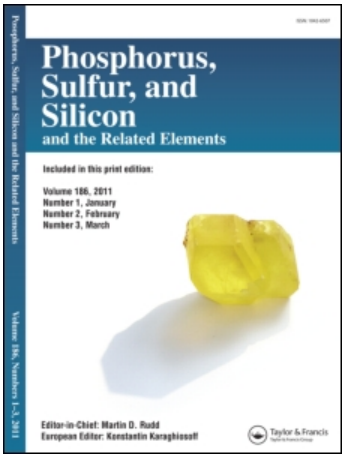

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Tris(trifluoromethyl) Cyclotriphosphine $(CF_3P)_3$: Formation and NMR Spectroscopy

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Tris(trifluoromethyl) Cyclotriphosphine $(CF_3P)_3$: Formation and NMR Spectroscopy

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The reaction of trifluoromethyl dichlorophosphine (CF_3PCl_2) with mild reducing agents results in the formation of CF_3-substituted cyclooligophosphines $(CF_3P)_n$ (n = 3–5). The hitherto unknown cyclotriphosphine $(CF_3P)_3$ is described here for the first time and is characterized by multinuclear (^{31}P, ^{19}F) NMR spectroscopy. A full analysis of the ^{19}F NMR signals of $(CF_3P)_3$ (X and Y part of $[AX_3]_2BY_3$ spectrum) is presented.

Keywords Cyclophosphanes; fluorine; NMR spectroscopy; phosphorus; trifluoromethyl

INTRODUCTION

The trifluoromethyl group (CF_3) is a very special substituent in organoelement chemistry.[1,2] In combination with phosphorus, it exerts a strong influence on the reactivity of the adjacent phosphorus atom. For example, unlike phosphinidenes with common alkyl and aryl substituents at phosphorus, trifluoromethylphosphinidene CF_3P forms a 1:1 adduct with trimethylphosphine; the compound $(CH_3)_3P{=}PCF_3$ was first reported 1961 by A. B. Burg and W. Mahler[3] and obtained by nucleophilic degradation of the corresponding cyclopolyphosphines $(CF_3P)_n$ (n = 4,5). It may be viewed as a source of monomeric trifluoromethylphosphinidene CF_3P, stabilized by coordination with a strong soft base. In the absence of such a base, trifluoromethylphosphinidene

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łodź, Poland, on the occasion of his 70th birthday.

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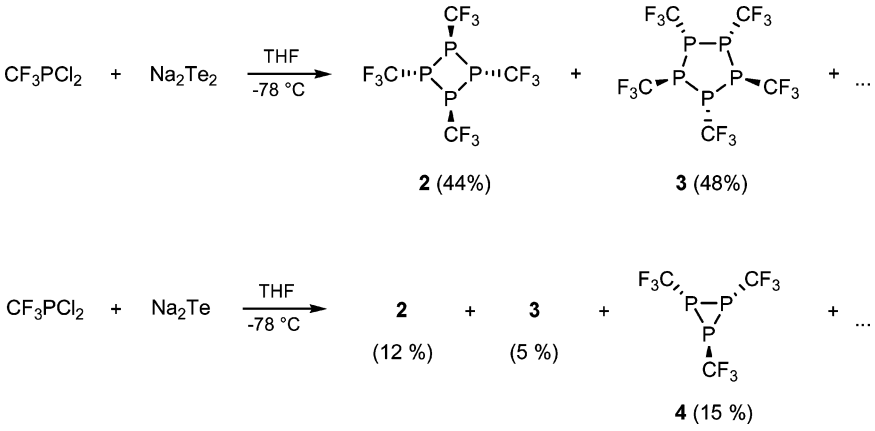
oligomerizes to form the tetramer $(CF_3P)_4$ and the pentamer $(CF_3P)_5$. Both cyclopolyphosphines were first obtained by W. Mahler and A. B. Burg from the reduction of the diiodide CF_3PI_2 with elemental mercury, which yields $(CF_3P)_4$ and $(CF_3P)_5$ in a 3:2 ratio.[4,5]

