An Unusual Reaction of Hexafluoroacetone with Methylenediphosphanes: Facile Synthesis of Carbodiphosphoranes

Igor Shevchenko,*[a] Rostislav Mikolenko,[a] Sandra Loss,[b] and Hansjörg Grützmacher*[b]

Keywords: Methylenediphosphane / Hexafluoroacetone / Carbodiphosphorane / Ylides / Carbenes

The oxidation of the methylenediphosphanes **3a,b** with hexafluoroacetone does not lead to the expected dioxaphospholane heterocycles, but yields quantitatively the carbodiphosphoranes **5a,b**. Compounds **5a,b** easily add HCl, HF or Cl_2 to the ylidic bonds. The chloro derivative **14b,** and its analogue **17** were used for the synthesis of phosphonium substituted carbenes.

It is well-known that the reaction of phosphanes with two equivalents of hexafluoroacetone (HFA) leads to the formation of phosphoranes in which the phosphorus atom is included in dioxaphospholane heterocycles.[1–4] It turns out that this is not the only possible pathway for this reaction. In one of our previous papers we described the formation of the phosphorus ylide **2** from the reaction of the methylenephosphinophosphorane **1** with one equivalent of HFA.[5] However, we considered this to be an exception to the rule as **1** possesses unique chemical properties due to the ability of the λ^5-phosphorus atom to form zwitterionic structures with tetra- and hexacoordinate phosphorus atoms bearing opposite charges.[6] According to the X-ray data **2** may indeed have the zwitterionic structure **2′**.[5]

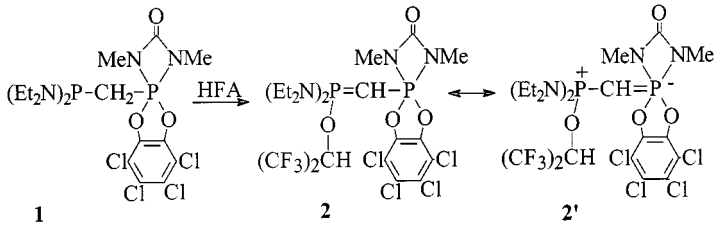
It appears, however, that this reaction is not an exception, but has a more common nature. In our preliminary communication[7] we reported an unusual reaction of the bis[bis(dialkylamino)phosphinyl]methanes **3a,b** with two equivalents of hexafluoroacetone, which quantitatively yields the carbodiphosphoranes **5a,b**. The addition of HFA to **3a,b** is accompanied by the migration of two protons from the $P-CH_2-P$ unit to the carbon atoms of HFA. Thus the presence of a methylene group between the two phosphorus atoms is a necessary condition for this reaction.

Formally, the mechanism of the formation of the carbodiphosphoranes **5a,b** can be considered to be an addition of the tautomeric P–H ylide form **3′a,b** to the carbonyl function of HFA. However, it is more likely that the migration of the proton from the $P-CH_2-P$ unit follows an electrophilic attack by HFA on the phosphorus. This reaction probably consists of two steps with the intermediate formation of the monoylides **4a** or **4b**. However, we could not detect these compounds by NMR spectroscopy. If only one equivalent of HFA was added to methylenediphosphanes **3a,b**, the reaction mixture was found to consist of starting material **3** and reaction product **5** in equal proportions. The reaction proceeds smoothly at room temperature by slow bubbling of gaseous HFA through a solution of **3a** or **3b** in hexane. The $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures show the presence of only one compound **5a** or **5b**, respectively (one singlet at $\delta = 33 - 37$). The location of the two equivalent protons in the α-positions to the CF_3 groups is confirmed by the ^{19}F-NMR spectra: all fluorine atoms are equivalent and appear as a doublet at $\delta = -73.0$ with a $^3J_{HF}$ coupling constant of 6.8 Hz. The $HC(CF_3)_2$ protons display the same coupling constant in the ^1H-NMR spectra, showing a characteristic low field multiplet at $\delta = 6.2$. NMR spectroscopic studies revealed an interesting phenomenon: this multiplet of nine slightly broadened lines is a combination of a septet, caused by $^3J_{FH}$coupling, and a triplet caused by $^3J_{PH}$coupling, with approximately equal coupling constants. The two marginal lines are of very low intensity and can only be distinguished at high signal-to-noise ratio and amplification. This unexpected $^3J_{PH}$ triplet was also found in the ^{31}P-NMR spectrum of **5a** or **5b** when measured with the selective decoupling of the protons of the NR_2 group. This means that the protons of the two $HC(CF_3)_2$ units are equivalent for each of the two phosphorus atoms and vice versa. This unusual P–H coupling is probably accounted for by a rapid exchange between the two protons of the $HC(CF_3)_2$ groups, as in **5′a,b**. Derivatives of **5a,b** – the hydrochloride salts **7a,b**, the tetrafluoroborate **16** and the dichloro- and tetrachloro derivatives **13, 14** – exhibit the same spectroscopic phenomenon (see below). It should be noted that the dimethylamino groups of **5a** appear in the ^1H-NMR spectrum not as a doublet, but as a pseudo-triplet, at $\delta = 2.59$, with a broadened central line which is consistent with the NMR spectroscopic data of known compounds. The analogous carbodiphosphorane, which has chlorine atoms instead of HFA groups at the two phosphorus atoms, shows the same pattern for the NMe_2 groups in its ^1H-NMR spectrum.[8]

