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# Molecular structures and reactivity of trifluoromethyltris(dialkylamino)phosphonium bromides [☆,☆☆]

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**Abstract**

Hexa-alkylphosphorus triamides and trifluoromethyl bromide react to give trifluoromethyltris(dialkylamino)phosphonium bromides which were used for the trifluoromethylation of benzaldehyde and copper(I) iodide in the presence of fluoride anions with different counterions; tris(diethylamino)difluorophosphorane proved to be a masked fluoride anion donor. The structures of $[CF_3P(NMe_2)_3]^+Br^-$ and $[CF_3P(NEt_2)_3]^+Br^-$ have been determined by single-crystal X-ray investigations and shown to exhibit a distorted tetrahedral bond configuration with a rather long $(F_3)C-P$ bond of 1.866(9) or 1.896(6) Å, respectively.

*Keywords:* Molecular structures; Reactivity; Trifluoromethyltris(dialkylamino)phosphonium bromides; Single-crystal X-ray determination; NMR spectroscopy

## 1. Introduction

Although trifluoromethyltris(dialkylamino)phosphonium halides, $[CF_3P(NR_2)_3]^+X^-$ (R = Me, X = Cl [1], R = Et, X = Br [2]) have been known for several years, their properties have not been investigated to any great extent. It has been shown only that $[CF_3P(NMe_2)_3]^+Cl^-$ decomposes slowly to give $CF_3H$ and $(Me_2N)_3PO$ in alkaline solution [1]. The salt $[CF_3P(NEt_2)_3]^+Br^-$ was formed as a by-product in the three-component system $CF_3Br/P(NEt_2)_3/PCl_3$ but has not been characterized [2]. Compounds of this kind are potential $CF_3$ group transfer reagents in the presence of ionic fluorides. We wish to report a simple procedure for preparing the phosphonium bromides $[CF_3P(NR_2)_3]^+Br^-$ and describe some of their properties.

## 2. Results and discussion

Hexa-alkylphosphorus triamides $P(NR_2)_3$ (**1a**: R = Me; **1b**: R = Et; **1c**: R = $^nPr$) reacted with trifluoromethyl bromide without a solvent in a closed system[1] to give $[CF_3P(NR_2)_3]^+Br^-$ (**2a**: R = Me; **2b**: R = Et; **2c**: R = $^nPr$) as colourless solids. Compounds **2a** and **2b** are hygroscopic, soluble in $CH_2Cl_2$ and $CH_3CN$, and sparingly soluble in ether and THF, whereas **2c** is non-hygroscopic and soluble in ether or THF.

$$\underset{\textbf{(1a–c)}}{P(NR_2)_3} + CF_3Br \xrightarrow{20\,^\circ C,\ 2\,d} \underset{\textbf{(2a–c)}}{[CF_3P(NR_2)_3]^+Br^-}$$

| | R |
|---|---|
| **a** | Me |
| **b** | Et |
| **c** | $^nPr$ |

In solvents such as THF, salt **2b** is precipitated in analytically pure form in 70% yield after 12 h. The reaction of **1a** and $CF_3Br$ in solution proceeded much slower with 27% conversion after 3 d. However, compound **2a** is the sole product formed contrary to the

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[☆] Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday.

[☆☆] Presented in part at the XIIth International Conference on Phosphorus Chemistry, Toulouse, France, 6–10 July, 1992, Abstract I 11.

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[1] Necessary to obtain a 93%–95% yield in the case of compounds **2a** and **2b**.

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similar reaction of **1a** and $CF_3I$ where $CF_3P(NMe_2)_2$ and $[P(NMe_2)_4]^+I^-$ were obtained [3]. The difference in the $CF_3Br$ and $CF_3I$ reactivity is probably due to their different electron affinities [4].

