Interaction of Some Methylenediphosphanes with Hexafluoroacetone and Hexafluorothioacetone Dimer

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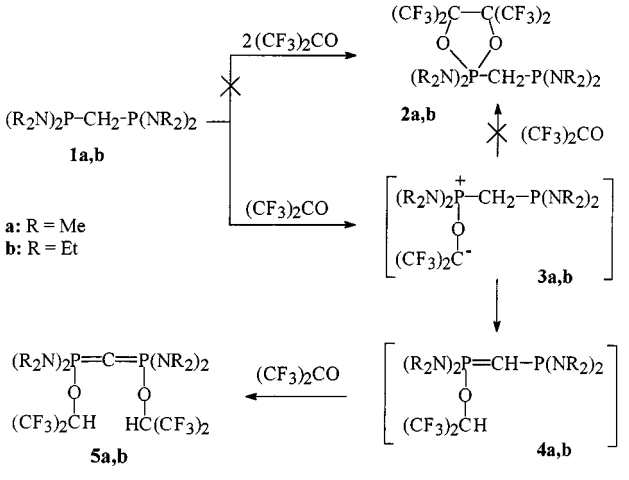
The reactions of methylenediphosphanes **1a–c** with hexafluoroacetone (HFA) and hexafluorothioacetone dimer (HFTA) gave the respective carbodiphosphoranes **5a**, **5b**, **6**, **15**, and **19**. The carbodiphosphoranes **6** and **19**, with phenyl groups at phosphorus, were able to react further with C=O or C=S functions. Compound **6** added one equivalent of HFA across one of the ylidic P=C bonds to give compound **9**, a stable intermediate of the Wittig reaction. The addition of HFTA to **19** gave, unexpectedly, the isomeric compound **21**. The molecular structures of **9**, **15**, and **21** were confirmed by X-ray investigations.

Introduction

It is well-known that the reaction of hexafluoroacetone (HFA) with phosphorus(III) derivatives can lead to the formation of 1,3,2- or 1,4,2-dioxaphospholanes.[1–4] Recently we found that the interaction of HFA with the methylenediphosphanes **1a** and **1b** proceeds in a different way to yield quantitatively the carbodiphosphoranes **5a** and **5b**,[5,6] but not the expected 1,3,2-dioxaphospholanes **2a** and **2b** (Scheme 1).

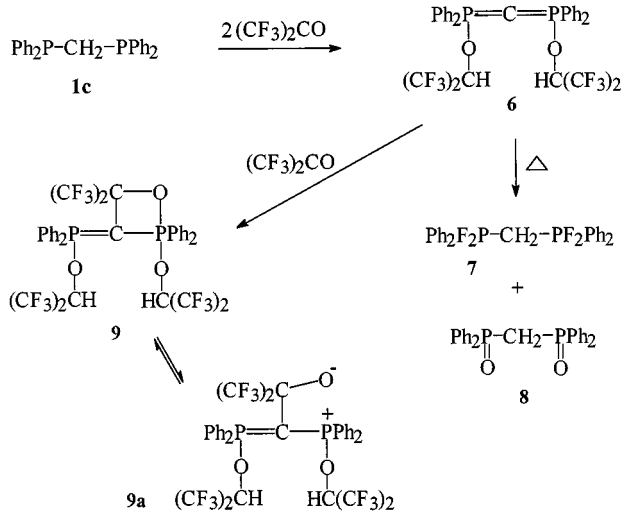


Scheme 1

The mechanism probably involves the intermediate formation of the unstable betaines **3a** and **3b**, which do not add a second molecule of hexafluoroacetone to give **2a** and **2b**, but undergo a proton migration from the $P-CH_2-P$ unit to the secondary carbon of the hexafluoroisopropoxy group forming the monoylides **4a** and **4b**. It is difficult to detect these products by NMR spectroscopy at room temperature since they react quickly with HFA to give the final products **5a** and **5b**. Thus, the presence of the methylene group with labile protons in the α-position to the phosphorus atoms is a necessary condition for this reaction.

Results and Discussion

In order to answer the question as to whether this reaction is an exception or it has more common character, we decided to use the *P*-phenyl-substituted starting material **1c** (Scheme 2).



Scheme 2

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Like compounds **1a** and **1b**, the bis(diphenylphosphanyl-methane) **1c** reacts with HFA to give the respective carbodiphosphorane **6**. After slow bubbling of gaseous HFA through a solution of **1c** in benzene at 20 °C, the ^{31}P NMR spectrum of the reaction mixture showed the presence of only compound **6** as a singlet at $\delta = 35.3$. The ^{19}F NMR spectrum displays only a doublet at $\delta = -72.45$ ($^3J_{HF} = 6.6$ Hz) confirming the equivalence of the all fluorine atoms and the presence of one proton in each $HC(CF_3)_2$ unit.

