An Unusual Oxidation of 1,5-Dimethyl-2,4-bis(dialkylamino)-1,5-diaza-2,4-diphosphinan-6-one with Hexafluoroacetone

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Dedicated to Professor Michael Lattman on the occasion of his 50th birthday

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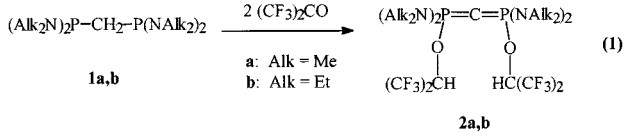
The oxidation of heterocycles **5a,b**, or **9** containing a methylenediphosphane unit, with hexafluoroacetone does not lead to the expected dioxaphospholane heterocycles, but yields unstable carbodiphosphoranes **6a,b** or ylide **10** respectively, which then react easily with HFA to give the stable intermediate products **7a,b** or **11** of the Wittig reaction.

Introduction

It is well-known that the oxidation of phosphanes with hexafluoroacetone (HFA) usually leads to the formation of 1,3- or 1,4-dioxaphospholane heterocycles.[1–4] Recently, however, we showed that this is not the only possible pathway for this reaction and that the presence of a methylene group in an α-position to the phosphorus atom may direct the reaction in an unusual way.[5,6] For example, bis[bis(dialkylamino)phosphinyl]methanes **1a,b** easily react with only two equivalents of HFA quantitatively, giving carbodiphosphoranes **2a,b** (Scheme 1).

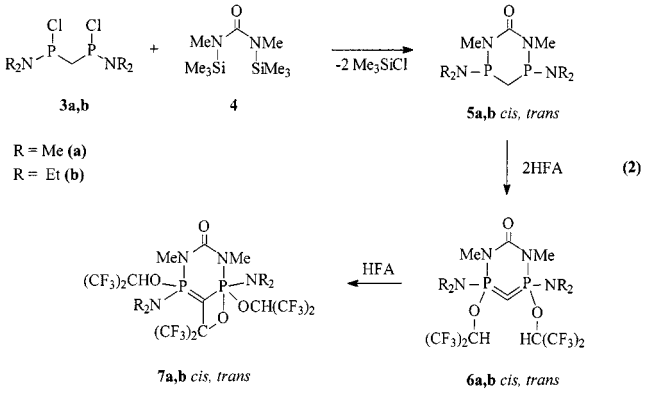


Scheme 1

Results and Discussion

In order to demonstrate the scope of this unusual reaction, we decided to employ other diphosphanes containing the structural fragment P–CH_2–P. It was interesting, for example, to investigate the reaction of HFA with compounds in which this fragment was a part of a heterocyclic system. As a model system we chose 1,5-dimethyl-2,4-bis(dialkylamino)-1,5-diaza-2,4-diphosphinan-6-one **5a,b**.[7]

The reactivity of **5a,b** in the reaction with HFA did not differ much from that of **1a,b**. The reaction proceeded smoothly at room temperature when gaseous HFA was slowly bubbled through a solution of **5a** or **5b** in dichloromethane at 20 °C. However, only small quantities of the expected cyclic carbodiphosphoranes **6a,b** could be detected in the reaction mixture by NMR spectroscopy. Unlike carbodiphosphoranes **2a,b**, compounds **6a,b** underwent addition of one more equivalent of HFA to give the heterocycles **7a,b**, which were the main product in this reaction (Scheme 2). The rate of addition of HFA to carbodiphosphoranes **6a,b** evidently exceeded the rate of their own formation; with HFA as limiting reagent, the content of **6a,b** did not grow and the starting material **5a,b** remained in the reaction mixture.



Scheme 2

These results are consistent with the only known example of the addition of HFA to hexaphenylcarbodiphosphorane.[8] Here, the same type of [1,2]oxaphosphetane was obtained by a cyclic addition. However the reaction required excess HFA and heating to 50 °C.