The unit cell of compound **2a** contains two symmetrically independent cations, **A** and **B**, two bromide ions and one solvating acetonitrile molecule (for geometrical parameters, see Table 1). The X-ray investigation showed that the P−N bonds in **2a** [1.584–1.605(5), average 1.598(5) Å] and in **2b** [1.597–1.605(5), average 1.602(5) Å] are noticeably shorter in comparison with, for example, the P−N bond lengths in $[CH_3P(NEt_2)_3]^+$ [1.625–1.633(3), average 1.628(3) Å] [5]. This effect reflects the electron-withdrawing capacity of the $CF_3$ group for lowering the energy of the outer orbitals and thus promoting more effective bonding towards nitrogen [6]. However, shortening of the P−N bonds is accompanied by elongation of P−C bonds from 1.783(3) Å to 1.866(9) Å in **2b** and 1.896(6) Å or 1.880(6) Å in **2aA** or **2aB** (see Figs. 1 and 2).

All the nitrogen atoms in **2a** and **2b** have nearly trigonal planar geometry. The arrangement of all the amino substituents is similar (Fig. 3). However, the phosphorus atoms have a noticeable distorted tetrahedral bond configuration: the N−P−N bond angles are increased to 111.3–115.5(3)° in **2a** and to 111.9–114.8(3)° in **2b**, while the C−P−N angles are reduced to 104.9–106.6(3)° in **2a** and to 105.0–105.4(3)° in **2b** (see Fig. 3). The geometrical parameters of the solvating acetonitrile molecule in the crystal of **2a** are N≡C 1.137(9) Å, C−C(Me) 1.47(2) Å, ∢N−C−C 179(1)° and are unexceptional [7].

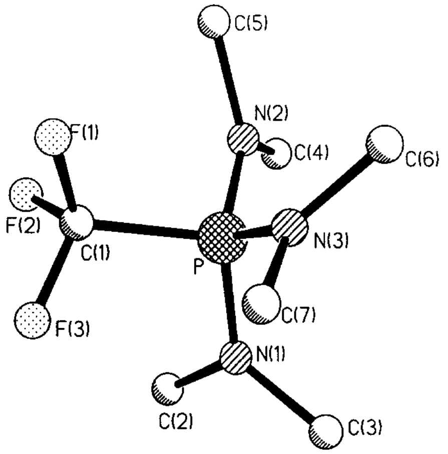

Fig. 1. General view of the cation **2aA** including the atomic numbering scheme.

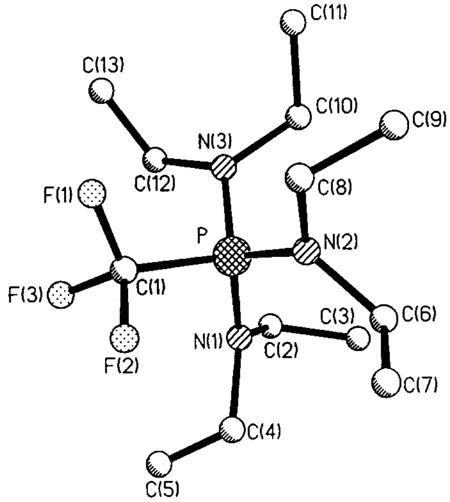

Fig. 2. General view of the cation **2b** including the atomic numbering scheme.

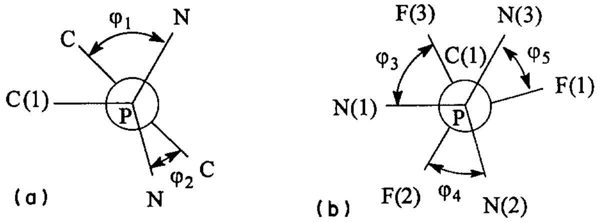

Fig. 3. Newman projections along (a) the P−N and (b) the P−C(1) bonds.

