Bis[bis(dialkylamino)phosphanyl]methanes and Bis(trifluoromethyl)acrylonitrile — Reactions and Derivatives

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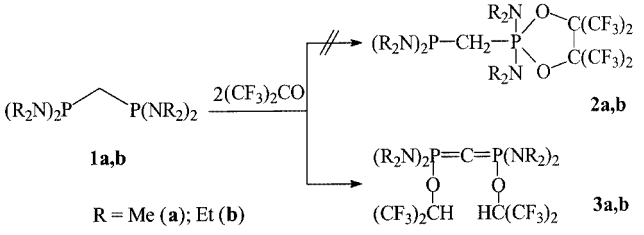
The reaction of bis[bis(dialkylamino)phosphanyl]methanes **1a,b** with bis(trifluoromethyl)acrylonitrile **8** led to the ylides **10a,b** which showed an interesting ability for self-fluorination involving trifluoromethyl groups to give the P–F derivatives **13a,b**. An X-ray analysis and NMR spectroscopic data showed that molecules of **10a,b** have different conformations in solution and in the crystal. Compounds **10a,b** reacted further with **8** to give either the symmetrical diylide **16a** or the P–F derivative **13b**. The addition of hexafluoroacetone to **10a,b** resulted in the formation of unsymmetrical diylides **19a,b**.

Introduction

Previously we have described the unusual reaction of hexafluoroacetone (HFA) with bis[bis(dialkylamino)phosphanyl]methanes **1a,b**, which does not lead to the expected phosphoranes **2a,b**,[1–4] in which one of the phosphorus atoms is included into 1,3,2-dioxaphospholane heterocycles, but yields quantitatively the carbodiphosphoranes **3a,b** (Scheme 1).[5,6]



Scheme 1

Taking into account the unusual nature of this reaction we were interested in studying its scope by substituting the carbonyl function of hexafluoroacetone with a C=C double bond. In this paper we describe the reaction of the bis[bis(dialkylamino)phosphanyl]methanes **1a,b** with alkenes in which the C=C double bond is activated by two trifluoromethyl groups.

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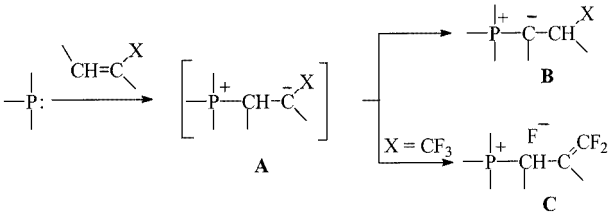
The interaction of tertiary phosphanes with compounds containing activated carbon-carbon double bonds to give phosphorus ylides is well known. The first step of this interaction is the formation of the intermediate zwitterionic compounds **A** (Scheme 2), containing a carbanion in the β-position to the phosphorus atom. Sometimes such intermediates can be isolated as stable compounds.[7–10] Then, a migration of the more acidic α-proton to the β-carbon is observed to give the appropriate ylides **B**. In some cases a similar migration is found for fluorine.[11,12] The forms **A** and **B** are in equilibrium with each other, and this equilibrium is usually shifted completely to the thermodynamically more stable form **B**. When this interconversion is separated by a high barrier, the two forms can be isolated as separate stable isomers.[13]

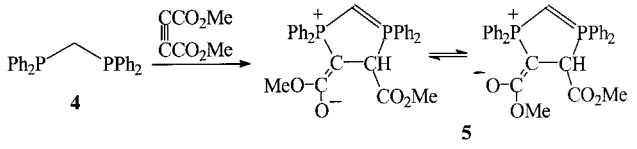


Scheme 2

We reasoned that if the C=C double bond of the starting alkene is activated by a CF_3 group (X = CF_3) the intermediate zwitterionic compound **A** can be alternatively stabilized by the elimination of a fluoride anion to give structure **C**. Such reactions have not been studied yet in the chemistry of phosphorus ylides, although the elimination of F^- from the α-position of a carbanion is well-known in fluorine chemistry.[14–17]

The second objective of the present investigation was to use methylenediphosphanes containing the fragment

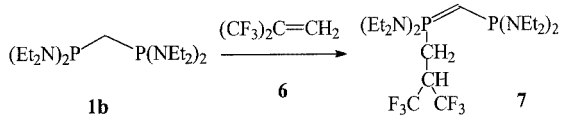
P−C−P. Such compounds have not yet been investigated in their reactions with alkenes, to the best of our knowledge. The only known close example is the reaction of methylenebis(diphenylphosphane) (**4**) with the methyl ester of acetylenedicarboxylic acid,[18] which gave a mixture of *E*/*Z* isomers of the stable cyclic ylide **5** (Scheme 3)