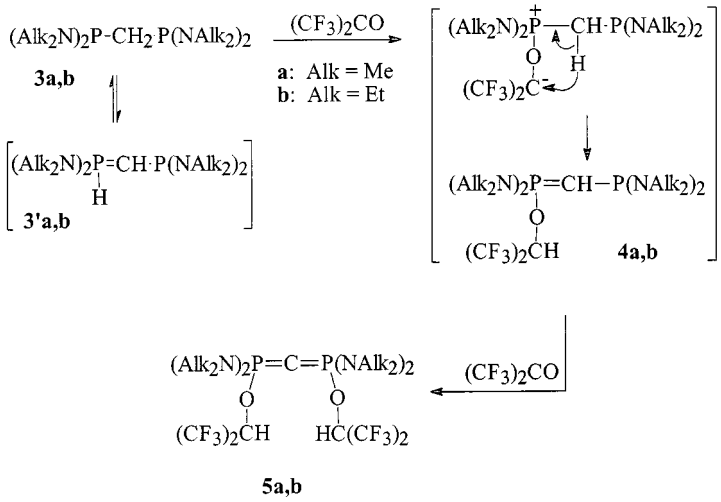
Theoretically, the reaction of **3a**,**b** with HFA can also lead to compounds **6a**,**b**, which are structural isomers of **5a**,**b** and which would have approximately the same spectral

[a] Institute of Bioorganic Chemistry,
Murmanskaya Street 1, 252660 Kiev, Ukraine
Fax: (internat.) + 38-044/573-2552
E-mail: ishev@bpci.kiev.ua; ishev@bioorg.kiev.ua
[b] Laboratorium für Anorganische Chemie,
ETH-Zentrum,
Universitätstrasse 6, CH-8092 Zürich
Fax: (internat.) + 41-1/632-1090
E-mail: gruetz@inorg.chem.ethz.ch

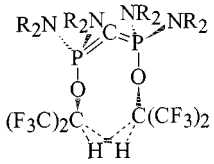
  1434–1948/99/1010–1665 $ 17.50+.50/0



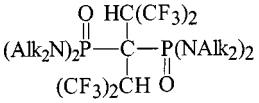
Scheme 1. Reaction of **1** with HFA



Scheme 2. Reaction of **3a,b** with HFA



5'a,b

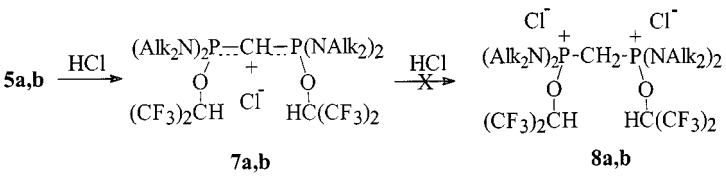


6a,b

data. However, unlike **6a,b**, the carbodiphosphoranes **5a,b** have an ylidic structure which was subsequently confirmed by treating them with HCl to form the stable salts **7a,b**. As strong bases, **5a**,**b** also react with ammonium chlorides. For this reason, small quantities of **7a**,**b** are always formed together with **5a,b** if the starting methylenediphosphanes **3a,b** are contaminated with dialkylammonium chlorides. However, compounds **7a,b** are not soluble in hexane and can easily be separated.

The structures of **7a,b** are entirely consistent with the NMR spectroscopic data obtained. The ^{13}C-NMR spectrum shows a triplet for the P−C−P carbon atom at δ = 7.35. Such an upfield chemical shift is indicative of a carbon atom bearing a negative charge. The ^{1}H-NMR spectrum of **7a** is shown in Figure 1. As in the case for **3a**, the $HC(CF_3)_2$ protons are equivalent towards each phosphorus atom and appear as a multiplet of nine lines at δ = 6.71. This signal, however, is not well resolved due to larger differences between the $^{3}J_{FH}$ and $^{3}J_{PH}$coupling constants. As in **3a,** the NMe_2 units of **7a** appear as pseudo triplets in the ^{1}H- and ^{13}C-NMR spectra. It is important to note that, despite their ylidic character, **7a,b** are very stable towards hydrolysis. With HCl no further reaction occurs and the expected diphosphonium salts **8a,b** cannot be obtained in this way.

The carbodiphosphorane **5a** slowly decomposes in hexane solution at room temperature and its signal in the ^{31}P-NMR spectrum disappears within several hours. Compound **5b,** containing bulkier diethylamino substituents, is more stable and a hexane solution of **5b** can be stored without decomposition for two days. However, subsequent evaporation of the solvent causes **5b** to decompose. The choice of hexane as solvent is very important for the preparation