Table 1
The main geometrical parameters of cations of compounds **2a** and **2b**

| | *2aA* | *2aB* | *2b* |
|---|---|---|---|
| *Bond lengths (Å)* | | | |
| P−N(1) | 1.600(5) | 1.596(5) | 1.605(5) |
| P−N(2) | 1.598(5) | 1.584(5) | 1.597(5) |
| P−N(3) | 1.605(5) | 1.605(5) | 1.605(5) |
| P−C(1) | 1.896(6) | 1.880(6) | 1.866(9) |
| $C-F_{avg.}$ | 1.331(8) | 1.325(8) | 1.339(8) |
| *Bond angles (°)* | | | |
| N(1)−P−N(2) | 112.7(3) | 115.5(3) | 114.8(3) |
| N(1)−P−N(3) | 111.9(3) | 112.4(3) | 113.5(3) |
| N(2)−P−N(3) | 114.1(3) | 111.3(3) | 111.9(3) |
| N(1)−P−C(1) | 105.4(3) | 105.4(3) | 105.4(4) |
| N(2)−P−C(1) | 105.3(3) | 106.4(3) | 105.2(3) |
| N(3)−P−C(1) | 106.6(3) | 104.9(3) | 105.0(3) |
| *Sum of the bond angles (°)* | | | |
| N(1) | 360.1(1.6) | 359.2(1.8) | 358.4(1.4) |
| N(2) | 360.0(1.7) | 359.6(1.7) | 359.8(1.4) |
| N(3) | 360.0(1.6) | 360.0(1.6) | 355.0(1.3) |
| *Torsion angles along P−N and P−C bonds (°)* | | | |
| P−N(1) | 65.2(7) | 68.9(6) | 60.9(7) |
| P−N(2) $\phi_1$ | 68.6(6) | 62.9(6) | 59.5(7) |
| P−N(3) | 58.7(6) | 65.2(6) | 58.0(7) |
| P−N(1) | 17.8(7) | 28.4(7) | 25.9(7) |
| P−N(2) $\phi_2$ | 14.6(6) | 5.1(7) | 4.5(7) |
| P−N(3) | 9.0(7) | 13.8(7) | 35.5(7) |
| $\phi_3$ | 42.0(6) | 38.7(7) | 44.4(7) |
| $\phi_4$ | 42.6(6) | 42.0(6) | 47.2(7) |
| $\phi_5$ | 42.1(6) | 41.1(6) | 45.2(7) |

In $CH_2Cl_2$, an equimolar mixture of **2b** and TAS fluoride **3**, $(Me_2N)_3S^+[F_2SiMe_3]^-$ [8], reacts immediately at −70 °C to give tris(dialkylamino)difluorophosphorane (**4**) [9] and $CF_3H$. Surprisingly, one-half of the amount of **2b** remained unreacted (carefully checked by $^{19}F$ and $^{31}P$ NMR spectroscopy), and at −30 °C began to interact with **4** to furnish the tris(diethylamino)fluorophosphonium cation (**5**) [10] and again $CF_3H$ (86% conversion of **4** at 0 °C).

$$[CF_3P(NEt_2)_3]^+ \xrightarrow[-2FSiMe_3]{\substack{+2[F_2SiMe_3]^- \\ (CH_2Cl_2)}} [CF_3PF_2(NEt_2)_3]^-$$

$$\xrightarrow[-\langle CF_3^- \rangle]{} \underset{(\mathbf{4})}{F_2P(NEt_2)_3} \xrightarrow[-\langle CF_3^- \rangle]{[CF_3P(NEt_2)_3]^+} \underset{(\mathbf{5})}{2[FP(NEt_2)_3]^+}$$

The first step in the reaction probably proceeds via a $\lambda^5\sigma^6P$ intermediate which furnishes the difluorophosphorane **4** and $CF_3H$ by proton abstraction from the solvent. Secondly, **4** acts as a fluoride donor [11] for unreacted **2b**. When **4** and **2b** were separately mixed (1:1 ratio) in $CH_2Cl_2$ an exothermic reaction occurred to give **5** in 95% yield after 1 h at ambient temperature.