Scheme 3

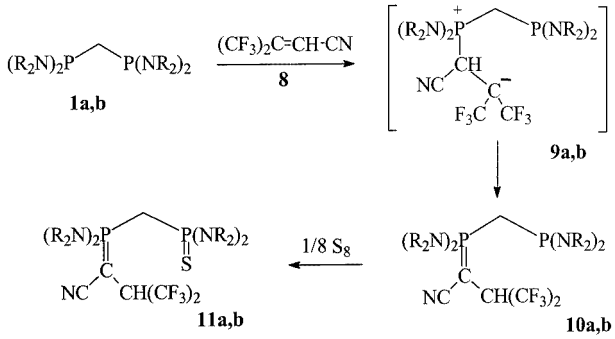
Results and Discussion

The activation of ethylene by two trifluoromethyl groups, as in compound **6**, turned out to be insufficient for the electrophilic attack of the trivalent phosphorus atom. The reaction of **1b** even with a threefold excess of 1,1-bis(trifluoromethyl)ethylene (**6**) proceeded very slowly (Scheme 4). After heating the reaction mixture in hexane in a sealed tube at 60 °C for 18 h, only traces of product **7** were detected by ^{31}P NMR spectroscopy as two characteristic doublets at δ = 34 and 78 ppm ($^2J_{P,P}$ = 76.4 Hz). The reaction rate increased in more polar solvents (CH_2Cl_2, $CHCl_3$), although it still required heating for a long period, which led to substantial decomposition of **7** and prevented its isolation in pure form.



Scheme 4

The presence of a nitrile group at the double bond, as in bis(trifluoromethyl)acrylonitrile (**8**), renders this compound much more reactive towards methylenediphosphanes **1a,b**. The reaction of **8** with **1a,b** proceeds rapidly in hexane solution at −15 °C to give ylides **10a,b** almost quantitatively (Scheme 5)



Scheme 5

The first step of this reaction is the formation of the intermediate betaines **9a,b**. However, at −15 °C the stability of these compounds is determined not by a fluoride ion elimination, but by a standard proton migration to give the ylides **10a,b**. Compounds **10a,b** can be isolated in good yields as colorless crystalline products. The structure of compounds **10a,b** and, in particular, the position of the ylidic bond, have been confirmed by NMR spectroscopy. For example the P−C−P carbon atom of **10a** appears as a doublet of doublets at δ = 26 ppm, whereas the negatively charged ylidic carbon atom P-*C*−CN appears with a characteristic high field chemical shift at δ = 10.8 ppm with a large $J_{P,C}$ coupling constant of 180 Hz. It is interesting to note that unlike the doublet of doublets of the $P-CH_2-P$ carbon atom in the ^{13}C NMR spectrum, the two equivalent protons of this unit appear in the ^1H NMR spectrum as only one doublet, probably because one of the two $^2J_{P,H}$ coupling constants is close to zero.

The second interesting peculiarity of compounds **10a,b** is the "through-space" spin-spin interaction between the $(CF_3)_2CH$ unit and the tricoordinate phosphorus atom. In the $^{31}P\{^1H\}$ NMR spectra the P^{III} phosphorus appears as a doublet of septuplets with $J_{P,F}$ = 3.0 Hz (**10a**) or 2.9 Hz (**10b**). All the fluorine atoms are equivalent and appear as a doublet of doublets in the ^{19}F NMR spectra, one of the doublets having the same $J_{P,F}$ coupling constant. In addition, the *C*H$(CF_3)_2$ carbon atom has a $J_{P,C}$ coupling constant of 6 Hz in the ^{13}C NMR spectrum. It should be noted that this spin-spin through-space interaction does not lead to a rigid cyclic conformation of compounds **10a,b**: the $(CF_3)_2CH$ group have a possibility for rotation, otherwise the equivalence of all fluorine nuclei should be accounted for by the appropriate symmetry of the molecule.

The structure of compound **10a** in the crystal was solved by X-ray analysis (Figure 1).