The carbodiphosphorane **6** is stable in solution at room temperature for several hours and quickly decomposes in the absence of the solvent. The decomposition of the molecule proceeds analogously to that of **5a** or **5b**, and gives methylene bis(difluorophosphorane) **7**[6] and methylenediphosphane oxide **8**. It is interesting that the formation of the dioxide **8** is not accounted for by the hydrolysis of the bisdifluorophosphorane **7**, as the reaction was carried out under anaerobic conditions. The formation of the analogous dioxide was also observed for **5a** and **5b**.[6]

Unlike compounds **5a** and **5b**, the carbodiphosphorane **6** is able to add one more equivalent of HFA across one of the ylidic P=C bonds with the formation of the cyclic product **9**, which is poorly soluble and crystallizes from the reaction mixture in good yield. It can be considered as a Wittig reaction intermediate, which are usually unstable at room temperature and cannot be isolated. Only a few compounds of this type are known. For example, an analogous addition has been observed for some other carbodiphosphoranes.[7–9] The proposed structure of compound **9** is in accordance with ^{31}P and ^1H NMR spectroscopy; the two different $HC(CF_3)_2$ groups display two characteristic multiplets at $\delta = 3.21$ and 4.36 in the ^1H NMR spectrum. However, the ^{19}F NMR spectrum displays an interesting peculiarity that may reflect the molecular structure of **9**. The two CF_3 groups connected to the four-membered ring are equivalent and display a common signal rather than the two quadruplets that we observed earlier for an analogous compound.[6] The equivalence of these CF_3 groups could be a result of the appropriate symmetry of the molecule: for example, if the plane of symmetry were to coincide with the four-membered cycle. However, the appearance of such symmetry in this molecule is very unlikely. Another explanation is that the four-membered cycle is open in solution, making the rotation of the $(CF_3)_2C$ unit possible. Looking for an answer to this question, we investigated this compound by X-ray analysis (Figure 1).

This analysis showed that the molecule does not have a plane of symmetry, which is why the equivalence of the CF_3 groups in solution can be only explained by the cleavage of one of the bonds of the four-membered ring. The ring is strained, as the C(1)−P(2)−O(1) angle is only 76° (in crystalline form), which should promote its opening. Although the C(1)−C(2) bond (152 pm) is somewhat longer then the normal $C_{sp^2}-C_{sp^3}$ bond, and is closer to normal $C_{sp^3}-C_{sp^3}$ bond lengths, its cleavage is unlikely, as this would result in the formation of the carbene structure, which, according to our previous results, should be unstable. We have already tried to obtain phosphonium-substituted carbenes, however they were very unstable and we could isolate only the products of their decomposition.[6]

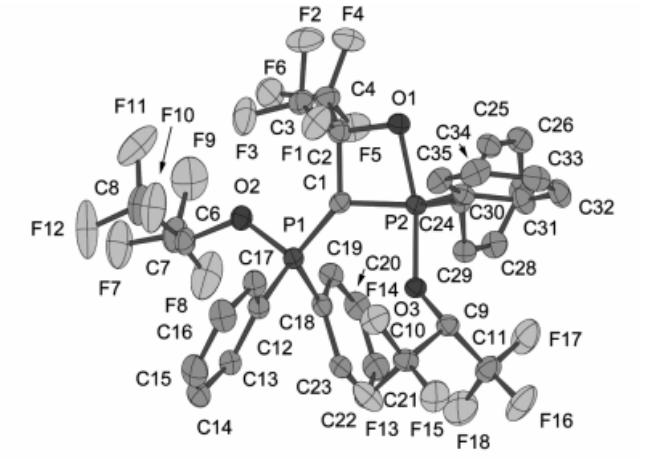
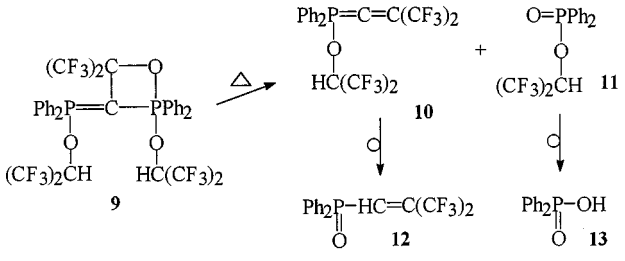


Figure 1. Perspective view and labeling scheme for the molecule **9**; selected bond lengths [pm] and angles [°]: P(1)−O(2) 162.16(19), P(1)−C(1) 170.3(3), P(1)−C(12) 179.2(3), C(1)−P(2) 175.1(3), C(1)−C(2) 151.5(4), C(2)−O(1) 141.0(3), P(2)−O(1) 178.38(19), P(2)−O(3) 177.80(18), P(2)−C(24) 182.4(3); P(1)−C(1)−P(2) 130.10(15), C(1)−P(2)−O(1) 76.00(11), C(1)−C(2)−O(1) 96.1(2), C(2)−O(1)−P(2) 94.96(15), C(2)−C(1)−P(2) 92.63(17), C(2)−C(1)−P(2)−O(1) 3.97(14)

We think that cleavage of the C(2)−O(1) bond [141.0(3) pm] is less preferable than that of the P(2)−O(1) bond, as in the latter case it would form the more stable zwitterionic structure **9a**. The reversible cleavage of the P−O bond of the intermediate oxaphosphetanes has also been postulated by other authors for the Wittig reaction mechanism.[10]