Evidence for the generation of $CF_3^-$ was provided by trapping experiments with benzaldehyde and copper(I) iodide. Slow addition of **3** at −30 °C to a solution of **2b** and benzaldehyde in THF/$CH_2Cl_2$ (1:1) led to **5** and 1-phenyl-2,2,2-trifluoroethylate (**6**). After 2 d, the phosphonium species **7** may be observed. Acidic work-up (HCl aq.) gave 1-phenyl-2,2,2-trifluoroethanol.

$$PhCHO \xrightarrow[\substack{-FSiMe_3, \\ -Br^-}]{\substack{1.\ CF_3P(NEt_2)_3{}^+Br^- \\ 2.\ [F_2SiMe_3]^-}}$$

$$\underset{(\mathbf{5})}{[FP(NEt_2)_3]^+} + \underset{(\mathbf{6})}{PhCH(CF_3)O^-} \xrightarrow{2\ d}$$

$$\underset{(7)}{[PhCH(CF_3)OP(NEt_2)_3]^+} + F^-$$

Using the system $CF_3Br/P(NEt_2)_3/PhCHO$, compound **7** was produced directly [12] at −70 °C ($\delta_P = 35.1$ ppm, $\delta_F = -80.4$ ppm). In this case, as a result of the bromophilic attack of **1b** at $CF_3Br$, the cation $[BrP(NEt_2)_3]^+$ is formed and $Br^-$ is readily replaced by $PhCH(CF_3)O^-$. A similar substitution in the less electrophilic $[FP(NEt_2)_3]^+$ took place very slowly even at ambient temperature as mentioned above.

Instead of **3**, spray-dried potassium fluoride in pyridine may be used as a source of fluoride ions; however, in this case, the reaction has to be accelerated by copper(I) iodide (~10 mol%). In the case of **2a**, benzaldehyde was also trifluoromethylated. If copper(I) iodide was used as an electrophile, a solution of $CF_3I$ and $CuCF_3$ ($\delta_F = -26.7$ ppm [13]) was obtained. In the presence of stabilizing hexamethylphosphoric triamide, iodine in 4-nitro-iodobenzene was substituted by the $CF_3$ group (5 h, 60–70 °C) to give 4-nitrotrifluoromethylbenzene in 98% yield.

## 3. Experimental details

Appropriate precautions in handling moisture and oxygen-sensitive compounds were observed throughout this work. Elemental analyses were undertaken by Mikroanalytisches Laboratorium Beller, Göttingen. NMR spectra were obtained on a Bruker AC 80 instrument operating at 80.13 MHz ($^1H$, internal standard TMS), 75.39 MHz ($^{19}F$, internal standard $CCl_3F$), 32.44 MHz ($^{31}P$, external standard 85% $H_3PO_4$) and 20.15 MHz ($^{13}C$, internal standard TMS), respectively.

### 3.1. *Crystal structure analysis of 2a and 2b*

The X-ray structural study of compounds **2a** and **2b** was performed on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ nm, the ratio of the scanning rates $\omega/\vartheta = 1.2$). The main crystallographic data for **2a** and **2b** are listed in Table 2. Both structures were solved by direct methods and refined by full-matrix least squares. The reflections with $I > 3\sigma$ were used. All hydrogen atoms in **2a** were located in the difference Fourier maps, whereas in **2b** only 50% of the H atoms were located; the positions of the remaining H atoms were calculated. The hydrogen atoms in both structures were included in the final refinement with the fixed positional and thermal ($B_{iso} = 4$ Å$^2$) parameters.

Corrections for Lorentz and polarization effects as well as the empirical correction for absorption (using the DIFABS program [14]) were applied. All structural calculations were carried out with a PDP-11/23$^+$ computer using the SDP-PLUS program package [15]. The atomic coordinates are listed in Tables 3 and 4.