Scheme 3. Reaction of **5a,b** with HCl

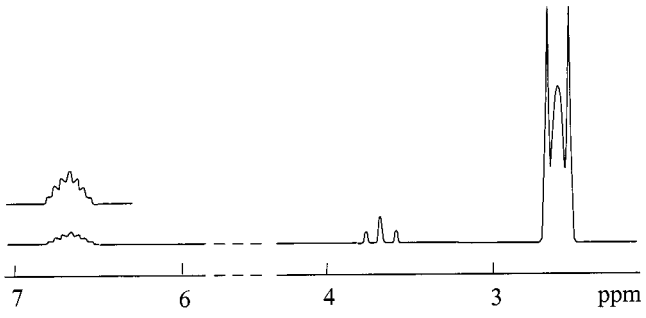


Figure 1. The ^{1}H-NMR spectrum of **7a**

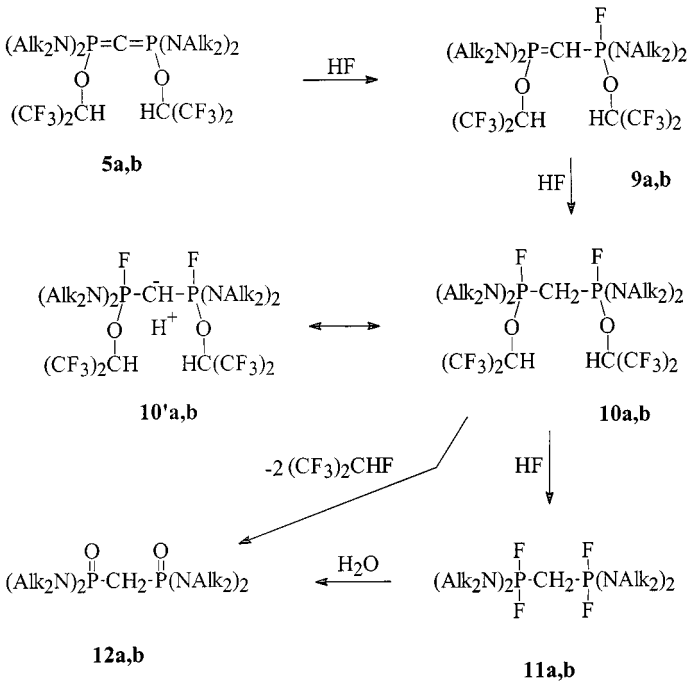
of carbodiphosphoranes **5a,b**. In other solvents they either cannot be obtained (CH_2Cl_2, $CHCl_3$) or are much less stable (C_6H_6, THF).

The decomposition of **5a,b** occurs by several steps (Scheme 4). All the intermediate compounds **9a,b - 12a,b** have been detected in the reaction mixture at different stages of the reaction. Due to the significant basicity of **5a,b** the reaction proceeds by an intermolecular abstraction of HF. In this way, half of the molecules of **5a,b** are used as a source of HF, that is why other compounds are also present in the reaction mixture. For example, small amounts of crystalline diethylammonium hexafluorophosphate (about 1%) can be isolated from the reaction mixture.

The proposed reaction pathway was confirmed by the reaction of **5a,b** with HF. The addition of one equivalent of HF gives the monofluorides **9a,b** which have, unlike their chloride analogues **7a,b,** two inequivalent phosphorus atoms and display two doublets of doublets with characteristic $^2J_{PP}$, $^1J_{FP}$ and $^3J_{FP}$ coupling constants of 45.9 Hz, 950 Hz and 13.7 Hz, respectively, in the ^{31}P-NMR spectra. In contrast to HCl, which does not add to **7a,b,** HF reacts with the monofluorides **9a,b** so readily that it is impossible to obtain **9a,b** without the difluorides **10a,b**. Compounds **10a,b** are also able to react further with HF to give the methylene-bis(difluorophosphoranes) **11a,b**. If a definite amount of HF (2.2 equiv.), or $Et_3N{\cdot}2HF$, is added, the reaction mixture consists only of the difluorides **10** and bis(difluorophosphoranes) **11**, which can easily be separated as compounds **10** are insoluble in hexane and precipitate as a light yellow oil, whereas compounds **11** remain in solution.

The difluorides **10a,b** possess interesting spectral characteristics. Their ^{31}P-NMR spectra display a complex resonance of the AA′XX′ spin system (Figure2) which does not vary in the temperature range from −60 to +60°C. A theoretical calculation of the FPPF system using the experimentally obtained coupling constants gives the same pattern. The carbon atom of the FP−CH_2−PF chain displays the expected triplet of triplets in the ^{13}C-NMR spectra. However, its upfield chemical shift (δ = 10), which is very close to that of the ylides **5a,b** or **7a,b**, shows that it bears a negative charge. The same conclusion can be drawn from the ^{1}H-NMR spectra, as the two acidic methylene protons show a broad signal at δ = 9.5. This indicates that the real structure of these compounds is probably closer to that of **10′a,b**.

The methylenebis(difluorophosphoranes) **11** were isolated as a low-melting crystalline product **11a** or light yellow oil **11b**. Their hydrolysis led to the dioxaderivatives **12a,b**. Interestingly, these compounds were also formed even if the decomposition of the carbodiphosphoranes **5a,b** was carried out under dry conditions. This can probably be explained by the removal of 1,1,1,2,3,3,3-heptafluoropropane from the difluorides **10a,b**. In order to confirm the formation of **12a,b** we tried to obtain them independently



Scheme 4. Reaction of **5a,b** with HF

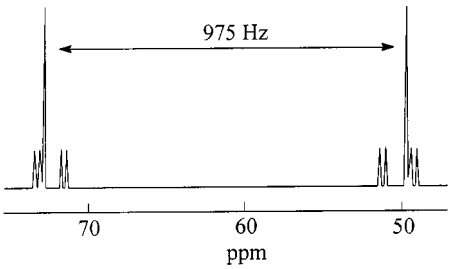


Figure 2. The ^{31}P-NMR spectrum of compounds **10a,b**

by the reaction of **3a,b** with oxygen. However, even after bubbling gaseous oxygen through a solution of **3a** or **3b** in dichloromethane, at room temperature, over long periods of time no reaction occurred, although it was later found that sulfur reacts very readily with **3a,b**.

The carbodiphosphorane structure of **5** is also confirmed by the rection with chlorine. Thus, **5b** very easily adds two equivalents of chlorine at room temperature to give the tetrachloro derivative **14**. The reaction initially forms the dichloro derivative **13** which, however, cannot be obtained in a pure form in this way, as a further reaction with chlorine occurs. This compound can be prepared by the abstraction of two chlorine atoms from **14** with $SnCl_2$ but, on a preparative scale, the use of the reaction between **14** and the starting carbodiphosphorane **5b** is more convenient. Compounds **13** and **14** were isolated as stable crystalline compounds which are insoluble in nonpolar solvents.