Interestingly, no CF_3-substituted cyclopolyphosphines with a smaller or larger ring size have been reported in the literature. Cyclotriphosphines $(RP)_3$ are known to form preferentially with large substituents R at phosphorus.[6] However A. H. Cowley et al. observed the formation of $(C_2F_5P)_3$,[7] which rearranged to the corresponding cyclotetraphosphine $(C_2F_5P)_4$ at ambient temperature.[8] R. A. Wolcott and J. L. Mills reported the synthesis of the stable heptafluoroisopropyl derivative $(iC_3F_7P)_3$.[8] In both cases, no satisfactory NMR data are available, however.

Here we report on the reaction of CF_3PCl_2 with Na_2Te and Na_2Te_2, which yields the cyclopolyphosphines $(CF_3P)_n$ (n = 3,4,5). The cyclotriphosphine $(CF_3P)_3$ is observed here for the first time and is characterized by ^{31}P NMR as well as by full analysis of its ^{19}F NMR spectrum.

RESULTS AND DISCUSSION

Trifluoromethyl dichlorophosphine CF_3PCl_2 (**1**) reacts with the equimolar amount of sodium ditelluride Na_2Te_2 in THF at −78°C to give the cyclotetraphosphine $(CF_3P)_4$ (**2**) and the cyclopentaphosphine $(CF_3P)_5$ (**3**) as the main products. When sodium telluride Na_2Te is used in the reaction with CF_3PCl_2 in addition to the cyclophosphines **2** and **3**, the cyclotriphosphine $(CF_3P)_3$ (**4**) also is formed (Scheme 1).



SCHEME 1

In contrast to the condensation of aminodichlorophosphines with $Te(SiMe_3)_2$, which yields phosphorus tellurium heterocycles $[(R_2N)_2P]_nTe_m$,[9] reduction of the dichlorophosphine by the sodium tellurides with formation of cyclopolyphosphines and elemental tellurium is the main pathway here.

The cyclotetraphosphine **2** is readily identified by its ^{31}P and ^{19}F NMR spectra (Figure 1). In the $^{31}P\{^{19}F\}$ NMR spectrum, a singlet at $\delta = -72.2$ is observed, which splits into a complex multiplet (a part of $[AX_3]_4$ spectrum) when coupling to fluorine is allowed. The ^{31}P chemical shift of **2** compares well to that of the methyl derivative $(CH_3P)_4$ ($\delta = -67.7$),[10] as well as to those of other cyclotetraphosphines $(RP)_4$ (e.g., $\delta = -72.8$ for R = 1-Ad,[11] $\delta = -58.0$ for R = *t*Bu[11]). The ^{19}F NMR signal for the CF_3 groups appears at $\delta = -50.9$ and displays the typical pattern for the X part of an $[AX_3]_4$ spectrum (Figure 1).