Table 2
Main crystallographic data for **2a** and **2b**

| | **2a** | **2b** |
|---|---|---|
| *a* (Å) | 8.170(2) | 13.595(4) |
| *b* (Å) | 12.807(4) | 10.187(3) |
| *c* (Å) | 11.774(4) | 13.678(4) |
| $\beta$ (°) | 90.00 | 96.77(2) |
| V (Å$^3$) | 1231.8 | 1881.0 |
| *Z* | 8 | 4 |
| $D_c$ (g cm$^{-3}$) | 1.53 | 1.40 |
| space group | $P2_12_12_1$ | $P2_1/c$ |
| $\mu$ (cm$^{-1}$) | 29.4 | 22.7 |
| $\vartheta_{max}$ (°) | 25 | 24 |
| Reflection number: | | |
| measured (unique) | 2602 | 2220 |
| used in the refinement | 1941 | 1244 |
| *R* | 0.035<br>0.054$^a$ | 0.046 |
| $R_w$ | 0.045<br>0.074$^a$ | 0.055 |

$^a$Discrepancy factors for inverted structure.

Table 3
Coordinates of non-hydrogen atoms and their equivalent isotropic temperature factors $B_{eq}$ (Å$^2$) in structure **2a**

| Atom | A | | | | Atom | B | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | $B_{eq}$ (Å$^2$) | | *x* | *y* | *z* | $B_{eq}$ (Å$^2$) |
| Br(A) | 0.2595(1) | 0.44806(4) | 0.72366(3) | 3.17(2) | Br(B) | 0.7782(1) | 0.39548(4) | 0.44306(3) | 2.66(1) |
| P(A) | 0.2177(2) | 0.4047(1) | 0.98530(8) | 1.73(3) | P(B) | 0.7108(3) | 0.7446(1) | 0.17353(8) | 1.75(3) |
| F(1A) | 0.3833(6) | 0.2970(3) | 1.0502(2) | 4.6(1) | F(1B) | 0.6257(7) | 0.6470(2) | 0.2662(2) | 4.6(1) |
| F2(A) | 0.1787(7) | 0.3457(3) | 1.1053(2) | 5.0(1) | F(2B) | 0.8772(7) | 0.6875(3) | 0.2765(2) | 5.5(1) |
| F3(A) | 0.1283(7) | 0.2684(3) | 1.0270(2) | 5.0(1) | F(3B) | 0.6701(7) | 0.7547(3) | 0.3051(2) | 4.5(1) |
| N(1A) | 0.7701(8) | 0.8292(3) | 0.1791(3) | 2.4(1) | N(1B) | 0.0223(7) | 0.4129(3) | 0.9673(3) | 1.9(1) |
| N(2A) | 0.2895(7) | 0.4752(3) | 1.0243(3) | 2.1(1) | N(2B) | 0.8275(7) | 0.6925(3) | 0.1302(3) | 2.0(1) |
| N(3A) | 0.3286(7) | 0.3811(3) | 0.9225(3) | 2.2(1) | N(3B) | 0.5165(7) | 0.7372(3) | 0.1525(3) | 2.1(1) |
| C(1A) | 0.229(1) | 0.3246(4) | 1.0458(3) | 2.7(2) | C(1B) | 0.720(1) | 0.7071(4) | 0.2599(3) | 3.3(2) |
| C(2A) | −0.111(1) | 0.4159(5) | 1.0173(4) | 3.6(2) | C(2B) | 0.926(1) | 0.8513(5) | 0.2162(4) | 3.8(2) |
| C(3A) | −0.044(1) | 0.4211(5) | 0.8991(3) | 3.2(2) | C(3B) | 0.697(1) | 0.8887(4) | 0.1414(4) | 4.0(2) |
| C(4A) | 0.201(1) | 0.5461(4) | 1.0285(3) | 3.0(2) | C(4B) | 0.972(1) | 0.7168(5) | 0.0923(4) | 4.1(2) |
| C(5A) | 0.447(1) | 0.4723(5) | 1.0618(4) | 3.5(2) | C(5B) | 0.808(1) | 0.6096(4) | 0.1321(4) | 2.9(2) |
| C(6A) | 0.4694(9) | 0.4257(4) | 0.8958(4) | 2.6(2) | C(6B) | 0.458(1) | 0.7022(4) | 0.0926(4) | 2.9(2) |
| C(7A) | 0.293(1) | 0.3124(4) | 0.8868(4) | 3.1(2) | C(7B) | 0.380(1) | 0.7636(5) | 0.1959(4) | 3.1(2) |
| N(4)[a] | 0.736(1) | 0.3731(4) | 0.1648(3) | 4.5(2) | | | | | |
| C(8)[a] | 0.727(1) | 0.4162(4) | 0.2056(4) | 3.2(2) | | | | | |
| C(9)[a] | 0.712(1) | 0.4710(4) | 0.2584(4) | 4.1(2) | | | | | |