We were interested in dichloride **13,** not only for confirmation of the structure of **5,** but also because of its possible application for the synthesis of carbenes. For this purpose we studied the reaction of **13** with silver tetrafluoroborate. The reaction is carried out in boiling chloroform for 2 hours. However, the phosphonium-substituted carbene **15** turned out to be unstable under these conditions and the only product which could be isolated from the reaction mixture was its derivative **16**. This compound is analogous to the salt **7b** and contains a hydrogen atom attached to the P−C−P carbon atom, which was subsequently confirmed by an X-ray structure analysis (Figure 3). The formation of

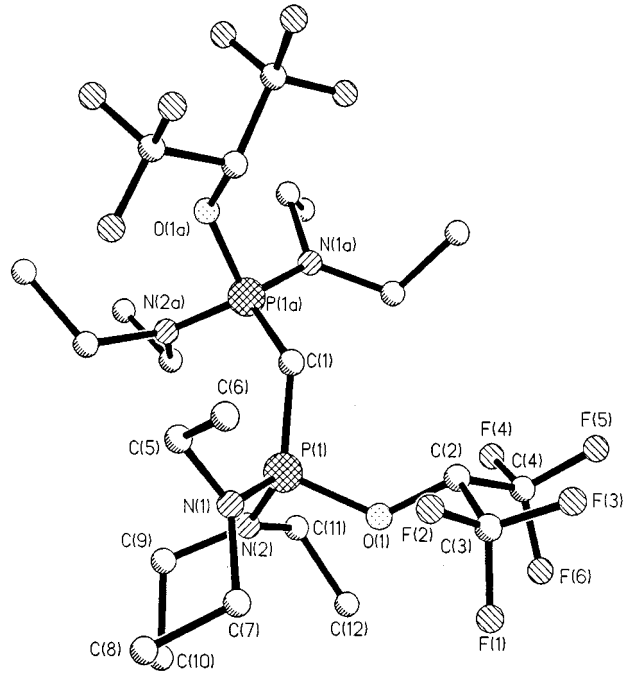
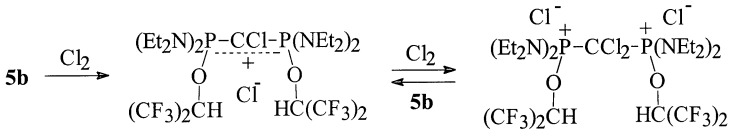


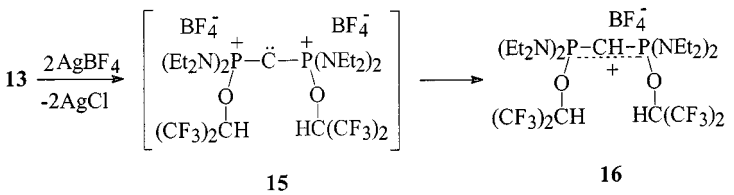
Figure 3. Molecular structure of **16**; selected bond lengths [Å] and angles [°]: P(1)−N(2) 1.618(6), P(1)−N(1) 1.619(6), P(1)−O(1) 1.625(4), P(1)−C(1) 1.681(6), O(1)−C(2) 1.408(6); P(1)#1−C(1)−P(1) 131.5(4); N(2)−P(1)−N(1) 109.27(13), N(2)−P(1)−O(1) 99.4(2), N(1)−P(1)−O(1) 105.5(2), N(2)−P(1)−C(1) 117.6(2), N(1)−P(1)−C(1) 113.66(11), O(1)−P(1)−C(1) 109.9(3), C(2)−O(1)−P(1) 127.5(2)

16 probably confirms the formation of the carbene **15** as an intermediate.

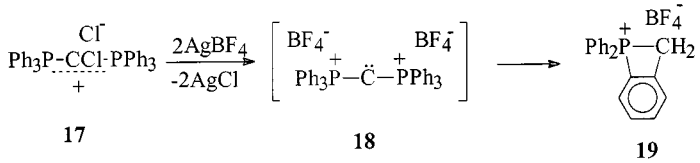
As was pointed out above, the tetrafluoroborate **16,** as well as the original carbodiphosphoranes **5a,b** and their derivatives **7a,b**, **13** and **14**, display an interesting spectroscopic phenomenon: the equivalence of the $HC(CF_3)_2$ protons for each of the two phosphorus atoms. This can be explained by a rapid exchange of the protons in solution on the NMR timescale. The crystal structure of **16** shows that these protons point towards the inside of the molecule and, if a rotation around the P−C−P bonds in solution is possible, they should be situated very close to each other thus



Scheme 5. Reaction of **5b** with Cl_2



Scheme 6. Reaction of **13** with $AgBF_4$



17 **18** **19**

Scheme 7. Reaction of **17** with $AgBF_4$

allowing the exchange process. Obviously, this rotation or flip-flop movement around the P−C−P bonds must be possible, as can be seen from the equivalence of the NMe_2 or NEt_2 protons in the NMR spectra, although in the solid state these groups are inequivalent as the molecule of **16** has C2 symmetry.