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Starting heterocycles **5a,b** were obtained in high yield by the addition of silylated urea **4** to methylene-bis(diethylaminochlorophosphanes) **3a,b** and were used in the reaction with HFA without purification. They existed as *cis*- and *trans*-isomers, depending on the position of the substituents at the phosphorus atoms with respect to the cycle. The *cis*-isomer of **5** is kinetically more stable and its formation is favored. The *trans*-isomer **5-*trans*** is thermodynamically more stable and the *cis*/*trans* ratio after reaching equilibrium between the isomers is 1:9. The rate of transformation of **5-*cis*** into **5-*trans*** depends on the solvent used in the reaction.[7] This gave us the possibility to use varying *cis*/*trans* ratios from 1:1 to 1:9 when **5a,b** was reacted with HFA.

The products of this reaction, compounds **7a,b**, also formed *cis*- and *trans*-isomers. However, unlike the starting heterocycles **5a,b**, they exist independently of each other and do not show any tendency to interconvert one into the other. That is why the observed ratio between the isomers of product **7** reflects the isomer distribution of the starting compound **5** before reaction with HFA.

When compounds **5a,b** were prepared in diethyl ether, the initial ratio between the isomers was 1:1 and after reaction with HFA the products **7a,b** were obtained with the same ratio of isomers. Each isomer displays two characteristic doublets in the ^{31}P NMR spectrum. Compounds **7a,b** are stable crystalline products and were isolated as a mixture of *cis*- and *trans*-isomers. The ratio of the isolated material corresponded to the one seen in solution and since both have equal solubility, they could not be separated. Attempts to separate them by liquid chromatography led to their substantial decomposition on the surface of silica gel, even though compounds **7a,b** do not react with water in the absence of silica gel.

When **5a,b** were prepared in dichloromethane, the *cis*/*trans* equilibrium ratio (1:9) was rapidly reached. The addition of HFA to this isomeric mixture gave the same distribution of isomers in the reaction products **7a,b**. The predominant content of **7a,b-*trans*** allowed for their isolation as pure crystalline substances. The structures of **7a,b-*trans*** are consistent with their NMR spectra. For example, the ^{31}P NMR spectrum of **7a** shows two doublets at −42 ppm and 33 ppm, which are characteristic of the ylide and spirophosphorane phosphorus atoms respectively. The ^{1}H and ^{13}C NMR spectra showed the non-equivalence of dialkylamino groups. All CF_3 groups of **7a,b-*trans*** are nonequivalent and give rise to six independent multiplets in the ^{19}F NMR spectra. Two of them do not show FH coupling, as they belong to the CF_3 groups connected to the four-membered ring.

The structure of compound **7b-*trans*** was confirmed by a single-crystal X-ray diffraction study. The general view of the molecule is shown in Figure 1. It should be noted that heterocycles of this type have not been studied by structural methods yet.[9]

The central 6-membered ring P(1)P(2)N(1)N(2)C(1)C(2) in this compound is almost planar: deviations from the least-square plane do not exceed 0.070 Å. The 4-membered heterocycle P(2)O(3)C(1)C(12) is planar within 0.026 Å.

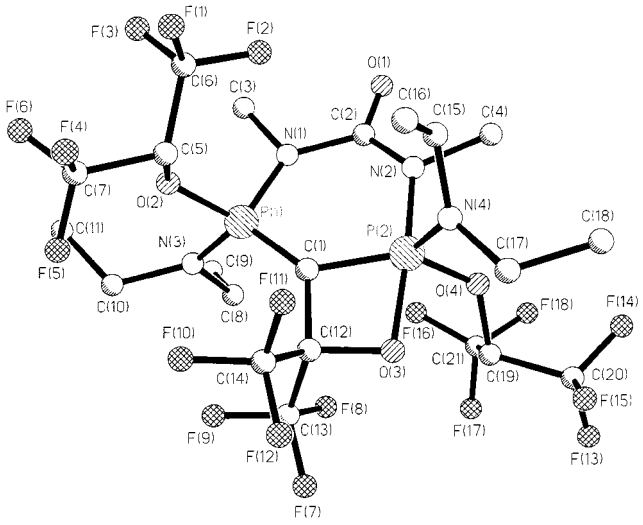
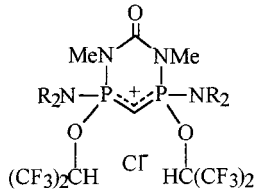