[a] Atoms of solvating molecule.

Table 4
Coordinates of non-hydrogen atoms and their equivalent isotropic temperature factors $B_{eq}$ (Å$^2$) in structure **2b**

| Atom | *x* | *y* | *z* | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Br | 0.89048(7) | 0.24546(8) | 0.40354(6) | 2.76(2) |
| P | 0.2587(2) | 0.2232(2) | 0.4903(2) | 2.10(5) |
| F(1) | 0.4057(4) | 0.2977(6) | 0.3861(4) | 5.1(1) |
| F(2) | 0.4116(4) | 0.0962(5) | 0.4285(4) | 5.8(2) |
| F(3) | 0.4579(4) | 0.2447(5) | 0.5336(4) | 5.5(1) |
| N(1) | 0.2617(5) | 0.1494(6) | 0.5943(4) | 2.0(2) |
| N(2) | 0.1931(5) | 0.1523(6) | 0.4010(5) | 2.2(2) |
| N(3) | 0.2335(5) | 0.3768(5) | 0.4956(5) | 2.5(2) |
| C(1) | 0.3882(7) | 0.2163(8) | 0.4581(7) | 3.5(2) |
| C(2) | 0.2052(6) | 0.1987(8) | 0.6713(6) | 2.5(2) |
| C(3) | 0.1024(7) | 0.1422(9) | 0.6679(7) | 3.7(2) |
| C(4) | 0.3018(6) | 0.0129(7) | 0.6080(6) | 2.6(2) |
| C(5) | 0.3919(6) | 0.0088(8) | 0.6851(6) | 3.0(2) |
| C(6) | 0.1326(6) | 0.0326(7) | 0.4134(5) | 2.1(2) |
| C(7) | 0.1695(7) | −0.0857(8) | 0.3584(6) | 3.2(2) |
| C(8) | 0.1989(6) | 0.1983(8) | 0.2977(5) | 2.6(2) |
| C(9) | 0.0984(7) | 0.2094(8) | 0.2386(6) | 3.3(2) |
| C(10) | 0.1300(6) | 0.4218(8) | 0.4692(6) | 2.5(2) |
| C(11) | 0.1202(7) | 0.5192(8) | 0.3828(6) | 3.5(2) |
| C(12) | 0.3003(7) | 0.4645(9) | 0.5655(8) | 5.3(3) |
| C(13) | 0.3457(8) | 0.569(1) | 0.5170(9) | 6.6(3) |

Table 5
Experimental details for the preparation of compounds **2a–c**

| Compound | Reactants [g (mmol)] | Yield [g (%)] | M.p. (°C) |
|---|---|---|---|
| **2a** | **1a**: 8.15 (50)<br>$CF_3Br$: 14.90 (100) | 95 | 107–109[a] |
| **2b** | **1b**: 12.35 (50)<br>$CF_3Br$: 14.90 (100) | 93 | 73–74 |
| **2c** | **1c**: 16.55 (50)<br>$CF_3Br$: 14.90 (100) | 40 | 151–152 |

[a] Decomposed at 180 °C.