In order to study the stability of carbenes in such systems, it was interesting to change the substituents at the phosphorus atoms of the P−C−P triad. We chose the dichloro derivative of hexaphenylcarbodiphosphorane[9] **17** as a suitable starting material. Its properties differ remarkably from those of **13**. For example, the chlorination of **17** does not give the tetrachloride but instead leads to the cleavage of a P−C bond.[10]

The reaction of **17** with $AgBF_4$ (Scheme 7) requires milder conditions and works at room temperature. However, the expected carbene **18** is also unstable. It decomposes with the cleavage of one P−C bond to give the cyclic phosphonium salt **19**, which is the main product in this reaction. Compound **19** has a methylene group in the α position to the phosphorus atom and can only be formed from the carbene **18**. It has already been shown that, when the benzene ring at the phosphorus atom has a suitable *ortho* substituent, carbene intermediates can undergo intramolecular reactions often leading to the formation of cyclic products.[11,12,13] Similar results were obtained with diisopropylamino groups attached to a phosphorus atom near the carbene centre.[14] Comparing these data with those known for stable carbenes,[15] one can postulate that the stabilization of a carbene centre requires substituents with σ-accepting and π-donating abilities. Phosphonium groups do not meet one of these conditions.

Experimental Section

All reactions and manipulations were carried out in a nitrogen atmosphere in a dry box or with standard Schlenk techniques, unless otherwise indicated. Solvents were dried by standard procedures and distilled in a nitrogen atmosphere and either used immediately or stored in the dry box prior to use. Glassware was oven-dried at 100°C overnight prior to use. NMR spectra were recorded on JEOL FX-90Q and Bruker WP-200 multinuclear NMR spectrometers. Chemical shifts were measured relative to residual solvent peaks and referenced to Me_4Si (^1H, ^{13}C) or to external 85% H_3PO_4 (^{31}P). Reagents **3a,b**[16] were prepared by standard methods.

Carbodiphosphorane 5a: Gaseous HFA (29.6 mL, 1.32 mmol) from a syringe was slowly bubbled through a solution of **3a** (0.139 g, 0.55 mmol) in 1 mL of hexane at 20°C. If the starting diphosphane is contaminated with dialkylammonium chloride an appropriate amount of salt **7a** is formed which can be easily separated as it is not soluble in hexane. ^1H NMR (200 MHz, [D_8]toluene):[17] δ = 2.59 (pseudo t, $^3J_{PH}$ = 11.6 Hz, 24 H, NCH_3), 6.25 (t of sept, $^3J_{FH}$ = 6.8 Hz, $^3J_{PH}$ = 6.8 Hz, 2 H, $CHCF_3$). − ^{19}F NMR (84.26 MHz, C_6H_{14}): δ = −73.0 (d, $^3J_{HF}$ = 6.8 Hz, 12 F). − ^{31}P NMR (36.2 MHz, C_6H_{14}): δ = 36.7.

Carbodiphosphorane 5b: This compound was obtained as described above from HFA (29.6 mL, 1.32 mmol) and **3b** (0.20 g, 0.55 mmol). − ^1H NMR (200 MHz, [D_8]toluene):[17] δ = 0.98 (t, $^3J_{HH}$ = 7.1 Hz, 24 H, NCH_2CH_3), 3.00 (m, 16 H, NCH_2CH_3), 6.09 (t of sept, $^3J_{FH}$ = 6.8 Hz, $^3J_{PH}$ = 6.8 Hz, 2 H). − ^{19}F NMR (84.26 MHz, C_6H_{14}): δ = −72.9 (d, $^3J_{HF}$ = 6.8 Hz, 12 F). − ^{31}P NMR (36.2 MHz, C_6H_{14}): δ = 33.6.

Phosphonium Chloride 7a: To a solution of **5a** in hexane 1 equiv. of HCl (as a solution in ether) was added at 20°C. The precipitate of **7a** which formed was separated by filtration and recrystallized from CH_2Cl_2/ether at −15°C. Yield 63%. − M.p. 183−185°C (dec.). − ^1H NMR (200 MHz, $CDCl_3$): δ = 2.71 (pseudo t, $^3J_{PH}$ = 10.7 Hz, 24 H, NCH_3), 3.67 (t, $^2J_{PH}$ = 10.0 Hz, 1 H, PCHP), 6.71 (t of sept, $^3J_{FH}$ = 5.9 Hz, $^3J_{PH}$ = 6.8 Hz, 2 H, $CHCF_3$). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 7.4 (t, $^1J_{PC}$ = 209 Hz, PCP), 37.3 (pseudo t, $^2J_{PC}$ = 4.9 Hz, 8 C, NCH_3), 70.3 [sept, $^2J_{FC}$ = 34 Hz, 2 C, $CH(CF_3)_2$], 120.8 (q, $^1J_{FC}$ = 285 Hz, 4 CF_3). − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −73.9 (d, $^3J_{HF}$ = 5.9 Hz, 12 F). − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 58.6. − $C_{15}H_{27}ClF_{12}N_4O_2P_2$(620.79): calcd. C 29.02, H 4.38; found C 28.77, H 4.32.

Phosphonium Chloride 7b: This compound was prepared as descibed above. Yield 52%. − M.p. 151−153°C. − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.06 (t, $^3J_{HH}$ = 6.8 Hz, 24 H, NCH_2CH_3), 3.05 (m, 16 H, NCH_2CH_3), 3.23 (t, $^2J_{PH}$ = 13.7 Hz, 1 H, PCHP), 6.75 (t of sept, $^3J_{FH}$ = 5.9 Hz, $^3J_{PH}$ = 6.8 Hz 2 H, $CHCF_3$). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 7.3 (t, $^1J_{PC}$ = 209 Hz, PCP), 13.7 (s, 8 C, NCH_2CH_3), 40.6 (s, 8 C, NCH_2CH_3), 70.4 [sept, $^2J_{FC}$ = 34 Hz, 2 C, $CH(CF_3)_2$], 120.8 (q, $^1J_{FC}$ = 285 Hz, 4 CF_3). − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −73.0 (d, $^3J_{HF}$ = 5.9 Hz, 12 F). − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 59.1. − $C_{23}H_{43}ClF_{12}N_4O_2P_2$(733.01): calcd. C 37.69, H 5.91; found C 28.77, H 4.32.