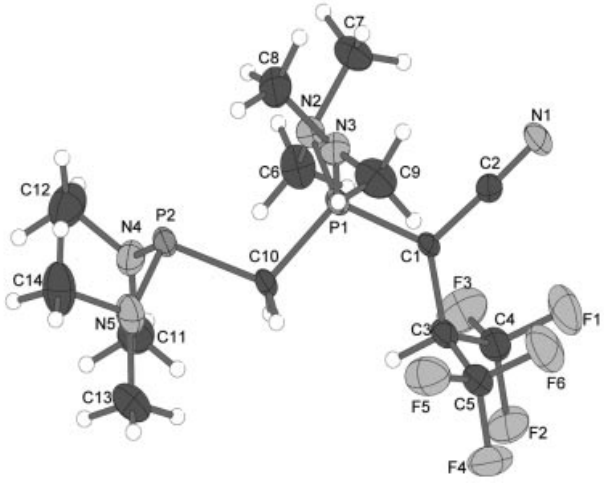


Figure 1. Perspective view and labeling scheme for the molecule **10a**; selected bond lengths [pm] and angles [°]: P(1)−C(1) 172.6(3), P(1)−C(10) 180.2(3), P(1)−N(2) 166.6(3), P(1)−N(3) 164.8(3), C(10)−P(2) 187.6(3), C(1)−C(2) 139.8(5), C(2)−N(1) 116.4(5), C(1)−C(3) 149.6(5); C(1)−P(1)−C(10) 109.07(16), P(1)−C(10)−P(2) 112.05(18), C(2)−C(1)−C(3) 121.3(3), C(2)−C(1)−P(1) 113.8(3), C(3)−C(1)−P(1) 124.9(2), N(1)−C(2)−C(1) 177.8(4); C(1)−P(1)−C(10)−P(2) −179.9(2), C(10)−P(1)−C(1)−C(2) −172.6(3), C(10)−P(1)−C(1)−C(3) 7.5(4)

In crystalline form the molecule of **10a** is rather symmetrical as the C(1), P(1), C(10), P(2) atoms are situated exactly in the same plane. The appropriate dihedral angle has a value of −179.9(2)°. The neighboring C(2) and C(3) atoms are only slightly deviated from this plane. For example, the C(10)−P(1)−C(1)−C(3) dihedral angle is 7.5(4)°. The two adjacent nitrogen atoms N(2) and N(3) have a slightly different configuration. The N(3) atom is almost flat, whereas the N(2) atom has a more pronounced tetrahedral geometry [the sums of angles are 357.3(8)° and 343.6(9), respectively]. In solution, however, both the dimethylamino groups are equivalent and display a common signal at δ = 2.49 ppm in the ^{1}H NMR spectrum.

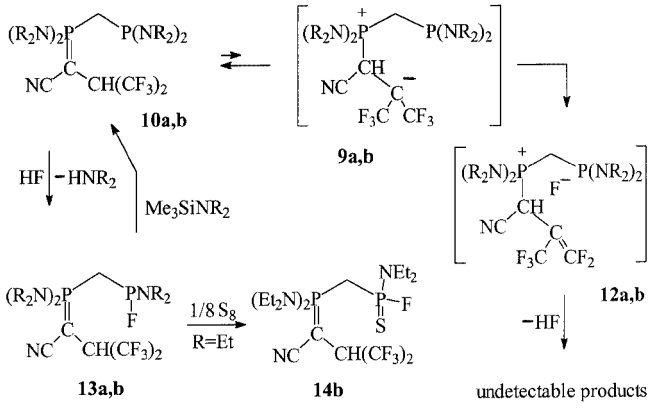
The ylidic carbon C(1) has an ideal flat conformation which is accounted for by the delocalization of the negative charge on the nitrile group; this is why the P(1)−C(1) bond (172.6 pm) is somewhat longer than the normal ylidic bond (168 pm),[19] whereas the C(1)−C(2) distance is considerably shorter (139.8 pm) than the average single C−C bond. These data are consistent with the structure of other nitrile-substituted phosphorus ylides.[20−22]

As is seen from the structure of **10a**, because of the large distance between P(1) and the fluorine atoms their spin-spin through-space interaction is hardly possible in the crystalline form. In solution, however, the molecule should have different conformations in which the bis(dimethylamino)-phosphane unit and the trifluoromethyl groups are close to each other due to rotation around the P(1)−C(10) and C(1)−C(3) bonds. This conclusion is also supported by the fact that the spin-spin through-space interaction in compounds **10a,b** disappears upon sulfuration of the phosphane center. All the fluorine atoms of the thio derivatives **11a,b** are equivalent and appear as one clear doublet in the ^{19}F NMR spectra at δ = −67 ppm ($^3J_{H,F}$ = 8 Hz).