Figure 1. Perspective view and labelling scheme for the molecule **7b-*trans*** (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P(1)−N(1) 1.634(3), P(1)−C(1) 1.668(4), P(2)−C(1) 1.738(4), P(2)−N(2) 1.773(3), P(2)−O(3) 1.779(3), O(3)−C(12) 1.407(4), N(1)−C(2) 1.421(5), N(2)−C(2) 1.352(5), C(1)−C(12) 1.507(5); N(1)−P(1)−C(1) 105.8(2), C(1)−P(2)−N(2) 98.3(2), C(12)−O(3)−P(2) 94.9(2), C(2)−N(1)−P(1) 129.3(3), C(2)−N(2)−P(2) 132.3(3), C(12)−C(1)−P(2) 93.1(2), P(1)−C(1)−P(2) 132.2(2), N(2)−C(2)−N(1) 121.1(3), O(3)−C(12)−C(1) 95.9(3)

The dihedral angle between the planes of the 6- and 4-membered cycles is 11.63°. All nitrogen atoms have a trigonal coordination sphere (corresponding sums of bond angles lie within a narrow range: 358.6−360.0°). Atom P(1) has significantly distorted tetrahedral coordination whereas atom P(2) has a trigonal bipyramidal coordination, with atoms O(3) and N(2) being in axial and atoms C(1), N(4), O(4) in equatorial positions.

Together with **7a,b**, small quantities of the cyclic carbodiphosphoranes **6a,b** were detected in the reaction mixture (about 5−10% based on ^{31}P NMR spectrum). These compounds also exist as *cis*- and *trans*-isomers. Each of them displays a singlet in the range of 40−44 ppm. This value is consistent with the chemical shifts of acyclic carbodiphosphoranes **2a,b**. As a strong base, **6a,b** can react with ammonium hydrochlorides to give salts **8a,b**. Since chlorophosphanes **3a,b** were frequently contaminated with small amounts of dialkylammonium chloride, salts **8a,b** were found in the reaction mixture with a yield of about 3−4%. When the reaction was carried out in THF, **8b** crystallized from the reaction mixture as a colorless crystalline product. *A priori*, this compound should also give rise to two isomers. However, only one isomer of **8b** was formed, as is evident from the ^{31}P NMR spectrum where only one singlet



8a,b

at 44.05 ppm is observed. The X-ray analysis of a single crystal revealed that this is the *cis*-isomer (Figure 2). The hexafluoroisopropoxide groups form two chelating units, which embrace the chlorine anion forming the thermodynamically stable structure. The chlorine atom is kept by the two hydrogen bonds which is only possible for the *cis*- but not for the *trans*-isomer (Cl···C(5) 3.323(9), Cl···C(12) 3.377(9) Å).