Methylenebis[bis(diethylamino)difluoro(1,1,1,3,3,3-hexafluoro-2-propoxy)phosphorane] 10b: To a solution of **5b** in hexane, obtained as described above, one molar equivalent of $Et_3N{\cdot}2HF$ was added. The colourless oil separated from the mixture after stirring for 20 min at room temperature was washed with hexane and dried in vacuo. Yield 26.5%. − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.14 (t, $^3J_{HH}$ = 7.07 Hz, 24 H, NCH_2CH_3), 3.13 (m, 16 H, NCH_2CH_3), 4.38 [sept, $^3J_{FH}$ = 6.8 Hz, 2 H, $HC(CF_3)_2$], 9.2 (broad s, 2 H, P−CH_2−P). − ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 10.32 (tt, $^1J_{PC}$ = 206.1 Hz, $^2J_{FC}$ = 24.4 Hz, FP−CH_2−PF), 13.3 (s, 8 C, NCH_2CH_3), 40.3 (d, $^2J_{PC}$ = 4.9 Hz, 8 C, NCH_2CH_3), 68.6 [sept, $^2J_{FC}$ = 32.2 Hz, 2 C, $CH(CF_3)_2$], 122.3 [q, $^1J_{FC}$ = 284.2 Hz, 4 C, $CHCF_3)_2$]. − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −76.4 (d, $^3J_{HF}$ = 6.8 Hz, 12 F, CF_3), −72.5 (d, $^1J_{PF}$ = 975.6 Hz, 2 F, FP−CH_2−PF). − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 63.1 [symmetrical multiplet, (see Figure 1), $^1J_{FP}$ = 975.6 Hz, $^2J_{PP}$ = 44.0 Hz, $^3J_{FP}$ = 7.8 Hz, 2 P, FP−CH_2−PF].

Methylenebis[bis(dimethylamino)difluorophosphorane] 11a: To a solution of carbodiphosphorane **5a**, prepared from **3a** (1.2 mmol) and HFA (2.88 mmol), in 4 mL of hexane, was added $Et_3N{\cdot}2HF$ (353 mg, 2.5 mmol). After stirring at room temperature for 30 min the reaction solution was separated from the residue formed. Evaporation of the solvent in vacuo gave 390 mg of a crude product which gave **11a** after recrystallisation from hexane. Yield 120 mg (30%). − M.p. 47−48°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.28 (t of quint, $^2J_{HP}$ = 23.4 Hz, $^3J_{HF}$ = 15.8 Hz, P−CH_2−P), 2.69 (dt, $^3J_{PH}$ = 10.5 Hz, $^4J_{FH}$ = 2.6 Hz, 24 H, NCH_3). − ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 39.6 (t of quint, $^1J_{PC}$ = 182.4 Hz, $^2J_{FC}$ = 44.9 Hz, $F_2P-CH_2-PF_2$), 39.9 (dt, $^2J_{PC}$ = 10.7 Hz, $^3J_{FC}$ = 6.8 Hz 8 C, NCH_3). − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −31.4 (dt, $^1J_{PF}$ = 720.2 Hz, $^3J_{HF}$ = 15.8 Hz, 4F). − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = −53.2 (t, $^1J_{FP}$ = 720.2 Hz, 2 P). − $C_9H_{26}F_4N_4P_2$ (328.28): calcd. C 32.93; H 7.98. found C 32.43; H 8.47.

Methylenebis[bis(diethylamino)difluorophosphorane] (11b): To a solution of carbodiphosphorane **5b**, prepared from **3b** (1.2 mmol) and HFA (2.88 mmol), in 4 mL of hexane, was added $Et_3N{\cdot}2HF$ (353 mg, 2.5 mmol). After stirring the mixture at room temperature for 30 min the reaction solution was separated from the residue formed. Evaporation of the solvent in vacuo gave 390 mg of a crude product from which **11b** was extracted with 1 mL of cold hexane at −15°C. Evaporation of the hexane in vacuo gave 11b as a light yellow oil of about 90% purity. Yield 180 mg (33%). Compound **11b** is thermally stable and can be purified by low-pressure distillation (0.03 Torr) at 110−115°C if prepared on a large scale. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.06 (t, $^3J_{HH}$ = 7.02 Hz, 24 H, NCH_2CH_3), 2.31 (m, broad, 2 H, P−CH_2−P), 2.97 (m, 16 H, NCH_2CH_3) − ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 15.73 (s, 8 C, NCH_2CH_3), 44.0 (m, $^2J_{PC}$ = 8.7 Hz, $^3J_{FC}$ = 7.8 Hz, 8 C, NCH_2CH_3), 45.2 (t of quint, $^1J_{PC}$ = 182.4 Hz, $^2J_{FC}$ = 43.9 Hz, $F_2P-CH_2-PF_2$) − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −38.0 (dt, $^1J_{PF}$ = 728.1 Hz, $^3J_{HF}$ = 14.0 Hz, 4 F) − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = −52.2 (t, $^1J_{FP}$ = 728.1 Hz, 2 P).