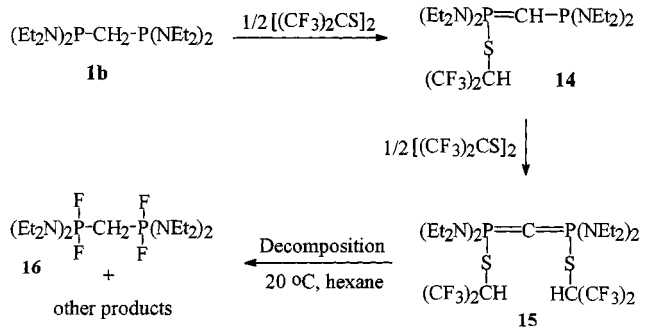
Indeed, heating compound **9** in chloroform or toluene solution at 60−100 °C led to the completion of the Wittig reaction, and gave a mixture of compounds **10**−**13** (Scheme 3), their relative amounts depending on the temperature and the solvent used. Compound **10** was not stable during the decomposition and was only detected by ^{31}P NMR spectroscopy as a singlet at $\delta = 36$. Compound **11** was isolated in low yield as a pure crystalline product. The formation of two other products **12** and **13** can be accounted for by the decomposition of the compounds **10** and **11**, in accordance with our above-mentioned conclusion about the formation of the dioxide **8**. Compound **12** showed two characteristic quadruplets for the two inequivalent CF_3 groups in the ^{19}F NMR spectra. Compound **13** was identified by comparison with a sample obtained independently.



Scheme 3

Thus, the substitution of the dialkylamino groups at phosphorus in methylenediphosphanes **1a** and **1b** by phenyl groups did not change the course of the reaction with HFA.

Our further interest was directed to the reaction of methylenediphosphanes **1a**−**c** with HFTA, whose properties are somewhat different from that of HFA (e.g. it easily dimerizes, and exists as a dimer at room temperature).[11] Therefore, one could expect that the softer sulfur atom might change the course of reaction (Scheme 1). However, compound **1b** and HFTA in hexane gave the carbodiphosphorane **15** quantitatively at −40 °C (Scheme 4). The ^{31}P NMR spectrum of the reaction mixture, taken immediately after the addition of HFTA to **1b**, displayed only one intense singlet at δ = 41.22 (similar to the chemical shift value found for **5b**), indicating two magnetically equivalent phosphorus nuclei of **15**. A two-step reaction is proposed with the intermediate formation of the mono ylide **14**, which was detected in the reaction mixture by ^{31}P NMR spectroscopy as two doublets at δ = 67.4 and 74.7 ($^2J_{PP}$ = 61 Hz) when only one equivalent of HFTA was added to the starting material.



Scheme 4

The carbodiphosphorane **15** turned out to be less stable than its oxygen analog **5b**. It decomposed in hexane solution at room temperature after several hours, whereas carbodiphosphorane **5b** was stable for two days under the same conditions. The choice of hexane as a solvent is very important for this reaction as in other solvents compound **15** is not stable or its synthesis may be accompanied by the formation of by-products. The decomposition of **15** gave a complex mixture with the predominant product being methylenebis(difluorophosphorane) **16**. This product was previously isolated after the decomposition of **5b** and showed the same signal in the ^{31}P NMR spectrum of a triplet at δ = −52.2 ($^1J_{FP}$ = 728 Hz).[6]

Despite the reduced stability of carbodiphosphorane **15**, it was possible to isolate it in a crystalline form, although all our efforts to obtain crystals of the more stable oxygen derivative **5b** failed. Colorless crystals of compound **15** can be stored at −25 °C, however they turn yellow and slowly decompose at room temperature. The X-ray analysis of **15** showed the following molecular structure (Figure 2).

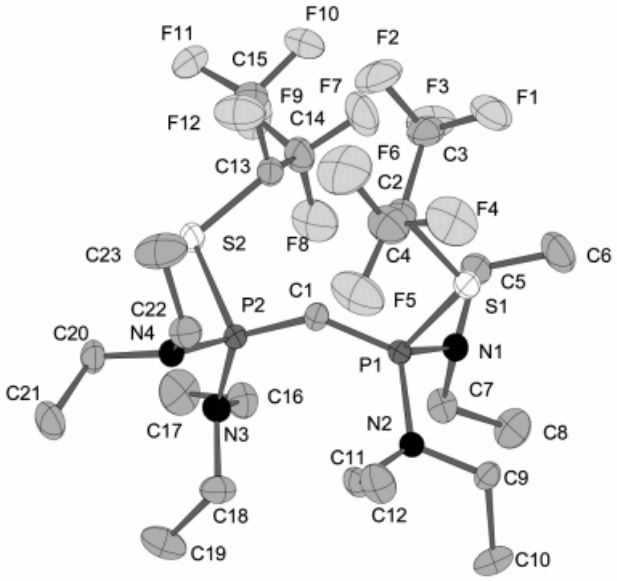
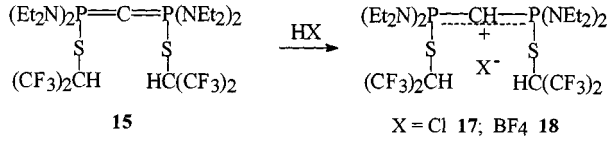