### *3.2. General preparative method (see Table 5)*

Trifluorobromomethane (4.9 g, 100 mmol) was condensed at −196 °C into an evacuated 100 ml steel cylinder containing 50 mmol of **1**. At this temperature, argon was added to bring the pressure to 1 atm. The cylinder was closed, warmed up and kept at 20 °C for 2–3 d. After opening the vessel, excess trifluoromethane was pumped off, the residue washed with 20 ml THF and 10 ml of diethyl ether, and dried at 20 °C in vacuum for 1 h.

Trifluoromethyltris(dimethylamino)phosphonium bromide (**2a**): $^1$H NMR δ: 3.00 (dq, $^3J_{PH}=9.20$, $^5J_{FH}=0.6$ Hz) ppm. $^{19}$F NMR δ: −59.25 ($^2J_{PF}=108.0$ Hz) ppm. $^{31}$P NMR δ: +36.05 ppm. $^{13}$C NMR δ: 36.98 ($CH_3$, $^2J_{PC}=4.3$ Hz); 120.90 ($CF_3$, dq, $^1J_{PC}=229.8$, $^1J_{CF}=319.4$ Hz) ppm. $C_7H_{18}BrF_3N_3P$ (312.11): Found: C, 26.91; H, 5.61; F, 18.00; P, 9.76%. Calc.: C, 26.92; H, 5.77; F, 18.27; P, 9.94%.

Trifluoromethyltris(diethylamino)phosphonium bromide (**2b**): $^1$H NMR δ: 1.21 ($CH_3$, t, 18H, $^3J_{HH}=7.08$ Hz); 3.27 ($CH_2$, dq, 12H, $J_{PH}=14.37$ Hz) ppm. $^{19}$F NMR δ: −65.63 ($^2J_{PF}=107.40$ Hz) ppm. $^{31}$P NMR δ: 35.20 ppm. $^{13}$C NMR δ: 12.25 ($CH_3$); 39.20 ($CH_2$, $^2J_{PC}=3.7$ Hz); 121.2 ($CF_3$, $^1J_{PC}=228.9$, $^1J_{CF}=296.3$ Hz) ppm. $C_{13}H_{30}BrF_3N_3P$ (396.27): Found: C, 39.16; H, 7.91;

F, 14.20; P, 7.75%. Calc.: C, 39.39; H, 7.58; F, 14.40; P, 7.60%.

Trifluoromethyltris(di-n-propylamino)phosphonium bromide (**2c**): $^1$H NMR δ: 0.87 ($CH_3$, 9,18H, $^{31}J_{HH}=7.0$ Hz); 1.60 ($CH_2$, m, 12H); 3.03 ($CH_2$, m, 12H) ppm. $^{19}$F NMR δ: −59.20 ($^2J_{PF}=106.8$ Hz) ppm. $^{31}$P NMR δ: 34.57 ppm. $C_{19}H_{42}BrF_3N_3P$ (480.44): Found: C, 47.35; H, 8.67; F, 11.59; P, 6.40%. Calc.: C, 47.50; H, 8.75; F, 11.88; P, 6.46%.

### 3.3. Reaction of 2b and 4

To a stirred solution consisting of 0.4 g (1 mmol) of **2b** in 1 ml of $CH_2Cl_2$ was added 0.3 g (1 mmol) of **4**. The exothermic reaction began immediately with evolution of $CF_3H$ (detected by $^{19}$F NMR spectroscopy). After 12 h, 100% of $[(Et_2N)_3PF]^+$ (**5**) was observed [10].