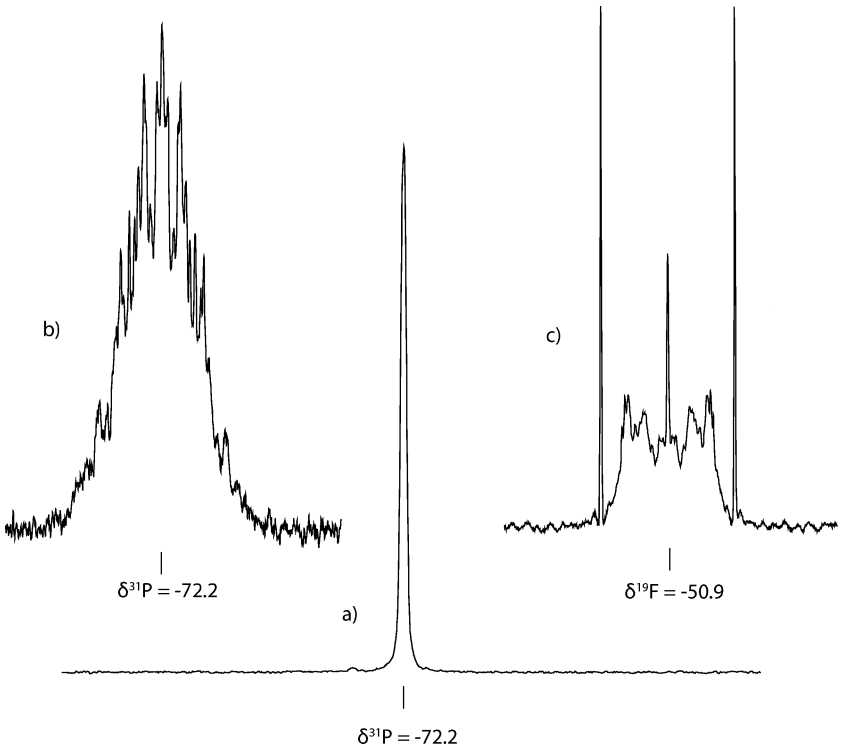


FIGURE 1 ^{31}P and ^{19}F NMR signals of $(CF_3P)_4$, ca. 0.1 M solution in THF: a) ^{31}P NMR signal with ^{19}F decoupling, b) ^{31}P NMR signal without ^{19}F decoupling (a part of $[AX_3]_4$), c) ^{19}F NMR signal (X part of $[AX_3]_4$).

For the cyclopentaphosphine **3**, a high order $^{31}P^{19}F$ NMR spectrum of AA'BB'C type is observed, in accord with the symmetry of the molecule (Figure 2). Pseudorotation of the five-membered ring in **3**[12] is slow on the NMR time scale at ambient temperature, and the spectrum displays a well resolved pattern of sharp lines. ^{31}P chemical shifts and P,P coupling constants result from a computer assisted iterative

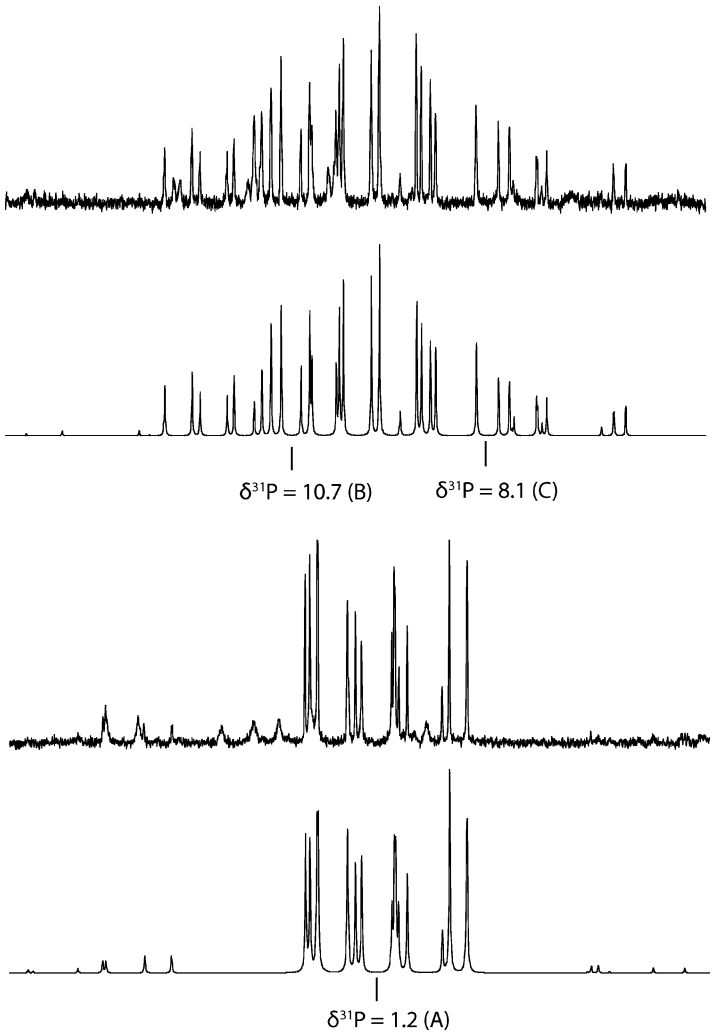
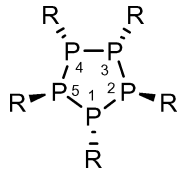


FIGURE 2 Observed (above) and calculated (below) $^{31}P\{^{19}F\}$ NMR spectrum of $(CF_3P)_5$ (**3**).