Figure 2. Perspective view and labeling scheme for the molecule **15** (H atoms are omitted for clarity); selected bond lengths [pm] and angles [°]: P(1)−N(1) 167.32(12), P(1)−C(1) 162.57(15), C(1) −P(2) 162.60(15), P(1)−S(1) 217.60(5), S(1)−C(2) 180.40(16), N(1)−C(5) 147.81(19), C(2)−C(3) 152.1(2); C(1)−P(1)−N(1) 122.84(7), C(1)−P(1)−S(1) 108.73(5), N(1)−P(1)−N(2) 101.47(6), N(1)−P(1)−S(1) 98.12(5), P(1)−C(1)−P(2) 139.52(9), P(1)−S(1)−C(2) 101.81(5)

Unlike allenes[12] and heteroallenes, in which the angle between the two double bonds is about 180°, the P=C=P angle in carbodiphosphoranes lies in the range 117−150°, depending on the structure and packing effects.[13−17] The only exception is hexa(dimethylamino)carbodiphosphorane, which has a linear structure and D_{3d} symmetry.[18] Here, the P=C=P angle of carbodiphosphorane **15** is 139.5° with a P=C bond length of 162.57 pm. Both phosphorus atoms of compound **15** have significantly distorted tetrahedral symmetry, with the largest deviation from the ideal angle being 13.3°. It is interesting that because of the low symmetry of the molecule in the solid state the ethyl groups of the diethyl substituents and CF_3 groups of the hexafluoroisopropoxy units are not equivalent. In solution, however, these groups are equivalent and have equal spectral characteristics. For example, all fluorine nuclei display a doublet at δ = −67.7 ($^3J_{HF}$ = 8.14 Hz) in the ^{19}F NMR spectra, which means that in a solution of **15** there is either a rotation or a rapid flip-flop movement around the P−C−P bonds.

The carbodiphosphorane **15**, as a strong base, reacts with acids: for example, with HCl or HBF_4 it gives the corresponding colorless salts **17** and **18** (Scheme 5). As was to be expected, the positive charge of the cation is delocalized over the P−C−P triad, resulting in the magnetic equivalence of the phosphorus nuclei. The ^{31}P NMR spectra of compounds **17** and **18** show only one singlet at δ = 62 and 68, respectively. The analogous salts have been obtained earlier for carbodiphosphoranes **5a** and **5b**, and showed the same spectroscopic data.[5] The chloride **17**, however, differs

from its oxygen derivative. After the addition of HCl to a solution of **15** in hexane compound **17** immediately precipitates from the reaction mixture as a colorless crystalline product that is insoluble in non-polar solvents. This product is stable at room temperature in the solid state. However, the dissolution of this compound leads to its transformation (slowly in [D_8]toluene and rapidly in $CDCl_3$) into another product, which shows two doublets at $\delta = 62.7$ and 71.1 ($^2J_{PP} = 42.6$ Hz) in the ^{31}P NMR spectrum. Since the analogous oxygen derivatives are stable in symmetrical form,[5] the decomposition of **17** can only be explained by the presence of sulfur atoms and by the nucleophilicity of the chlorine anion. Although the appearance of substantial amounts of by-products was not observed in the ^{31}P NMR spectra, we could not isolate the unknown product in a crystalline form and investigate it more thoroughly.



Scheme 5

In contrast to the chloride anion, the tetrafluoroborate is less nucleophilic and the corresponding salt **18** was stable and did not decompose even in boiling $CDCl_3$ solution. This compound crystallized easily allowing us to establish its structure by X-ray analysis (Figure 3).

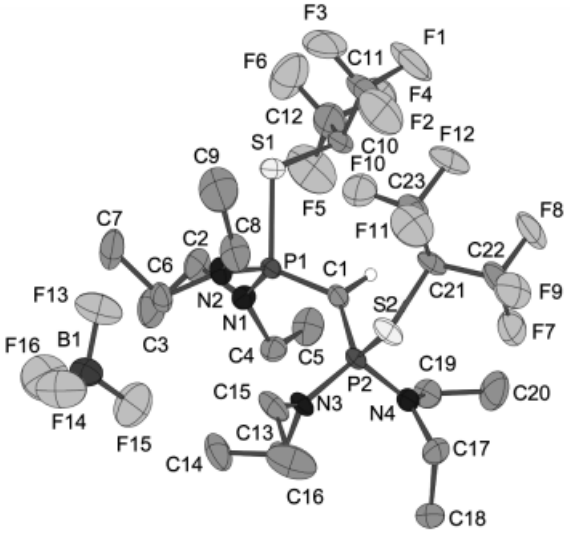
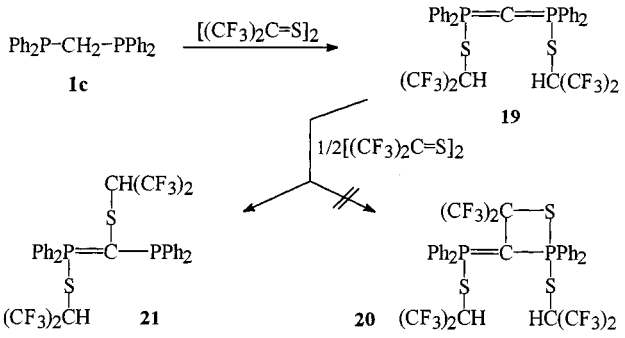