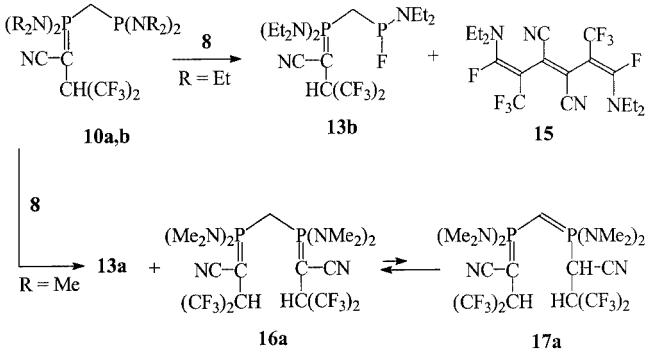
Compounds **10a,b** are rather stable in the crystalline form and in solution at −15 °C. At room temperature, however, they slowly decompose (over several days) into the monofluorides **13a,b** (Scheme 6). At 60 °C this process takes several hours. The stability of **10a,b** is probably determined by the presence of CF_3 groups in the α-position to the carbanion of the equilibrium forms **9a,b**. The elimination of the fluoride ion from the non-phosphorus analogs of **9a,b** can lead, in some cases, to stable products containing a perfluoroisopropenyl unit.[17] However, the elimination of F^- from **10a,b** probably goes via the unstable intermediates **12a,b**, which quickly decompose forming HF and a complex mixture of unidentified products. Thus, one half of the ylide molecules **10a,b** is formally used in their decomposition as a source of HF, which then reacts with the second half to give the monofluoro derivatives **13a,b**. Further transformation of **13a,b** into difluoro derivatives was not observed. The proposed mechanism was confirmed by the addition of HF (as $Et_3N{\cdot}3HF$) to compounds **10a,b**, giving the monofluorides **13a,b**. This result is consistent with the decomposition of carbodiphosphoranes **3a,b** and the formation of P−F bonds.[6]

The structure of compounds **13a,b** was confirmed by NMR spectroscopy and by their reaction with silylated amines, which led to the starting materials **10a,b**. One of the two phosphorus atoms in **13a,b** is asymmetric, which is why these compounds exist as a mixture of enantiomers. The diethylamino derivative **13b** was isolated as a crystalline product. Although the nucleophilicity of the phosphorus atom P^{III} in this compound is substantially reduced, it can be sulfurated with elemental sulfur to give **14b**. This process leads to the disappearance of the free rotation around one of the P−C bonds, hence **14b** was isolated as a mixture of diastereomers. Unlike starting compound **13b** the two trifluoromethyl groups in **14b** are inequivalent and appear as two quadruplets in the ^{19}F NMR spectrum. An interesting peculiarity of the sulfurated derivative is that the P−F fluorine is coupled with only one proton of the P−CH_2−P unit, the second coupling constant being equal or very close to zero. The presence of only one proton between two phosphorus is excluded as the chemical shift of the appropriate carbon atom in the ^{13}C NMR spectrum does not differ from that of compound **13b**.

The trivalent phosphorus of compounds **10a,b** is able to react further with **8**. However, the pathway of this reaction depends on the steric situation in compounds **10a,b**. The diethylamino derivative **10b** reacts slowly with **8** at room temperature and does not give the expected diylide but yields the monofluoro derivative **13b** as the main product (Scheme 7). According to the spectroscopic data the yield of monofluoride **13b** is about 70%, which is why its formation cannot be accounted for by the decomposition of the start-



Scheme 6



Scheme 7

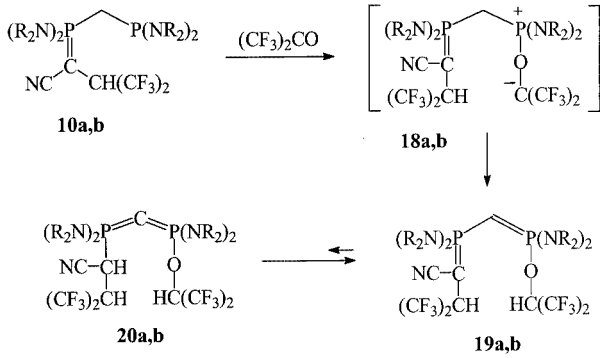
ing material. Bis(trifluoromethyl)acrylonitrile (**8**) acts as a fluorinating agent in this unusual reaction, transforming into the novel fluorinated triene **15**.[23] It is interesting to note that one of the trifluoromethyl groups of the acrylonitrile **8** looses two fluorine atoms and adds one of the diethylamino groups which was initially connected to one trivalent phosphorus atom of **10b**. Triene **15** was isolated as a slightly yellow crystalline product. The detailed structure of this compound was determined by X-ray analysis.[23]