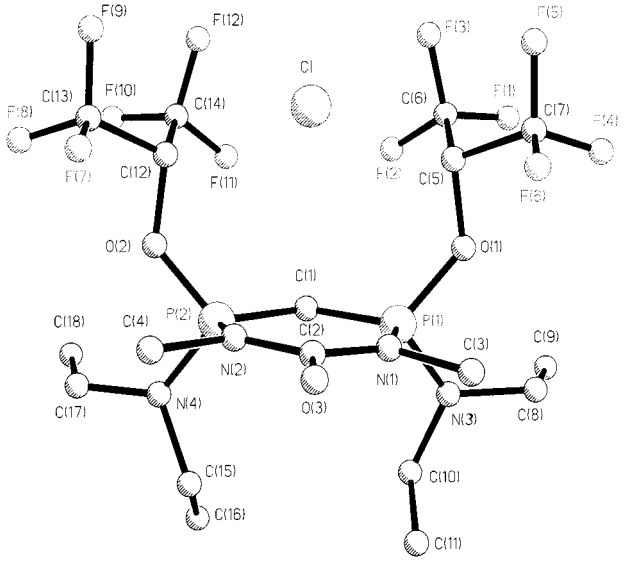
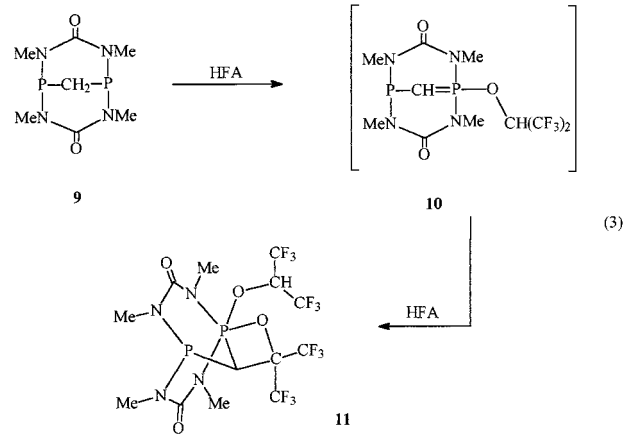


Figure 2. Perspective view and labelling scheme for the molecule **8b-*cis*** (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P(1)−N(1) 1.654(10), P(1)−C(1) 1.671(11), P(2)−C(1) 1.662(11), P(2)−N(2) 1.661(10), N(1)−C(2) 1.39(2), N(2)−C(2) 1.364(14); N(1)−P(1)−C(1) 107.4(5), C(1)−P(2)−N(2) 106.3(5), C(2)−N(1)−P(1) 129.5(9), C(2)−N(2)−P(2) 130.9(9), P(1)−C(1)−P(2) 125.5(7), N(2)−C(2)−N(1) 119.5(13)

As in compound **7b-*trans***, the central 6-membered ring P(1)P(2)N(1)N(2)C(1)C(2) of **8b-*cis*** is almost planar: deviations do not exceed 0.060 Å. Atoms P(1) and P(2) have significantly distorted tetrahedral coordination. These data differ from the results of X-ray analyses, which we obtained earlier for the *cis*- and *trans*-isomers of the sulfur-derivative of heterocycle **5b**. These isomers showed noticeably distorted ring conformations, while the distortions at the phosphorus atoms were less pronounced than in **7b**-*trans* and **8b**-*cis*.[10] Owing to the $n_{N(1,2)}-\pi_{C=O}$ conjugation, the N(1)−C(2) and N(2)−C(2) bonds of **8b-*cis*** and **7b-*trans*** are noticeably shorter than the standard value of 1.45 Å for the $N(sp^2)-C(sp^2)$ single bond.[11] Comparison of the geometrical parameters of **8b-*cis*** and **7b-*trans*** with the corresponding values in related systems[10,12−14] shows delocalization of electron density over the N(1)−P(1)−C(1)−P(2)−N(2) bond system for the former molecules. It is noteworthy that unlike compound **7b-*trans***, in which the P(1)=C(1) double bond is localized as is indicated by the rather different bond lengths [P(1)−C(1) 1.668(4), P(2)−C(1) 1.738(4) Å], charge delocalization over the P(1)−C(1)−P(2) system [P(1)−C(1) 1.671(11), P(2)−C(1) 1.662(11) Å] is observed in **8b-*cis***.

For the further studies of the reactions of $P-CH_2-P$-containing heterocycles with HFA we used compound **9**. Its structure is rather close to that of **5a,b**, but instead of dialkylamino groups the two phosphorus atoms are bridged by one more urea unit. The reaction of compound **9** with HFA is slower and after 48 h in a sealed tube, a polymeric product of uncertain structure (82%) and compound **11** (18%) were obtained (Scheme 3). Since compound **11** is poorly soluble in dichloromethane, which was used as a solvent, it crystallized directly from the reaction mixture as colorless crystals.