Figure 3. Perspective view and labeling scheme for the molecule **18**; selected bond lengths [pm] and angles [°]: P(1)−N(1) 163.6(3), P(1)−C(1) 169.6(4), C(1) −P(2) 169.7(4), P(1)−S(1) 212.72(14), S(1)−C(10) 182.5(4), N(1)−C(2) 148.2(5), C(10)−C(11) 152.2(6); C(1)−P(1)−N(2) 116.21(19), C(1)−P(1)−S(1) 111.42(14), N(1)−P(1)−S(1) 107.61(13), N(1)−P(1)−N(2) 108.99(17), P(1)−C(1)−P(2) 129.2(2), P(1)−S(1)−C(10) 111.86(15)

The addition of one proton to the P=C=P carbon atom of **15** leads to certain changes in the geometry of the product. As one would expect, the P−C−P angle in **18** becomes significantly narrower (129.2° versus 139.5°). The angles between the phosphorus atoms bonds become closer to those for a tetrahedral geometry. The P−C−P bond lengths of **18** are larger than those of **15** [169.6(4) versus 162.57(15) pm]. However, the other bonds at the phosphorus atoms are shorter in **18** than in **15**. The largest difference (4.9 pm) was found for the P−S bonds, which may indicate the possible participation of the sulfur atoms in delocalization of the positive charge.

The interaction of the dimer of HFTA with methylenebis(diphenylphosphane) **1c** turned out to be quite unusual. The first phase of this reaction, the addition of the two HFTA units to **1c**, does not differ from the analogous reaction with HFA and gives carbodiphosphorane **19** (Scheme 6). Unlike carbodiphosphoranes **5**, **6**, and **15**, which are relatively stable in solution at room temperature, compound **19** exists in diethyl ether solution only at −70 °C and can be detected spectroscopically only at this temperature. There is no doubt about the symmetrical structure of this compound as the ^{31}P NMR spectrum at this temperature shows only one intense singlet at $\delta = 22.5$. The oxygen derivative **6** displays similar spectroscopic data. At −40 °C the carbodiphosphorane **19** decomposes completely in solution within 30−40 min.



Scheme 6

In contrast to carbodiphosphorane **6**, which reacts further with HFA very slowly at room temperature, carbodiphosphorane **19** is very active and easily reacts even at low temperature (−70 °C) with HFTA. However, the character of this interaction is not quite clear. If 1.5 equivalents of the dimer of HFTA were added to the methylenediphosphane **1c** the reaction mixture only showed two doublets in the ^{31}P NMR spectrum at $\delta = 65.2$ and −4.5, with a coupling constant of 185.3 Hz. The same spectroscopic data were found for the colourless crystalline product that was isolated from the reaction mixture in good yield. We were sure that this was the cyclic product **20**, which is analogous to compound **9**. However, the ^{19}F NMR spectrum showed the presence of only two fragments of HFTA in the molecule. Beside this, the mass spectrum together with the analytical data pointed to a molecular weight of 748.56, the same as in carbodiphosphorane **19**. The X-ray analysis solved

this puzzle and gave structure **21** (Figure 4) which is the constitutional isomer of compound **19**.

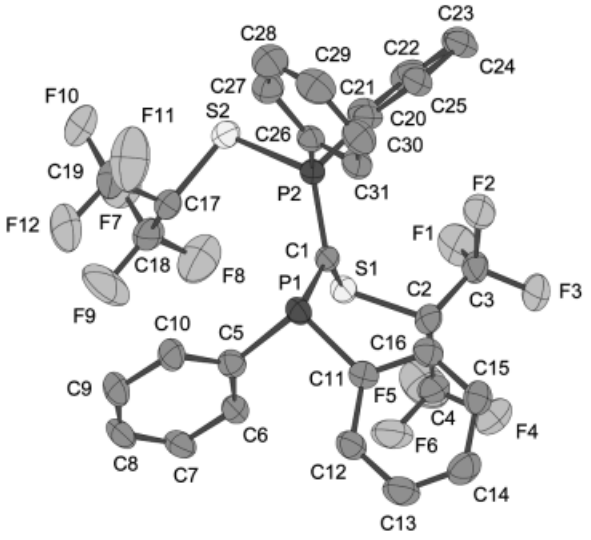


Figure 4. Perspective view and labeling scheme for the molecule **21**; selected bond lengths [pm] and angles [°]: P(1)−C(1) 181.4(5), C(1)−P(2) 170.4(5), P(2)−S(2) 215.55(19), C(1)−S(1) 176.8(5), P(1)−C(5) 183.1(5), P(2)−C(20) 181.3(5); P(1)−C(1)−P(2) 117.6(3), C(1)−P(1)−C(5) 106.2(2), P(1)−C(1)−S(1) 125.5(3), P(2)−C(1)−S(1) 113.4(3), C(1)−P(2)−S(2) 117.22(18), C(1)−P(2)−C(20) 116.0(2)

These two isomers exist independently from each other and do not interconvert. Carbodiphosphorane **19** is unstable and decomposes with the formation of a mixture of compounds that does not contain signals of the other isomer. Thus, in order to transform the symmetric carbodiphosphorane **19** into its asymmetrical isomer **21** the presence of HFTA is necessary. HFTA most likely plays a catalytic role in this process. However in this case it is not clear why the same yield of **21** cannot be obtained with only a small excess of HFTA.