The reaction of the less bulky dimethylamino derivative **10a** with **8** is much easier and gives a mixture of monofluoro derivative **13a** and the expected diylide **16a** in the ratio 35:65. The same result was obtained when two equivalents of **8** were added to the starting bis[bis(dialkylamino)phosphanyl]methane (**1a**). The formation of compound **13a** is not a result of decomposition of **16a**, as this ratio does not change after completion of the reaction. The mechanism of fluorination of **10a** by **8** does not, therefore, include the formation of **16a** as an intermediate product.

Diylide **16a** was isolated as a stable crystalline product, the structure of which was confirmed by NMR spectroscopy. Despite the fact that the $P-CH_2-P$ hydrogen atoms are situated between the two positively charged phosphorus atoms and are therefore rather acidic, the possible unsymmetrical structure **17a** was not detected. Thus, the equilibrium between **16a** and **17a** is completely shifted to the symmetrical form. The NMR spectroscopic data showed that the two phosphorus atoms and all their substituents are equivalent. The methylene group $P-CH_2-P$ appears as a triplet and the two ylidic carbon atoms as a characteristic doublet at $\delta = 12.0$ ppm ($^1J_{P,C} = 197$ Hz) in the ^1H and ^{13}C NMR spectra. Analogously to other symmetrical compounds containing central P−P or P−C−P fragments in which two phosphorus atoms are divided by a plane of symmetry, the diylide **16a** shows characteristic signals of an AA′XX′ spin system. The two tertiary carbon atoms of the $(CF_3)_2CH$ units are equivalent and appear as a clear septet of triplets in the ^{13}C NMR spectrum, each carbon having the same coupling constants with the two phosphorus atoms and vice versa. The two protons of the $(CF_3)_2CH$ groups show the same effect. However, because of the equality of the $^3J_{P,H}$ and $^3J_{H,F}$ coupling constants the spectrum appears as a multiplet of nine lines. Earlier we observed the analogous coupling for the same protons of carbodiphosphoranes **3a,b**.[5]

The presence of ylidic and trivalent phosphorus bridged by a methylene group makes compounds **10a,b** interesting synthons for further investigations. We were interested in the reaction of **10a,b** with hexafluoroacetone as it could answer the question as to whether the formation of carbodiphosphoranes described at the beginning of this paper is an exception or is more common.

We found that HFA reacts easily with ylides **10a,b** giving compounds **19a,b**, which were isolated as stable crystalline products, quantitatively (Scheme 8). The reaction proceeds via the intermediate zwitterionic structure **18a,b**, followed by proton migration from the $P-CH_2-P$ unit to the $(CF_3)_2C^-$ carbanion. As ylidic bonds are extremely polarized, the compounds **19a,b** can be considered as structures with alternating charges $P^+-C^--P^+-C^-$. Compounds **19a,b** should be in equilibrium with the carbodiphosphorane structures **20a,b**, although according to NMR spectroscopic data this equilibrium is shifted towards **19a,b**. For example, the $P-HC^--P$ proton appears in the ^1H NMR spectra as a doublet of doublets at high field ($\delta =$ 0.63 ppm). The two negatively charged ylidic carbon atoms are clearly seen in the ^{13}C NMR spectra at $\delta = 7.6$ and 15.6 ppm. The latter value, corresponding to the $C-CN$ carbon atom, is shifted slightly to low field compared with starting ylides **10a,b** which can be accounted for by the presence of the isomeric forms **20a,b**.



Scheme 8

Experimental Section

General Remarks: All operations were performed under nitrogen in a dry box. The solvents were dried by standard procedures. The NMR spectra were recorded with a JEOL FX-90Q and Varian 300 MHz spectrometers. The ^1H and ^{13}C chemical shifts are referenced to external tetramethylsilane (TMS). The ^{31}P chemical shifts are referenced to 85% aqueous orthophosphoric acid as an external standard. As usual, downfield shifts are given positive signs. The digital resolutions were 0.25, 0.5 Hz and 1.25 Hz for ^1H, ^{13}C and ^{31}P NMR spectra respectively.