Scheme 3

Unlike **5**, the phosphorus atoms of compound **9** are less nucleophilic, as they are bonded to two amide nitrogen atoms. That is why the reaction of **9** with HFA involves only one of the two phosphorus atoms. Although we could not detect it, we assumed that in this case the first reaction product, the ylide intermediate **10**, undergoes two simultaneous processes: polymerization and addition of HFA across the P=C bond to give **11**.

The structure of **11** was determined by NMR spectroscopic and analytical data. The ^1H NMR spectrum shows the non-equivalence of the all four methyl groups, the characteristic multiplet of the $(CF_3)_2CH$ unit at 5.48 ppm and doublet of doublets of the P−CH−P proton at 4.82 ppm. All CF_3 groups are also non-equivalent and display separate multiplets in the ^{19}F NMR spectrum. The interesting feature of this compound is that the two CF_3 groups at the four-membered cycle show a through-space coupling with the tricoordinated phosphorus atom. This phosphorus atom appears as a multiplet at 61 ppm in the ^{31}P NMR spectrum, whereas the other phosphorus atom gives rise to a doublet at −43 ppm.

Thus, the reaction of the $P-CH_2-P$ containing heterocycles **5** and **9** with hexafluoroacetone did not lead to the formation of the expected 1,3,2- or 1,4,2-dioxaphospholane heterocycles with a pentacoordinated phosphorus atom, but yielded derivatives of cyclic carbodiphosphoranes with tetracoordinated ylide phosphorus atoms.

Experimental Section

All operations were performed under nitrogen in a dry box. The solvents were dried by the usual procedures. The NMR spectra were recorded on JEOL FX-90Q and Varian 300 MHz spectro-

meters. The ^{1}H and ^{13}C NMR chemical shifts were referenced to tetramethylsilane (TMS). The ^{31}P NMR chemical shifts were measured using 85% aqueous orthophosphoric acid as an external standard. As usual, high frequency shifts were 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 Compounds 3a,b: Compounds **3a,b** can be obtained with a 35−40% yield (after distillation) from methylene-bis(dichlorophosphane)[17] and dialkylamine. Use of silylated dialkylamine increases the yield to 50%. It is more convenient, however, to prepare fully substituted tetra(dialkylamino)methylenediphosphane **1a,b**, which can be isolated by distillation in 75−80% yield, and mix it subsequently with one equivalent of starting methylene-bis(dichlorophosphane) without solvent.