It is interesting to note that the value of the $^2J_{PP}$ coupling constant of compounds containing the P−C−P system may vary in the range from less then 1 Hz to over 100 Hz. The $^2J_{PP}$ coupling constant of the compound **21** was unusually large 185 Hz. However, the largest value of this constant has been recently reported for $1\sigma^4,3\sigma^2$-diphosphaallene.[19]

Although, to the best of our knowledge, this unusual isomerization does not have direct analogies in the literature, it may be related to other migration processes observed for phosphorus compounds.[19,20]

Experimental Section

All operations were performed under nitrogen in a glove box. The solvents were dried by standard procedures. − The NMR spectra were measured with a JEOL FX-90Q, Bruker DPX 200 or Bruker AMX 360 spectrometer. The ^{1}H and ^{13}C chemical shifts are referenced to tetramethylsilane (TMS). The ^{31}P chemical shifts were measured using 85% aqueous orthophosphoric acid as an external standard. As usual, high frequency shifts are given positive signs. The digital resolutions were 0.25 Hz, 0.5 Hz, and 1.25 Hz for ^{1}H, ^{13}C, and ^{31}P NMR spectra, respectively.

Synthesis of Compound 6: A solution of methylenebis(diphenylphosphane) **1c** (30 mg, 0.078 mmol) in [D_6]benzene (0.5 mL) was placed in a tube with diameter 4−5 mm (a 5 mm NMR tube can be used) and 3.8 mL (0.172 mmol) of gaseous HFA were slowly bubbled through it at room temperature using a syringe with a thin needle. The end of the needle was placed at the bottom of the tube. The reaction mixture showed the following spectral parameters: ^{1}H NMR (89.56 MHz, C_6D_6): δ = 6.27 [br. sept., $^3J_{HF}$ = 6.58 Hz, 2 H, *H*C(CF_3)$_2$], 6.95 (m, 12 H, Ph), 7.70 (m, 8 H, Ph). − ^{19}F NMR (84.26 MHz, C_6D_6): δ = −72.46 (d, $^3J_{HF}$ = 6.58 Hz, 12 F, C*F*$_3$). − ^{31}P NMR (36.2 MHz, C_6D_6): δ = 35.3 (s, 2P).

Synthesis of Compound 9: Gaseous hexafluoroacetone (19 mL, 0.832 mmol) was condensed into a solution of methylenebis(diphenylphosphane) **1c** (100 mg, 0.260 mmol) in benzene (1 mL) in a glass tube. The tube was sealed and kept at room temperature for 3 days. According to the NMR spectroscopic data the reaction was complete in 30 h, and the rest of the time was needed for the crystallization of the product as a colorless crystals. The crystals were filtered off, washed with 0.4 mL of dichloromethane and dried in vacuo 0.05 mm. Yield 145 mg (63%), m.p. 121−124 °C. − ^{1}H NMR (89.56 MHz, $CDCl_3$): δ = 3.57 [d. sept., $^3J_{PH}$ = 10.6 Hz, $^3J_{FH}$ = 6.6 Hz, 1 H, C*H*(CF_3)$_2$], 4.72 [d. sept., $^3J_{PH}$ = 13.2 Hz, $^3J_{FH}$ = 5.6 Hz, 1 H, C*H*(CF_3)$_2$], 7.25−8.12 (m, 20 H, Ph). − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −70.98 (d, $^3J_{FH}$ = 6.6 Hz, 6 F, CF_3), −72.26 (s, 6 F, CF_3), −74.39 (s, 6 F, CF_3). − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = −32.5 (d, $^2J_{PP}$ = 56.0 Hz), 58.8 (d, $^2J_{PP}$ = 56.0 Hz). − $C_{34}H_{22}F_{18}O_3P_2$ (882.46): calcd. C 46.28, H 2.51; found C 46.26, H 2.53.

Synthesis of Compound 11: A solution of compound **9** (100 mg, 0.113 mmol) in toluene (1 mL) was heated at 100 °C for 5 h. The solvent was removed in vacuo (0.05 mm), the remaining oil was dissolved in boiling hexane and the solution was left at 20 °C overnight. A mixture of compounds **11**−**13** with predominant content of **11** was separated, and the mother liquid was kept for two weeks at 20 °C followed by two weeks at −20 °C. Colourless crystals of **11** (7 mg, 16%) were separated from the precipitated oil and dried in vacuo. − ^{1}H NMR (89.56 MHz, $CDCl_3$): δ = 5.41 [d. sept., $^3J_{PH}$ = 12.29 Hz, $^3J_{FH}$ = 5.86 Hz, 1 H, C*H*(CF_3)$_2$], 7.35−7.95 (m, 10 H, Ph). − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −73.96 (d, $^3J_{FH}$ = 5.86 Hz, 6 F, CF_3). − ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 68.33 [d. sept., $^2J_{PC}$ = 4.8 Hz, $^2J_{FC}$ = 35.1 Hz, 1 C, *C*H(CF_3)$_2$], 120.4 (d, $^1J_{PC}$ = 274.9 Hz, 2 C, Ph), 128.5 (d, $^2J_{PC}$ = 14.7 Hz, 4 C, Ph), 131.2 (d, $^3J_{PC}$ = 11.7 Hz, 4 C, Ph), 132.95 (d, $^4J_{PC}$ = 2.9 Hz, 2 C, Ph),. − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 39.85 (s, 2 P). − $C_{15}H_{11}F_6OP_2$ (368.22): calcd. C 48.93, H 3.01; found C 48.21, H 3.13.

