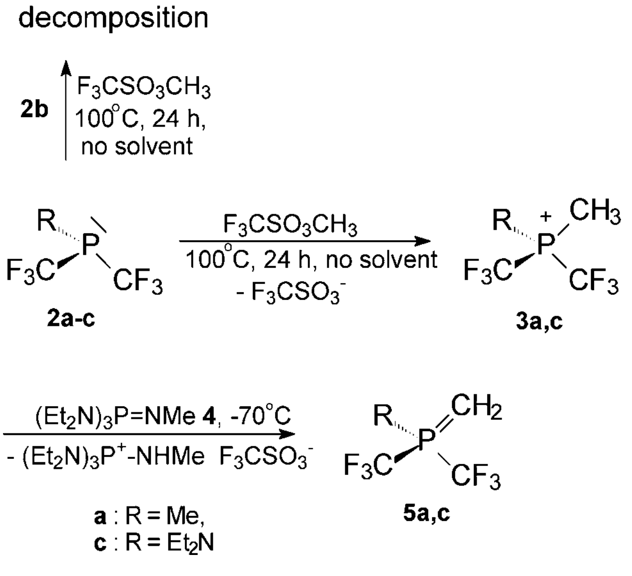
$$RPCl_2 + 2\,CF_3Br \xrightarrow[-\,2(Et_2N)_3PCl^+\,Br^-]{2\,(Et_2N)_3P} RP(CF_3)_2$$

SCHEME 1

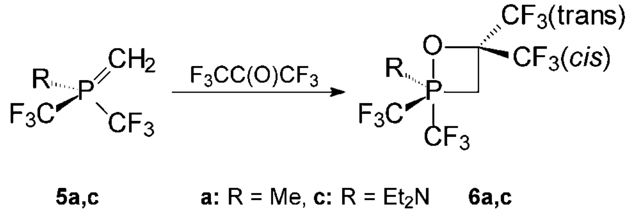
temperatures as low as −50°C. It was of advantage to obtain the nonvolatile amidophosphonium salt, $[(Et_2N)_3PNHMe]^+CF_3SO_3^-$, which could easily be separated (Scheme 2).

The reaction of the bis(trifluoromethyl) ylides **5a** and **5c** with hexafluoroacetone furnished the 2,2,4,4-tetrakis(trifluoromethyl)-1,2$\lambda^5\sigma^5$-oxaphosphetanes, **6a** and **6c**, as colourless, moisture-sensitive liquids (Scheme 3).

The structure of the compounds **2–6** was confirmed by their NMR spectra (see Table 1). The ylides **5a** and **5c** were characterized at −70°C. In the ^{19}F NMR spectra for the *P*-CF_3 groups at 308 K, broad doublets were observed, while sharp singlets were recorded for the *C*-CF_3 groups. Because of *Berry*-pseudorotation, which was fast on the NMR time scale, axial and equatorial CF_3 substituents at phosphorus could not be distinguished. Cooling a solution of phosphetane **6c** (R = Et_2N) in toluene-d_8 slowed down the ligand permutation process, resulting in the magnetic inequivalence of the *P*-CF_3 groups and, also of the *C*-CF_3 groups (cis and trans with respect to the equatorial *P*-CF_3) below the coalescence temperature of 273 K. At 213 K, a doublet of quartets for the axial *P*-CF_3 was observed ($\delta = -62.6$, $^2J_{FP} = 52.4$, $^4J_{FF} = 13.9$ Hz), a doublet of quartets for the equatorial *P*-CF_3 group ($\delta = -67.0$, $^2J_{FP} = 123.0$, $^4J_{FF} = 13.9$ Hz) split further by "through-space" coupling ($J_{F\cdots F} = 7.0$ Hz) between *C*-CF_3(cis) and *P*-CF_3(equatorial). The smaller absolute value of $^2J_{FP} = 52.4$, compared to $^2J_{FP} = 123.0$ H, is typical of an axially bonded CF_3 moiety [4,9]. In a similar oxaphosphetane, F· · ·F "through-space" coupling *C*-CF_3(cis) · · *P*-CF_3(equatorial) was found ($J_{F\cdots F} = 4.7$ Hz) [9].



SCHEME 2



SCHEME 3

TABLE 1 NMR Data of **2a–c, 3a, 3c, 5a, 5c, 6a**, and **6c** at 308 K (*J* in Hz)

Compound	*δH (P-CH)*[a] *($^2J_{HP}$)*	*δF (P-CF3)*[a]	*δF (C-CF3)*[a]	*δP*[a] *($^2J_{FP}$)*
2a	0.95 (4.4)	−62.2		−5.0 (75.7)
2b[b]	2.47 (6.8)	−53.1		13.9 (65.2)
2c[c]		−59.8		41.7 (86.6)
3a[d]	2.95 (16.8)	−54.7		59.8 (108.8)
3c[e]	3.08 (13.8)	−61.9		47.7 (113.4)
5a[f]		−67.0		17.8 (79.3)
5c[f]		−71.9		32.2 (87.5)
6a	1.25, 3.45[g] (15.5), (17.1)	−66.9	−78.5	−60.7 (80.5)
6c[h,i]	3.03[g] (16.0)	−64.0	−77.0	−51.5 (88.0)

[a] High-field shifts from TMS, CCl_3F, and 85% H_3PO_4 were given negative signs.