Synthesis of Compound 7a-*trans*: *N,N′*-Dimethyl-*N,N′*-bis(trimethylsilyl)urea[18] **4** (154 mg, 0.663 mmol) was added to a solution of methylene-bis(dimethylaminochlorophosphane) **3a** (150 mg, 0.638 mmol) in dichloromethane (1.5 mL), and the mixture was stirred at room temperature for 15 min. The reaction mixture was then placed in a 5-mm NMR tube and gaseous HFA (40 mL, 1.79 mmol) was slowly bubbled through it at room temperature using a syringe with a thin needle. The solvent was removed in vacuo 10 min after the addition of HFA and the residue was extracted with hexane (2 × 5 mL). The hexane solution was concentrated in vacuo to a volume of 5 mL and then cooled to −15 °C. In 48 h colorless crystals of **7a-*trans*** were separated and dried in vacuo. Yield 120 mg (25%), m.p. 101−102 °C. − ^{1}H NMR (89.56 MHz, $CDCl_3$): δ = 2.59 (d, $^{3}J_{PH}$ = 13.2 Hz, 6 H, N(CH_3)$_2$), 2.75 (d, $^{3}J_{PH}$ = 15.1 Hz, 6 H, N(CH_3)$_2$), 2.78 (d, $^{3}J_{PH}$ = 16.8 Hz, 3 H, NCH_3), 2.86 (d, $^{3}J_{PH}$ = 10.0 Hz, 3 H, NCH_3), 5.18 (m, 1 H, CHCF$_3$), 5.42 (m, 1 H, CHCF$_3$). − ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 28.6 (s, 1 C, NCH$_3$), 35.7 (s, 1 C, NCH$_3$), 36.8 (s, 2 C, N(CH$_3$)$_2$), 37.6 (d, $^{2}J_{PC}$ = 8.5 Hz, 2 C, N(CH$_3$)$_2$), 67.0−75.5 (m, 3 C, CH(CF$_3$)$_2$), 120.4 (q, $^{1}J_{FC}$ = 282.8 Hz, 2 C, CF$_3$), 121.3 (q, $^{1}J_{FC}$ = 279.2 Hz, 2C, CF$_3$), 123.5 (q, $^{1}J_{FC}$ = 289.0 Hz, 2C, CF$_3$), 153.8 (dd, $^{2}J_{PC}$ = 10.9 Hz, $^{2}J_{PC}$ = 11.2 Hz, C=O). − ^{19}F NMR (282.2 MHz, $CDCl_3$): δ = −72.99 (m, CF$_3$), −73.47 (m, CF$_3$), −74.08 (m, CF$_3$), −74.62 (m, CF$_3$), −76.17 (m, CF$_3$), −77.27 (m, CF$_3$). − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = −42.0 (d, $^{2}J_{PP}$ = 75.6 Hz), 33.1 (d, $^{2}J_{PP}$ = 75.6 Hz). − $C_{17}H_{20}F_{18}N_4O_4P_2$ (748.29): calcd. C 27.29, H 2.69; found C 27.18, H 2.82.

Synthesis of Compound 7b-*trans*: *N,N′*-Dimethyl-*N,N′*-bis(trimethylsilyl)urea[18] **4** (128 mg, 0.550 mmol) was added to a solution of methylene-bis(dimethylaminochlorophosphane) **3b** (150 mg, 0.515 mmol) in dichloromethane (2 mL), and the mixture was stirred at room temperature for 45 min. The solvent was then removed in vacuo and the remaining oil was allowed to stay at 25 °C for 30 min in order for the *cis*- and *trans*-isomers of **3b** to reach equilibrium. Subsequently, the oil was dissolved in CH_2Cl_2 (1 mL), the solution was placed in a 5-mm NMR tube and gaseous HFA (32 mL, 1.44 mmol) was slowly bubbled through the solution using a syringe equipped with a thin needle. The solvent was removed in vacuo 10 min after the addition of HFA, and the residue was extracted with hexane (2 × 3 mL). The hexane solution was concentrated in vacuo to a volume of 1 mL and then cooled to −15 °C. The colorless crystals of **7b-*trans*** formed over 24 h were separated and dried in vacuo. Yield 116 mg (29%), m.p. 120−121 °C. − ^{1}H NMR (89.56 MHz, $CDCl_3$): δ = 1.04 (t, $^{3}J_{HH}$ = 7.1 Hz, 6 H, NCH$_2$CH_3), 1.17 (t, $^{3}J_{HH}$ = 7.1 Hz, 6 H, NCH$_2$CH_3), 2.84 (d, $^{3}J_{PH}$ = 7.3 Hz, 3 H, NCH_3), 2.91 (d, $^{3}J_{PH}$ = 10.3 Hz, 3 H, NCH_3), 3.09 (m, 8 H, NCH_2CH$_3$), 5.11 (m, 1 H, CHCF$_3$), 5.35 (m, 1 H, CHCF$_3$). − ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 11.97 (s, 1 C, NCH$_2$CH_3), 12.14 (s, 1 C, NCH$_2$CH_3), 14.0 (s, 2 C, NCH$_2$CH_3), 30.0 (s, 1 C, NCH$_3$), 36.1 (s, 1 C, NCH$_3$), 37.7 (d, $^{2}J_{PC}$ = 8.6 Hz, 2 C, NCH$_2$CH$_3$), 42.3 (s, 2 C, NCH$_2$CH$_3$), 65.0−76.2 (m, 3 C, CH(CF$_3$)$_2$), 120.5 (q, $^{1}J_{FC}$ = 286.5 Hz, 2 C, CF$_3$), 121.5 (q, $^{1}J_{FC}$ = 284.1 Hz, 2C, CF$_3$), 123.5 (q, $^{1}J_{FC}$ = 286.4 Hz, 2C, CF$_3$), 153.8 (dd, $^{2}J_{PC}$ = 10.9 Hz, $^{2}J_{PC}$ = 11.1 Hz, 1 C, C=O). − ^{19}F NMR (282.2 MHz, $CDCl_3$): δ = −72.29 (m, 3 F, CF_3), −72.86 (m, 3 F, CF_3), −74.10 (m, 3F, CF_3), −74.17 (m, 3 F, CF_3), −74.39 (m, 3 F, CF_3), −75.51 (m, 3 F, CF_3). − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = −38.2 (d, $^{2}J_{PP}$ = 74.2 Hz), 36.0 (d, $^{2}J_{PP}$ = 74.2 Hz). − $C_{21}H_{28}F_{18}N_4O_4P_2$ (804.40): calcd. C 31.36, H 3.51; found C 31.69, H 3.58.