Synthesis of Compounds 12 and 13: A solution of compound **9** (150 mg, 0.170 mmol) in chloroform (1.5 mL) was heated to 60 °C for 48 h and then the solvent was removed in vacuo (0.05 mm). Crystallization of the residue from dichloromethane/hexane gave a mixture of two types of crystals for compounds **12** and **13** (24 mg), which were mechanically separated.

12: − ^{1}H NMR (89.56 MHz, $CDCl_3$): δ = 7.37 (d, $^2J_{PH}$ = 11.6 Hz, 1 H), 7.44−7.92 (m, 10 H, Ph). − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −65.7 (q, $^4J_{FF}$ = 7.33 Hz, 3 F, CF_3), −59.1 (q, $^4J_{FF}$ = 7.33 Hz, 3 F, CF_3). − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 17.1 (s, 2 P).

13: − ^{1}H NMR (89.56 MHz, $CDCl_3$): δ = 7.28−7.90 (m, 10 H, Ph), 8.81 (br. s, 1 H) − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 26.5 (s, 2 P).

Synthesis of Compound 15: A solution of HFTA (50 mg, 0.137 mmol) in hexane (1.2 mL), cooled to −40 °C, was quickly added to a solution of methylenebis[bis(diethylamino)phosphane] **1b** (50 mg, 0.137 mmol) in hexane (1.2 mL) at the same temperature. The reaction mixture was stirred at −20 °C for 5 min. and then kept at this temperature for 20 min. The colorless crystalline product **16** was filtered off and dried in vacuo. Yield of the crystals 48 mg (48%). According to the ^{31}P NMR spectrum the mother liquor contained compound **15** only. − ^{1}H NMR (360.13 MHz, C_6H_{14}): δ = 1.33 (t, $^{1}J_{HH}$ = 7.1 Hz, 24 H, CH_2CH_3), 3.33 (m, 16 H, CH_2CH_3), 5.02 [sept, 2 H, $CH(CF_3)_2$]. − ^{19}F NMR (188.31 MHz, C_6H_{14}): δ = −67.7 (d, $^{3}J_{HF}$ = 8.14 Hz, 12 F, CF_3). − ^{31}P NMR (145.78 MHz, C_6H_{14}): δ = 41.4 (s, 2 P). − $C_{23}H_{42}F_{12}N_4P_2S_2$ (728.67): calcd. C 37.91, H 5.81; found C 37.57, H 5.79.

Synthesis of Compound 18: The reaction mixture of the carbodiphosphorane **15** obtained as described above was diluted with hexane (2 mL) and warmed to 20 °C. At this temperature the crystals of **15** dissolved completely. The solution was then quickly cooled to −20 °C and the equivalent amount of HBF_4 (solution in ether) was added to it. The colourless crystalline product that precipitated immediately was filtered off and dried in vacuo. Yield 98 mg (88%); after crystallization from CH_2Cl_2/diethyl ether at −25 °C the yield is 61% (68 mg). − ^{1}H NMR (360.13 MHz, $CDCl_3$): δ = 1.20 (t, $^{3}J_{HH}$ = 7.06 Hz, 24 H, NCH_2CH_3), 1.91 (t, $^{2}J_{PH}$ = 4.9 Hz, 1 H, P−CH−P), 3.27 (m, 16 H, NCH_2CH_3), 4.25 [br. sept., $^{3}J_{FH}$ = 7.1 Hz, 2 H, $HC(CF_3)_2$]. − ^{19}F NMR (188.31 MHz, $CDCl_3$): δ = −69.5 (d, $^{3}J_{HF}$ = 7.1 Hz, 12 F, CF_3), −151.2 (s, BF_4). − ^{31}P NMR (145.78 MHz, $CDCl_3$): δ = 68.2 (s, 2 P). − $C_{23}H_{43}BF_{16}N_4P_2S_2$ (816.48): calcd. C 33.83, H 5.31; found C 33.71, H 5.02.