Compound 10a: Bis(trifluoromethyl)acrylonitrile (**8**; 400 mg, 2.12 mmol) in 2 mL of diethyl ether was cooled to −15 °C and added to a solution of methylenebis(dimethylaminophosphane) (**1a**; 500 mg, 1.98 mmol) in 10 mL of hexane at the same temperature. The reaction mixture was maintained at −15 °C for 48 h. The colorless crystals of **10a** formed over this time were separated and recrystallized from chloroform/diethyl ether (1:2) at −15 °C, (681 mg, 78%), m.p. 72−74 °C. ^1H NMR ($CDCl_3$): $\delta = 2.13$ [d, $^2J_{P(1),H} = 13.5$, $^2J_{P(2),H} = 0$ Hz, 2 H, $P-CH_2-P$], 2.45 [d, $^3J_{P,H} =$ 10.0 Hz, 12 H, $N(CH_3)_2$], 2.49 [d, $^3J_{P,H} = 10.0$ Hz, 12 H, $N(CH_3)_2$], 3.34 [m, 1 H, $CH(CF_3)_2$] ppm. ^{13}C NMR ($CDCl_3$): $\delta = 10.78$ (dm, $J_{P,C} = 180.0$ Hz, 1 C, PCCN), 26.22 (dd, $^1J_{P,C} = 25.4$, $^1J_{P,C} =$ 85.8 Hz, PCP), 36.60 (d, $^2J_{P,C} = 2.9$ Hz, 2 C, NMe_2), 36.76 (d, $^2J_{P,C} = 3.9$ Hz, 2 C, NMe_2), 40.40 (d, $^2J_{P,C} = 15.6$ Hz, 4 C, NMe_2), 45.62 [sept. dd, $^2J_{P,C} = 16.6$, $J_{P,C} = 5.9$, $^2J_{F,C} = 29.3$ Hz, 1 C, $CH(CF_3)_2$], 124.20 (q, $^1J_{F,C} = 282.9$ Hz, 2 C, CF_3), 125.02 (d, $^2J_{P,C} = 10.8$ Hz, CN) ppm. ^{19}F NMR ($CDCl_3$): $\delta = -67.5$ (dd, $^3J_{H,F} = 8.3$, $J_{P,F} = 3.0$ Hz, 6 F) ppm. ^{31}P NMR ($CDCl_3$): $\delta =$ 66.94 (d, $^2J_{P,P} = 85.3$ Hz), 79.19 (sept. d, $^2J_{P,P} = 85.3$, $J_{F,P} =$