Synthesis of Compound 8b-*cis*: *N,N′*-Dimethyl-*N,N′*-bis(trimethylsilyl)urea[18] **4** (134 mg, 0.578 mmol) was added to a solution of methylene-bis(dimethylaminochlorophosphane) **3b** (160 mg, 0.550 mmol) in THF (4 mL), and the mixture was stirred at room temperature for 15 min. The solvent and all volatiles were then removed in vacuo (0.05 Torr) for 15 min, and the remaining oil was dissolved again in THF (4 mL). The solution was then placed in a 10-mm NMR tube and gaseous HFA (17 mL, 0.755 mmol) was slowly bubbled through the solution using a syringe equipped with a thin needle. The reaction mixture was allowed to stay at −15 °C. Colorless crystals of **8b-*cis*** formed over 24 h were separated and dried in vacuo. Yield 13 mg (3.6%). − ^{1}H NMR (89.56 MHz, $CDCl_3$): δ = 1.22 (t, $^{3}J_{HH}$ = 7.1 Hz, 12 H, NCH$_2$CH_3), 3.04 (d, $^{3}J_{PH}$ = 6.2 Hz, 6 H, NCH_3), 3.25 (m, 8 H, NCH_2CH$_3$, 1 H, PCHP), 7.46 (m, 2 H, CHCF$_3$). − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −72.98 (d, $^{3}J_{FH}$ = 41.0 Hz, 12 F, CF_3). − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 44.0 (s, 2 P).

Synthesis of Compound 11: Gaseous hexafluoroacetone (20.5 ml; 0.914 mmol) was condensed into a solution of bicyclic compound **9** (113 mg; 0.456 mmol) in dichloromethane (1 mL) in a glass tube. The tube was sealed and kept at room temperature for 3 d. The colorless crystalline product formed in the reaction mixture was then filtered off, washed with dichloromethane (0.3 mL) and dried in vacuo (0.05 mm). Yield 49 mg (18.5%), m.p. 120−121 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.93 (d, $^{3}J_{HP}$ = 9.4 Hz, 3 H, NCH_3), 2.99 (d, $^{3}J_{HP}$ = 10.2 Hz, 3 H, NCH_3), 3.14 (d, $^{3}J_{HP}$ = 9.4 Hz, 3 H, NCH_3), 3.18 (d, $^{3}J_{HP}$ = 12.6 Hz, 3 H, NCH_3), 4.82 (dd, $^{2}J_{HP}$ = 6.1 Hz, $^{2}J_{HP}$ = 26.1 Hz, 1 H, P−CH−P), 5.48 (d of hept., $^{3}J_{HP}$ = 14.9 Hz, $^{3}J_{HF}$ = 5.6 Hz, 1 H, HC(CF$_3$)$_2$). − ^{19}F NMR (84.26 MHz, $CDCl_3$): δ = −77.93 (m, CF$_3$), −74.11 (m, CF$_3$), −73.18 (m, CF$_3$), −70.98 (m, CF$_3$). − ^{31}P NMR ($CDCl_3$): δ = −43.3 (d, $^{2}J_{PP}$ = 65.0 Hz, 1 P), 61.3 (m, $^{2}J_{PP}$ = 65.0 Hz, 1 P). − $C_{13}H_{14}F_{12}N_4O_4P_2$ (580.21): calcd. C 26.91, H 2.43; found C 27.07, H 2.54.