Methylenebis[bis(diethylamino)phosphane oxide] (12b): A solution of **11b** (115 mg, 0.261 mmol) in 0.5 mL of dichloromethane was added to a solution of sodium carbonate (55 mg, 0.52 mmol) in 0.5 mL of water and the reaction mixture stirred at room temperature for 0.5 h. The organic layer was then separated and volatiles evaporated in vacuo. The residue was extracted with 2 mL of hexane. Evaporation of hexane in vacuo gave 54 mg of pure **12b** as a light yellow oil (yield 52%). Compound **12b** is thermally stable and can be purified by low-pressure distillation (0.03 Torr) at 130−135°C if prepared on a large scale. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.10 (t, $^3J_{HH}$ = 7.07 Hz, 24 H, NCH_2CH_3), 2.24 (t, $^3J_{PH}$ = 16.7 Hz, 2 H, P−CH_2−P), 3.08 (dq, $^3J_{PH}$ = 10.7 Hz, $^3J_{HH}$ = 7.07 Hz, 16 H, NCH_2CH_3) − ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 14.13 (s, 8 C, NCH_2CH_3), 24.75 (t, J_{PC} = 105.3 Hz, P−C−P), 38.88 (m, 8 C, NCH_2CH_3) − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 26.7 (s, 2 P). − MS: M_{calc} = 396.5; M_{exp}(EI) = 396; $M_{exp.}$(CI pos.) = 397.

Dichloro Derivative 13: To a solution of **14** (255 mg, 0.304 mmol) in 4 mL of THF at −20°C was added one molar equivalent of the carbodiphosphorane **5b** in hexane. A ^{31}P-NMR spectrum of the reaction mixture showed only one signal at 59.9 ppm. The mixture was allowed to react at this temperature for 15 min. The fine colourless crystals of **13** formed during this time were separated, washed with hexane and dried in vacuo. Yield 391 mg (84%). The product can be recrystallized from dichloromethane-ether. M.p. 160−162°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{HH}$ = 7.08 Hz, 24 H, NCH_2CH_3), 3.17 (dq, $^3J_{PH}$ = 11.7, $^3J_{HH}$ = 7.08 Hz, 16 H, NCH_2CH_3), 6.71 [m, 2 H, $CH(CF_3)_2$]. − ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 6.96 (t, $^1J_{PC}$ = 207.73 Hz, P−CCl_2−P), 13.81 (s, 8 C, NCH_2CH_3), 40.72 (s, 8 C, NCH_2CH_3), 70.24 [sept, $^2J_{FC}$ = 33.2 Hz, 2 C $CH(CF_3)_2$], 120.67 [q, $^1J_{FC}$ = 284.78 Hz, 4 C, $CH(CF_3)_2$]. − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −72.8 [d, $^3J_{HF}$ = 5.9 Hz, 12 F, $CH(CF_3)_2$]. − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 59.9 (s, 2 P). − $C_{23}H_{42}Cl_2F_{12}N_4O_2P_2$ (767.46): calcd. C 36.00, H 5.52; found C 36.68, H 6.17.

Tetrachloro Derivative 14: To a stirred solution of the carbodiphosphorane **5b**, prepared from **3b** (0.42 mmol) and HFA (1.01 mmol), in 1 mL hexane, chlorine (0.84 mmol, as a solution in CCl_4) was added at room temperature. The precipitated yellow oil (257 mg) was separated and recrystallized from dichloromethane-ether. (NB: If the ^{31}P-NMR spectrum of the oil shows a second signal of the intermediate dichloride at 59.9 ppm, more chlorine solution should be added). Yield 138 mg (38%), colourless crystalline product. M.p. 109−113°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.19 (t, $^3J_{HH}$ = 6.82 Hz, 24 H, NCH_2CH_3), 3.19 (dq, $^3J_{PH}$ = 11.7, $^3J_{HH}$ = 6.82 Hz, 16 H, NCH_2CH_3), 5.80 [m, 2 H, $CH(CF_3)_2$]. − ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 13.05 (s, 8 C, NCH_2CH_3), 30.26 (t, $^1J_{PC}$ = 229.2 Hz, P−CCl_2−P), 40.66 (s, 8 C, NCH_2CH_3), 71.12 [sept, $^2J_{FC}$ = 35.1 Hz, 2 C, $CH(CF_3)_2$], 119.91 [q, $^1J_{FC}$ = 285.7 Hz, 4 C, $CH(CF_3)_2$]. − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −71.85 [d, $^3J_{HF}$ = 5.9 Hz, 12 F, $CH(CF_3)_2$]. − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 55.0 (s, 2 P). − $C_{23}H_{42}Cl_4F_{12}N_4O_2P_2$ (838.38): calcd. C 32.95, H 5.05; found C 33.83, H 5.72.

Phosphonium Tetrafluoroborate 16: To a solution of **13** (300 mg, 0.391 mmol) in 3 mL of $CHCl_3$ was added $AgBF_4$ (90 mg, 0.469 mmol). After refluxing for 3 h the hot reaction mixture was filtered and kept at room temperature for 24 h. The colourless crystals of **16** formed during this time were separated, washed with hexane and dried in vacuo. Yield 69 mg (21%). − M.p. 192−193°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.19 (t, $^3J_{HH}$ = 7.08 Hz, 24 H, NCH_2CH_3), 3.18 (dq, $^3J_{PH}$ = 11.7, $^3J_{HH}$ = 7.08 Hz, 16 H, NCH_2CH_3), 5.30 [m, 2 H, $CH(CF_3)_2$]. − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −72.9 [d, $^3J_{HF}$ = 5.86 Hz, 12 F, $CH(CF_3)_2$], −151.3 (s, BF_4). − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 58.4 (s, 2 P). − $C_{23}H_{43}BF_{16}N_4O_2P_2$ (784.35): calcd. C 35.22, H 5.53; found C 36.82; H 5.63.