[b] ^1H: $\delta = 1.19$ (6 H, *Me*$_2$CH, dd, $^3J_{HH} = 6.9$, $^3J_{HP} = 16.2$).

[c] ^1H: $\delta = 0.88$ (6 H, *Me*CH$_2$, t, $^3J_{HH} = 7.1$), 2.95 (4 H, CH$_3$*CH*$_2$, dq, $^3J_{HP} = 10.7$).

[d] ^{19}F: $\delta = -74.8$ (s, $F_3CSO_3^-$).

[e] ^1H: $\delta = 1.27$ (6 H, *CH*$_3$CH$_2$, t, $^3J_{HH} = 7.1$), 3.48 (4 H, CH$_3$*CH*$_2$, dq, $^3J_{HP} = 12.8$); ^{19}F: $\delta = -74.2$ (s, $F_3CSO_3^-$).

[f] 1H: Not observed because of overlapping signals of $(Et_2N)_3PNMe$.

[g] P*CH*$_2$.

[h] ^1H: $\delta = 0.77$ (6 H, *CH*$_3$CH$_2$, t, $^3J_{HH} = 6.9$), 3.03 (4 H, CH$_3$*CH*$_2$, dq, $^3J_{HP} = 13.9$).

[i] ^{19}F at 213 K: −62.6 (P-C*F*$_3$ (ax), $^2J_{FP} = 52.4$, $^4J_{FF} = 13.9$), −67.0 (P-C*F*$_3$ (eq), $^2J_{FP} = 123.0$, $J_{F\cdots F} = 7.0$), −77.6 (C-C*F*$_3$ (cis), qq, $^4J_{FF} = 7.8$, $J_{F\cdots F} = 7.0$), −77.0 (C-C*F*$_3$ (trans), $^4J_{FF} = 7.8$).

TABLE 2 Experimental Details for the Synthesis of Compounds **2a–c**

	1 (g)[a]	*CF_3Br (g)*[a]	*$(Et_2N)_3P$ (g)*[a]	*Solvent (ml)*	*Yield (g)*[b]	*bp (°C)*[c]
2a[d]	**1a** 11.1 (95)	34.3 (230)	46.9 (190)	Triglyme 150	8.3 (47)	30 (1013)
2b	**1b** 11.6 (80)	30.0 (200)	39.5 (160)	CH_2Cl_2 120	4.2 (25)	85 (1013)
2c	**1c** 8.7 (50)	22.4 (150)	24.7 (100)	CH_2Cl_2 150	7.7 (64)	59 (100)

[a] Values in parentheses are in millimoles.
[b] Values in parentheses are the percent values.
[c] Values in parentheses are in millibars.
[d] See Ref. [6].

EXPERIMENTAL

Mass-spectra (EI, 70 eV) were recorded on a Finnigan MAT 8222 spectrometer. NMR spectra were obtained on a Bruker AC 80 instrument operating at 75.39 MHz (^{19}F, internal standard CCl_3F) and 32.44 MHz (^{31}P, external standard 85% H_3PO_4). All reactions and manipulations were conducted under an atmosphere of dry nitrogen.

General Procedure for the Synthesis of Compounds **2a–c**

In the respective solvent, bromotrifluoromethane and the dichlorophosphine (**1a–c**) were cooled to −60 to −80°C. Hexaethylphosphorus triamide was added, and the reaction mixture was allowed to warm to ambient temperature. All volatiles were pumped off in vacuo (10^{-3} mbar) and the residue distilled. (See Table 2 for data of **2a–c**.)

*Isopropylbis(trifluoromethyl)phosphine (***2b***).* Anal calcd for $C_5H_7F_6P$ (212.07): C, 28.30; H, 3.33; F, 53.76; P, 14.61. Found: C, 28.13; H, 3.18; F, 53.10; P, 14.36.

*Diethylaminobis(trifluoromethyl)phosphine (***2c***)* [7]. MS: $m/e\,(\%) = 241$ (M^+, 8), 226 ($M^+ - CH_3$, 5), 172 ($M^+ - CF_3$, 22), 122 (Et_2NPF^+, 100), 94 ($Et(H)NPF^+$, 7), 69 (CF_3^+, 18), 29 ($C_2H_5^+$, 45), and other fragments.