TABLE I ^{31}P NMR Chemical Shifts and P,P Coupling Constants (in Hz) for $(CF_3P)_5$ (3) and $(CH_3P)_5$[14]



		3[a]	$(CH_3P)_5$
δ^{31}P	P1	8.1	−49.8
	P2,5	10.7	−49.2
	P3,4	1.2	−47.5
$^1J_{PP}$	P1,P2; P1,P5	−215.7	−248.6
	P2,P3; P4,P5	−224.0	−236.4
	P3,P4	−346.7	−310.3
$^2J_{PP}$	P1,P3; P1,P4	+36.6	+23.3
	P2,P4; P3,P5	−5.2	−8.1
	P2,P5	−0.4	−3.6

[a]The relative signs of the coupling constants result from the iterative fitting of the spectrum and are given assuming a negative sign for $^1J_{PP}$.[16]

fitting of the spectrum, and are given in Table I. The NMR parameters thus obtained mainly confirm those reported by J. P. Albrand and J. B. Robert, derived from ^{31}P[^{31}P] tickling experiments.[13]

The ^{31}P NMR parameters of the related methyl substituted cyclopentaphosphine $(CH_3P)_5$[14] are also included in Table I for comparison. The CF_3 substituent at phosphorus affects mainly the position of the ^{31}P NMR signals, which in the case of **3** are shifted to the lower field by about 50 ppm. Interestingly, the P,P coupling constants are much less affected and are quite similar in both cyclophosphines. For both molecules, the substituents at adjacent phosphorus atoms will prefer positions on alternate sides of the five-membered ring in order to minimize steric repulsion. This is possible for all except one pair of phosphorus atoms, for which the substituents are oriented to the same side of the ring. This situation, shown for the solid state in the case of **3**,[15] is confirmed also for the solution by the symmetry of the spin system and by the large value of $^1J_{PP}$ between P3 and P4, as well as by the positive and relatively large values of $^2J_{PP}$ between P1 and P3(4) (Table I).

The CF_3-substituted cyclotriphosphine **4** is observed only in the reduction of CF_3PCl_2 with Na_2Te and is reported here for the first time.

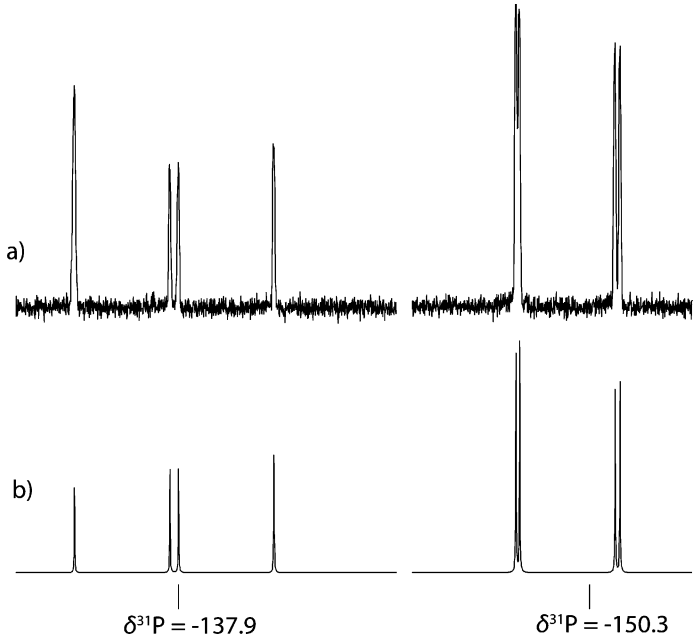


FIGURE 3 $^{31}P\{^{19}F\}$ NMR spectrum of cyclotriphosphine $(CF_3P)_3$ (**4**): a) observed and b) calculated spectrum.