Bicyclic Phosphonium Salt 19: To a solution of **17** (300 mg, 0.494 mmol) in 3 mL of CH_2Cl_2, $AgBF_4$ (385 mg, 1.98 mmol) was added and the reaction mixture stirred at room temperature for 48 h. The liquid phase of the reaction mixture was separated and ether was added until it became turbid. The precipitate formed during 24 h at room temperature was separated and dissolved in 1.5 mL of CH_2Cl_2. This solution was washed with 1 mL of water and then ether was added until it became turbid. The crystalline product formed over 24 h at room temperature was separated and dried in vacuo (0.03 Torr). Yield 85 mg (47%). − M.p. 195−197°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.22 (d, $^2J_{PH}$ = 5.9 Hz, 2 H, CH_2), 7.76 (m, 14 H, Ar). − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −152.4 (s, BF_4). − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 22.95 (s). − $C_{19}H_{16}BF_4P$ (362.11): calcd. C 63.02, H 4.45; found C 59.00, H 4.76. Mass spectrum: $M_{calc.}$ = 362.11; $M(cation^+)_{calc.}$ = 275.3; $M(cation^+)_{exp.}$(EI) = 277.

X-ray Crystal Structure Determination of Compound 16: Crystal data: $C_{23}H_{43}BF_{16}N_4O_2P_2$, M_r = 784.36, d = 1.484 Mg/m^3; μ = 0.24 mm^{-1}, orthorhombic, space group *Pbcn*; a = 9.74(4), b = 317.53(7), c = 20.53(8) Å; V = 350(2) Å^3; Z = 4, rhombic colourless crystal 0.8 × 0.7 × 0.6 mm. Data collection and reduction: Data were collected to $2\Theta_{max}$ = 48.1° with a STOE Image plate system using monochromated (graphite monochromator) Mo-K_α

radiation. 17227 reflections were collected (hemisphere), of which 2717 were independent (R_{int} = 0.0700). The structure was solved by direct methods and subjected to full-matrix least-squares refinement based on F^2 with SHELXTL (Version 5.0). R_1 = 4.06%, wR_2 = 9.57% (based on F^2) for 247 parameters and 1570 reflections with $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The fluorine atoms of the BF_4^- anion were split, resulting in positions having reasonable occupancy factors and B−F bond lengths and F−B−F angles. Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112955. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: + 44-1223/336033 or E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

We are indebted to Ms. D. Döring and Mr. T. Kaschner for their cooperation and to the Swiss National Science Foundation and the DAAD for financial support.

[1] M. Witt, K. S. Dathathreyan, H. W. Roesky, *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 223−312.
[2] R. Burgada, R. Setton, "Preparation, Properties and Reactions of Phosphoranes", in: *The Chemistry of Organophosphorus Compounds* (Ed.: F. R. Hartley), in *The Chemistry of Functional Groups* (Series Ed.: S. Patai), Wiley, Chichester, New York, Brisbane, Toronto, Singapore, **1994**, vol. 3; ch. 3, p. 185−272.
[3] F. U. Seifert, G.-V. Röschenthaler, *J. Fluorine Chem.* **1995**, *70*, 171−174.
[4] I. Neda, C. Melnicky, A. Vollbrecht, A. Fischer, P. G. Jones, R. Schmutzler, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1047−1059.
[5] I. V. Shevchenko, A. Fischer, P. G. Jones, R. Schmutzler, *Polyhedron* **1993**, *12*, 435−444.
[6] I. V. Shevchenko, *Tetrahedron Lett.* **1995**, *36*, 2021−2024.
[7] I. V. Shevchenko, *Chem Commun.* **1998**, 1203−1204.
[8] A. P. Marchenko, G. N. Koydan, N. A. Oleynik, I. S. Zal′tsman I.S., A. M. Pinchuk, *Zh. Obshch. Khim.* **1988**, *58*, 1665−1666; *Chem. Abstr.* **1989**, *110*, 173342f.
[9] R. Appel, F. Knoll, H. Scholer, H.-D. Wihler, *Angew. Chem.* **1976**, *88*, 769−770.
[10] R. Appel, F. Knoll, W. Michel, W. Morbach, H.-D. Wihler, H. Veltmann, *Chem. Ber.* **1976**, *109*, 58−70.
[11] D. V. Griffith, K. Karim, B. J. Whitehead, *Zh. Obshch. Khim*. **1993**, 63, 2245; *Chem. Abstr.* **1994**, *121*, 205523m.
[12] D.V.Griffiths, P. A. Griffiths, K. Karim, B. J. Whitehead, *J. Chem. Res.* **1996**, 176−177.
[13] D. V. Griffiths, P. A. Griffiths, K. Karim, B. J. Whitehead, *J. Chem. Soc., Perkin Trans., 1* **1996**, 555.
[14] M.-J. Menu, Y. Dartiguenave, M. Dartiguenave, A. Baceiredo, G. Bertrand, *Phosphorus Sulfur Silicon* **1990**, *47,* 327−334.
[15] A. J. Arduengo, III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.
[16] Compound **3a** was prepared in 79% yield (bp 68−70°C, 0.03 Torr) in a similar manner to its diethylamino derivative **3b**: M. Fild, J Heinze, W. Krueger, *Chem.-Ztg.* **1977**, *101*, 259.
[17] The ^{1}H-NMR spectra of **5a** and **5b** were recorded in hexane or in [D_8]toluene immediately after HFA had been added to the solution of **3a** or **3b**.

Received February 19, 1999
[I99057]