General Procedure for the Synthesis of Compounds **3a–c**

Compounds **2a–c** and one equivalent, methyltrifluoromethansulfonate were heated in a glass ampoule at 100°C for 16 h. The remaining solid was recrystallized in dichloromethane at −50°C and dried in vacuo (10^{-3} mbar). (See Table 3 for data of **3a–c**.)

*Dimethylbis(trifluoromethyl)phosphonium triflate (***3a***).* Anal calcd for $C_5H_6F_9O_3PS$ (348.12): C, 17.24; H, 1.74; F, 49.14; P, 8.90. Found: C, 17.72; H, 1.89; F, 48.90; P, 8.57.

*Diethylaminomethylbis(trifluoromethyl)phosphonium triflate (***3c***).* Anal calcd for $C_8H_{13}F_9NO_3PS$ (405.21): C, 23.70; H, 3.23; F, 42.22, P, 7.65. Found: C, 24.02; H, 3.38; F, 41.30: P, 7.42.

General Procedure for the Synthesis of Compounds **5a** *and* **5c**

To compounds **3a** (0.18 g, 0.52 mmol) and **3c** (0.28 g, 0.69 mmol) one equivalent of $(Et_2N)_3PNMe$ **4** (0.15 g, 0.52 mmol in the case of **3a**; 0.20 g, 0.69 mmol in the case of **3c**) in 3 ml toluolene-d_8 was added at −80°C. The reaction mixture was allowed to warm, first to −50°C, then to ambient temperature, and was NMR-spectroscopically characterized. There was no change in the NMR parameters for 2 days. *Methyl-bis(trifluoromethyl)methylene phosphorane* (**5a**) and *diethylamino-bis(trifluoromethyl)methylene phosphorane* (**5c**), according to the NMR evidence, were quantitatively formed.

General Procedure for the Synthesis of Compounds **6a** *and* **6c**

To a solution of **3a** (2.61 g, 7.5 mmol) and **3c** (3.49 g, 8.4 mmol) one equivalent of $(Et_2N)_3PNMe$ **4** (1.93 g,

TABLE 3 Experimental Details for the Synthesis of Compounds **3a** and **3c**

	2 (g)[a]	*Yield (g)*[b]	*mp (°C)*
3a	**2a** 3.68 (20)	6.9 (99)	131
3b[c]	**2b** 4.24 (20)	100 (12)	
3c	**2c** 8.44 (35)	12.5 (89)	53

[a] Values in parentheses are in millimoles.
[b] Values in parentheses are the percent values.
[c] Nonseparable mixture of decomposition products.

7.0 mmol in the case of **3a**; 2.21 g, 8.0 mmol in the case of **3c**) in 10 ml THF was added at −80°C and stirred for 1 h. The reaction mixture was cooled to −196°C, evacuated and 1.5 equivalents of hexafluoroacetone (2.57 g, 15.5 mmol in the case of **3a**; 2.94 g, 17.7 mmol in the case of **3c**) added. Within 12 h the reaction mixture was allowed to warm to ambient temperature and the volatiles were pumped off in vacuo. The residue was extracted with 5 ml of pentane, which was pumped off in vacuo to yield pure products.

2-Methyl-2,2,4,4-tetrakis(trifluoromethyl)-1,2$\lambda^5\sigma^5$*-oxaphosphetane (***6a***).* mp −15°C. MS: *m*/*e* (%): 345 ($M^+ - F$, 13); 295 ($M^+ - CF_3$, 85); 245 ($M^+ - CF_3$—CF_2, 100); and other fragments. Anal calcd for $C_7H_5F_{12}OP$ (364.07): C, 23.90; H, 1.38; F, 62.62, P, 8.51. Found: C, 24.02; H, 1.40; F, 61.80: P, 8.42.

2-Diethylamino-2,2,4,4-tetrakis(trifluoromethyl)-1,2$\lambda^5\sigma^5$*-oxaphosphetane (***6c***).* mp −5°C. MS: *m*/*e* (%): 402 ($M^+ - F$, 8); 352 ($M^+ - CF_3$, 42); 257 [$Et_2N(CF_3)_2PO^+$, 19]; 242 [$Et_2N(CF_3)_2PH^+$, 100]; 214 [$EtHN(CF_3)_2PH^+$, 83]; 164 [$F_3CC(CH_2)CF_3^+$, 41]; 145 [$H_2CC(CF_3)CF_2^+$, 33]; 95 [$H_2CCCF_3^+$, 34]; 69 (CF_3^+, 36); and other fragments. Anal calcd for $C_{10}H_{12}F_{12}NOP$ (421, 16): C, 28.50; H, 2.87; F, 54.15, P, 7.36. Found: C, 28.84; H, 3.02; F, 54.50: P, 7.39.

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