In THF solution at room temperature, it converts within three weeks completely to the cyclotetraphosphine **2**, as was also reported for the pentafluoroethyl derivative.[8] The identity of the cyclotriphosphine **4** results unequivocally from its $^{31}P\{^{19}F\}$ NMR spectrum and from the full analysis of its ^{19}F NMR spectrum. It represents the first perfluoroalkyl-substituted cyclotriphosphine, for which detailed NMR spectroscopic data are now available.

The $^{31}P\{^{19}F\}$ NMR spectrum of cyclotriphosphane **4** displays the characteristic eight-line pattern for an A_2B type spin system (Figure 3), in accordance with the symmetry of the molecule. Including the fluorine nuclei of the three CF_3 groups, it expands to a 12 spin system of $[AX_3]_2BY_3$ type. The ^{19}F NMR spectrum (Figure 4) shows two signals in a 2:1 integral ratio, representing the X and Y part, respectively. The signal of the Y nuclei at $\delta = -53.6$ can be analyzed according to first order (doublet of triplets of septets), due to the symmetric position of the Y nuclei with respect to the other coupling nuclei. The signal for the X nuclei at $\delta = -52.9$ is of high order, however. Its computer assisted iterative analysis yields in addition to the values for $^2J_{PF}$, $^3J_{PF}$, and

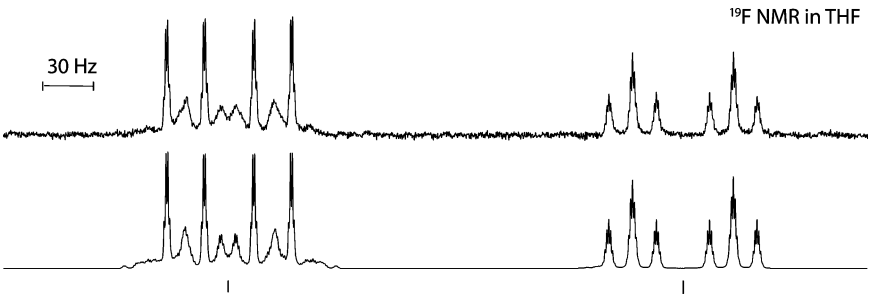
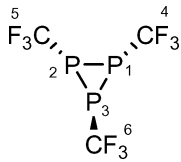


FIGURE 4 Observed (above) and calculated (below) ^{19}F NMR spectrum of cyclotriphosphine $(CF_3P)_3$ (**4**).

$^5J_{FF}$ and also the "hidden" coupling constant between the isochronous A nuclei (Table II).

The ^{31}P NMR signals of cyclotriphosphine **4** appear at high field in a region typical for P_3-rings. They are shifted to low field compared to those of the related methyl substituted cyclotriphosphine $(CH_3P)_3$ (P_A: $\delta = -171.0$, P_B: $\delta = -157.3$, $^1J_{PP} = -170.8$ Hz).[10] The signals of

TABLE II ^{31}P and ^{19}F NMR Data of Cyclotriphosphine $(CF_3P)_3$ (4)



δ^{31}P	P1,2	−150.3
	P3	−137.9
$^1J_{PP}$	P1,P3; P2,P3	−171.3
	P1,P2	−199.0
δ^{19}F	F4,5	−52.9
	F6	−53.6
$^2J_{PF}$	P1,F4; P2,P5	+82.5
	P3,F6	+58.6
$^3J_{PF}$	P1,F5; P2,F4	−32.0
	P1,F6; P2,F6	−13.9
	P3,F4; P3,F5	−21.9
$^5J_{FF}$	F4,F5	−2.5
	F4,F6; F5,F6	−1.1

Coupling constants J in Hz.