Synthesis of Compound 21: A solution of thiohexafluoroacetone (72 mg, 0.198 mmol) in ether (2 mL) was cooled to −70 °C and quickly added to a solution of methylenebis(diphenylphosphane) **1c** (50 mg, 0.130 mmol) in ether (3 mL) at the same temperature. The reaction mixture was stirred at −70 °C for 10 min. The reaction solution was then concentrated to a volume of about 0.6 mL. Hexane (1 mL) was added and solution was kept at −25 °C for 3 days. The colourless crystalline product formed over this time was filtered off and dried in vacuo. Yield of the crystals 50 mg (50%). According to the ^{31}P NMR spectrum the mother liquid contained compound **21** only. − ^{1}H NMR (360.13 MHz, $CDCl_3$): δ = 3.20 [sept., $^{3}J_{FH}$ = 8.07 Hz, 1 H, $CH(CF_3)_2$], 4.36 [d. sept., $^{3}J_{FH}$ = 7.34 Hz, $^{3}J_{PH}$ = 1.98 Hz, 1 H, $CH(CF_3)_2$], 6.85−7.18 (m, 12 H, Ph), 7.78−8.08 (m, 8 H, Ph). − ^{19}F NMR (188.31 MHz, $CDCl_3$): δ = −66.15 (dd, $^{3}J_{HF}$ = 7.4 Hz, J_{PF} = 2.6 Hz, 6 F, CF_3), −65.75 (d, $^{3}J_{HF}$ = 7.4 Hz, 6 H, CF_3) − ^{31}P NMR (145.78 MHz, $CDCl_3$): δ = −4.5 (d, $^{2}J_{PP}$ = 185 Hz, 1 P, P−C−P), 65.2 (d, $^{2}J_{PP}$ = 185 Hz,

Table 1. Crystal data and structure refinement parameters of compounds **9**, **15**, **18**, **21**

	9	**15**	**18**	**21**
Formula	$C_{34}H_{22}F_{18}O_3P_2$	$C_{23}H_{42}F_{12}N_4P_2S_2$	$C_{23}H_{43}BF_{16}N_4P_2S_2$	$C_{31}H_{22}F_{12}P_2S_2$ x 1/2 $C_4H_{10}O$
Mol. wt.	882.46	728.67	816.48	785.57
Temperature K	173(2)	173(2)	173(2)	173(2)
Wavelength pm	71.073	71.073	71.073	71.073
Crystal size [mm]	0.6 × 0.4 × 0.3	0.8 × 0.6 × 0.5	0.6 × 0.4 × 0.3	1.0 × 0.5 × 0.3
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*Cc*	$P2_1/n$	$P2_1/n$
a [pm]	1826.7(5)	2162.7(2)	1151.8(3)	1675.8(4)
b [pm]	948.75(11)	1030.60(10)	1798.8(3)	1083.0(2)
c [pm]	3989.7(6)	1799.4(2)	1730.8(3)	1917.0(2)
α [°]	90	90	90	90
β [°]	6.83(1)	123.420(10)	96.14(2)	96.86(2)
γ [°]	90	90	90	90
V [nm^3]	3.3475(6)	3.3475(6)	3.5654(13)	3.4542(11)
Z	8	4	4	4
$D_{calcd.}$ [Mg/m^3]	1.716	1.446	1.521	1.501
Absorption coefficient [mm^{-1}]	0.263	0.343	0.346	0.337
2θ range [°]	2.52 to 25.00	2.71 to 27.51	2.26 to 25.00	2.55 to 22.49
F(000)	3536	1512	1680	1576
Index range	$-21 \le h \le 21$, $-1 \le k \le 11$, $-47 \le l \le 47$	$-28 \le h \le 28$, $-1 \le k \le 13$, $-23 \le l \le 18$	$-11 \le h \le 13$, $-1 \le k \le 21$, $-20 \le l \le 20$	$-18 \le h \le 1$, $-11 \le k \le 1$, $-20 \le l \le 20$
Reflections collected	13731	8241	7844	5706
Independent reflections	6012 [*R*(int) = 0.0432]	7255 [*R*(int) = 0.0161]	6235 [*R*(int) = 0.0294]	4477 [*R*(int) = 0.0471]
Completeness to θ_{max}	99.9	99.8	99.2	99.0
Max. and min. transmission	0.9251 and 0.8579	0.8472 and 0.7709	0.9033 and 0.8193	0.9056 and 0.7292
Data/Restraints/Parameter	6012/0/517	7255/2/401	6235/0/446	4477/1/462
Goodness-of-fit on F^2	1.020	1.040	1.024	1.033
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0448, *wR*2 = 0.1021	*R*1 = 0.0249, *wR*2 = 0.0655	*R*1 = 0.0677, *wR*2 = 0.1687	*R*1 = 0.0544, *wR*2 = 0.1276
Largest difference peak and hole [e·Å^{-3}]	0.427 and −0.462	0.330 and −0.225	0.827 and −0.832	0.368 and −0.388 The solvent molecule is disordered.
Absolute structure parameter	−	0.44(3) The structure was refined as a merohedric twin	−	−

1 P, P−C−P). − $C_{23}H_{42}F_{12}N_4P_2S_2$ (748.57): calcd. C 49.74, H 2.96; found C 49.35, H 3.11.

X-ray Crystal Structure Determination of Compounds 9, 15, 18, and 21: All crystallographic measurements were performed at 173(2) K on a Siemens P4 diffractometer, using graphite monochromated Mo-K_α radiation (λ = 71.073 pm) and an LT2 low temperature device. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELX-97 (Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically and the position of the hydrogen atoms were calculated using a riding model. Crystal data, data collection and processing parameters are given in Table 1.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-150573 (**9**), CCDC-150574 (**15**), CCDC-150575 (**18**), and CCDC-150576 (**21**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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