### 3.4. Reaction of 2b and benzaldehyde

A solution of benzaldehyde (1.06 g, 10 mmol) and 4.75 g (12 mmol) of **2b** in 25 ml of $CH_2Cl_2$/THF (1:1) was gradually treated at −30 °C with $(Me_2N)_3S^+$ $[F_2SiMe_3]^-$ (2.75 g, 10 mmol). The reaction mixture was held for 30 min at 20 °C, diluted with 10 ml of 20% HCl and stirred for 2 h. The product was extracted, washed with $NaHSO_3$ solution to remove unreacted benzaldehyde and dried over $Na_2SO_4$. Distillation gave 1.43 g (81%) of 1-phenyl-2,2,2-trifluoroethanol (b.p. 84–86 °C/14 mmHg). $^{19}$F NMR δ: 79.35 (d, $^3J_{HF}=6.89$ Hz) ppm.

Similarly, compound **2a** (1.4 g, 4.5 mmol), benzaldehyde (0.4 g, 3.8 mmol) and CuI (0.1 g, 0.5 mmol) in 4.5 ml of pyridine were treated with 0.26 g (4.5 mmol) of spray-dried KF. The slight exothermic reaction was complete within 1.5 h. 1-Phenyl-2,2,2-trifluoroethanol was again obtained, 0.36 g (55%), identified by its $^{19}$F and $^1$H NMR spectra.

### 3.5. Preparation of trifluoromethylcopper(I)

A mixture of **2a** (0.31 g, 1 mmol), spray-dried KF (0.06 g, 1 mmol) and CuI (0.20 g, 1 mmol) in 3 ml of DMF was stirred for 2 h at 20 °C. Complete conversion to furnish $CF_3Cu$ occurred as determined by $^{19}$F NMR spectroscopy ($\delta_F=-26.7$ ppm).

The same reaction mixture was kept at 0 °C for 3 h, 3 ml of hexamethylphosphoric triamide and *p*-nitroiodobenzene (2.23 g, 1 mmol) were added and the mixture warmed up to 60 °C. After 5 h, the reaction mixture contained 98% of *p*-nitrotrifluoromethylbenzene [13] ($\delta_F=-67.7$ ppm).

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## References

[1] D.S. Paulin, A.J. Tomlinson and R.G. Cavell, *Inorg. Chem., 16* (1977) 24.

[2] W. Volbach and I. Ruppert, *Tetrahedron Lett., 24* (1983) 5509.

[3] H.J. Ang, J. Manoussakis and Y.O. El-Nigumi, *J. Inorg. Nucl. Chem., 30* (1968) 175.

[4] C.P. Andrieux, L. Gélis, Medebielle, J. Pinson and J.-M. Savéant, *J. Am. Chem. Soc., 112* (1990) 3509.

[5] H. Schmidbaur, R. Pichl and G. Müller, *Z. Naturforsch., 41b* (1986) 395.

[6] A.N. Chernega, M.Yu. Antipin, Yu.T. Struchkov and V.D. Romanenko, *Zh. Strukt. Khim., 27* (1986) 130.

[7] M.J. Barrow, *Acta Crystallogr., A39* (1983) 158.

[8] W.J. Middleton, *Org. Synth., 64* (1985) 221.

[9] G.I. Drozd, M.A. Sokalskij, O.G. Strukov and S.Z. Ivin, *Zh. Obshch. Khim., 40* (1970) 2396.

[10] R. Bartsch, O. Stelzer and R. Schmutzler, *Z. Naturforsch., 36b* (1981) 1349.

[11] T. Martini, *Tetrahedron Lett., 22* (1976) 1857.

[12] A. Kruse, G. Siegemund, A. Schumann and I.W. Ruppert, Ger. Patent DE 3 801248, 1989; [*Chem. Abs., 112* (1990) 77 537u].

[13] D.J. Burton and Zh.-Y. Yang, *Tetrahedron, 48* (1992) 189.

[14] N. Walker and D. Stuart, *Acta Crystallogr., A39* (1983) 158.

[15] B.A. Frenz, in H. Schenk et al. (eds.), *Computing in Crystallography,* Delft University Press, Delft, 1976, pp. 64–74.