[a]The relative signs of the coupling constants result from the iterative fitting of the spectrum and are given assuming a negative sign for $^1J_{PP}$.[16]

cyclotriphosphines $(RP)_3$ with bulky organic substituents (R = 1-Ad: $P_A\delta = -81.0$, $P_B\delta = -69.4$, $^1J_{PP} = -197.9$ Hz[11]; R = *t*Bu: $P_A\delta = -71.0$, $P_B\delta = -109.6$, $^1J_{PP} = -201.1$ Hz[11]) are found at a still lower field. The value of the "hidden" coupling constant $^1J_{PP}$ between P1 and P2 is with −199.0 Hz larger than between P3 and P1(2) in accord with the *cis* orientation of the CF_3 substituents at these phosphorus atoms.

CONCLUSION

Trifluoromethyl dichlorophosphine CF_3PCl_2 is reduced by Na_2Te or $Na_2Te_2$to yield the cyclophosphines $(CF_3P)_4$ (**2**) and $(CF_3P)_5$ (**3**). In the case of the reaction with Na_2Te, the cyclotriphosphine $(CF_3P)_3$ (**4**) also is formed and is reported here for the first time. Although cyclotriphosphine **4** slowly converts in solution to the cyclotetraphosphine **2**, it is stable enough to allow characterization by ^{31}P and ^{19}F NMR spectroscopy. A comparison of the ^{31}P NMR data of $(CF_3P)_n$ (n = 3−5) with those of the related methyl substituted cyclophosphines $(CH_3P)_n$ (n = 3–5) reveals that the substitution of CH_3 by CF_3 effects mainly the ^{31}P chemical shifts and, to a much lower extent, the P,P coupling constants.

EXPERIMENTAL

All reactions were carried out under inert gas atmosphere using Schlenk techniques. Argon (Messer Griesheim, purity 4.6 in 50 l steel cylinder) was used as inert gas. All glass vessels were stored in a 130°C drying oven and were flame dried in vacuum at 10^{-3} mbar before use. Tetrahydrofurane was freshly distilled from sodium/benzophenone before use. Na_2Te and Na_2Te_2 were prepared following the procedure for Na_2Se and Na_2Se_2[17] and stored in a dry box under nitrogen atmosphere. CF_3PCl_2 was prepared as described in the literature.[18,19]

NMR spectra were recorded with a Jeol EX 400 Eclipse instrument at 161.997 MHz (^{31}P) and 376.548 MHz (^{19}F). Chemical shifts are referred to 85% H_3PO_4 (^{31}P) and $CFCl_3$ (^{19}F) as external standards. All spectra were mesured at 25°C. For the iterative fitting of the ^{31}P and ^{19}F NMR spectra, the PERCH program package[20] was used.

Reaction of CF_3PCl_2 with Na_2Te_2

In a Schlenk flask, Na_2Te_2 (602 mg, 2 mmol) was suspended in 4 mL of dry THF. The suspension was cooled down to −78°C using an acetone/dry ice bath, and CF_3PCl_2 (342 mg, 2 mmol) in 4 mL of toluene was added dropwise with stirring during 10 min. The reaction mixture

was allowed to warm up to 0°C, and stirring was continued overnight at that temperature. The precipitate formed was separated using a centrifuge, and the clear liquid phase was transferred via a syringe into a Schlenk flask and stored at −20°C. The ^{31}P and ^{19}F NMR spectra of the solution showed the presence of **2** (48%), **3** (52%). For the NMR data of **2**, see Figure 1; for the ^{31}P NMR data of **3**, see Table I. ^{19}F NMR of **3** (THF): $\delta = -41.7$ (m, 6F, 2,5- or 3,4-CF_3), −45.0 (m, 6F, 2,5- or 3,4-CF_3), −45.8 (m, 3F, 1-CF_3).

Reaction of CF_3PCl_2 with Na_2Te

Na_2Te (347 mg, 2 mmol) in 4 mL THF was reacted with CF_3PCl_2 (342 mg, 2 mmol) in 4 mL toluene as described above. The workup of the reaction mixture followed the procedure described for the analogous reaction of Na_2Te_2 and CF_3PCl_2 (see above). The ^{31}P and ^{19}F NMR spectra of the clear filtrate showed the signals of **2** (12%), **3** (5%), and **4** (15%) together with the signals of other still unidentified products.

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