X-ray Crystal Structure Determination of Compounds 7b-*trans* and 8b-*cis*: Crystal data, data collection and processing parameters are given in Table 1. All crystallographic measurements were performed at 20 °C on a CAD-4-Enraf−Nonius diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) and ω-2θ scan mode (the ratio of the scanning rates ω/2θ = 1.2). Unit-cell parameters were calculated from the setting angles of 22 strong, high-angle carefully centered reflections with $13 > \theta > 12°$ for **7b-*trans*** and $11 > \theta > 10°$ for **8b-*cis***. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation control reflections were measured every 147 reflection. Correction for crystal decay (ca. 13% for **7b-*trans*** and 8% for **8b-*cis***) was applied during the processing of data sets. All data were corrected for Lorentz and polarization effects but not for absorption. Both structures were solved by direct methods.[15] Non-hydrogen atoms were refined against F by the full-matrix least-squares technique[16] in the anisotropic approxi-

Table 1. Crystal data and structure refinement parameters of compounds **7b-*trans***, **8b-*cis***

	7b-*trans*	**8b-*cis***
Empirical formula	$C_{21}H_{28}F_{18}N_4O_4P_2$	$C_{18}H_{29}ClF_{12}N_4OP_2$
a [Å]	10.452(2)	13.314(5)
b [Å]	11.732(1)	12.896(4)
c [Å]	14.908(3)	17.613(6)
α [°]	68.00(1)	90
β [°]	78.81(1)	105.48(3)
γ [°]	73.79(1)	90
V [Å^3]	1619	2914
Z	2	4
d [g × cm^{-3}]	1.65	1.54
Crystal system	Triclinic	Monoclinic
Space group	P-1 (N2)	$P2_1/c$ (N14)
μ [mm^{-1}]	0.27	0.34
F(000)	812	1376
Crystal size [mm]	0.27 × 0.40 × 0.50	0.03 × 0.15 × 0.15
Index ranges	$0 < h < 10$	$0 < h < 14$
	$-11 < k < 12$	$0 < k < 13$
	$-15 < l < 15$	$-19 < l < 18$
θ_{max} [°]	22	22.7
No. of reflections:		
Collected	4220	4314
Independent	3953	3894
in refinement ($I > 0$)	3069	3037
with $I > 2\sigma(I)$	2789	1418
R(int)	0.015	0.043
No. of refined parameters	442	281
Final R factors ($I > 2\sigma(I)$):		
R_1 (F)	0.042	0.098
R_w (F^2)	0.112	0.178
GOF	1.044	1.005
Weighting coefficients:		
A	0.065	0.082
B	1.238	0
Largest peak/hole [e cm^{-3}]	0.21/−0.24	0.28/−0.29

mation. All hydrogen atoms in **7b-*trans*** were located in the difference Fourier maps. For **8b-*cis*** all hydrogen atoms were placed in calculated positions. In both structures, the hydrogen atoms were included in the final refinement riding their supporting carbon atoms. The weighting scheme $\omega^{-1} = \sigma^2(F_o^2) + (AP)^2 + BP$, with $P = (F_o^2 + 2F_c^2)/3$ was used. − Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141691 (**7b-*trans***) and CCDC-141692 (**8b-*cis***). 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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