3.0 Hz) ppm. $C_{14}H_{27}F_6N_5P_2$ (441.34): calcd. C 38.10, H 6.17; found C 37.18, H 5.82.

Compound 10b: Bis(trifluoromethyl)acrylonitrile (**8**; 233 mg, 1.23 mmol) in hexane (3 mL) was cooled to −15 °C and added to a solution of methylenebis(diethylaminophosphane) (**1b**; 418 mg, 1.15 mmol) in hexane (5 mL) at the same temperature. The reaction mixture was maintained at −15 °C for 24 h. The colorless or light-yellow crystals of **10b** formed over this time were separated and washed with hexane (2 × 2 mL). Yield 496 mg (78%), 68−72% after crystallization from diethyl ether/hexane at −15 °C, m.p. 62−64 °C. ^{1}H NMR ($CDCl_3$): δ = 1.01 (t, $^3J_{H,H}$ = 7.07 Hz, 12 H, CH_2CH_3), 1.14 (t, $^3J_{H,H}$ = 7.07 Hz, 12 H, NCH_2CH_3), 2.27 [d, $^2J_{P(1),H}$ = 16.1, $^2J_{P(2),H}$ = 0 Hz, 2 H, P−CH_2−P], 3.09 (m, 16 H, N NCH_2CH_3), 3.44 [m, 1 H, $CH(CF_3)_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 13.13 (d, $^3J_{P,C}$ = 1.9 Hz, 4C, NCH_2CH_3), 13.17 (dm, $J_{P,C}$ = 214.6 Hz, 1C, $PCCN$), 13.5 (d, $^3J_{P,C}$ = 3.9 Hz, 4C, NCH_2CH_3), 28.09 (dd, $^1J_{P,C}$ = 21.5, $^1J_{P,C}$ = 80.0 Hz, PCP), 39.19 (d, $^2J_{P,C}$ = 3.9 Hz, 2C, NCH_2CH_3), 39.34 (d, $^2J_{P,C}$ = 2.9 Hz, 2C, NCH_2CH_3), 42.20 (d, $^2J_{P,C}$ = 16.6 Hz, 4C, NCH_2CH_3), 46.40 [sept. dd, $^2J_{P,C}$ = 17.8, $J_{P,C}$ = 9.0, $^2J_{F,C}$ = 29.3 Hz, 1C, $CH(CF_3)_2$], 124.12 (q, $^1J_{F,C}$ = 282.0 Hz, 2C, CF_3), 125.66 (d, $^2J_{P,C}$ = 9.9 Hz, CN) ppm. ^{19}F NMR ($CDCl_3$): δ = −66.93 (dd, $^3J_{H,F}$ = 7.8, $J_{P,F}$ = 2.9 Hz, 6F) ppm. ^{31}P NMR ($CDCl_3$): δ = 73.78 (d, $^2J_{P,P}$ = 102.4 Hz), 67.18 (sept. d, $^2J_{P,P}$ = 102.4, $J_{F,P}$ = 2.9 Hz) ppm. $C_{22}H_{43}F_6N_5P_2$ (553.56): calcd. C 47.74, H 7.83; found C 47.69, H 7.75.

Compounds 11a, 11b: Sulfur (16 mg) was added to a solution of **10a** or **10b** (0.4 mmol) in 2 mL of CH_2Cl_2 at 20 °C. After 2 h the solution was filtered, the solvent was evaporated and the residue was recrystallized from CH_2Cl_2/hexane (1:2) at −15 °C.

11a: Yield 142 mg (75%), m.p. 125−128 °C. ^{1}H NMR ($CDCl_3$): δ = 2.48 [d, $^3J_{P,H}$ = 12.6 Hz, 6 H, $N(CH_3)_2$], 2.63 [d, $^3J_{PH}$ = 10.3 Hz, 6 H, $N(CH_3)_2$], 2.83 (t, $^2J_{P(1),H}$ = $^2J_{P(2),H}$ = 15.8 Hz, 2 H, P−CH_2−P), 3.54 [m, 1 H, $CH(CF_3)_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 12.81 (dm, $J_{P,C}$ = 186.3 Hz, 1C, $PCCN$), 27.73 (dd, $^1J_{P,C}$ = 88.8, $^1J_{P,C}$ = 90.7 Hz, PCP), 36.56 (d, $^2J_{P,C}$ = 2.9 Hz, 4C, NMe_2), 37.23 (d, $^2J_{P,C}$ = 3.9 Hz, 4C, NMe_2), 46.27 [sept.d , $^2J_{P,C}$ = 14.6, $^2J_{F,C}$ = 29.3 Hz, 1C, $CH(CF_3)_2$], 124.20 [q, $^1J_{F,C}$ = 284.8 Hz, 2(CF_3)], 124.70 (d, $^2J_{P,C}$ = 13.7 Hz, CN) ppm. ^{19}F NMR ($CDCl_3$): δ = −66.95 (d, $^3J_{H,F}$ = 7.8 Hz, 6F) ppm. ^{31}P NMR ($CDCl_3$): δ = 61.46 ($^2J_{P,P}$ = 1.2 Hz), 72.12 ($^2J_{P,P}$ = 1.2 Hz) ppm. $C_{14}H_{27}F_6N_5P_2S$ (473.40): calcd. C 35.52, H 5.75; found C 35.14, H 5.35.

11b: Yield 176 mg (75%), m.p. 106−109 °C. ^{1}H NMR ($CDCl_3$): δ = 1.11 (t, $^3J_{H,H}$ = 7.03 Hz, 12 H, NCH_2CH_3), 1.16 (t, $^3J_{H,H}$ = 7.03 Hz, 12 H, NCH_2CH_3), 2.7−3.2 (m, 2 H, P−CH_2−P, 16 H, NCH_2CH_3), 3.09 (m, 16 H, NCH_2CH_3), 3.45 [m, 1 H, $CH(CF_3)_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 13.43 (d, $^3J_{P,C}$ = 3.9 Hz, 4C, NCH_2CH_3), 13.67 (d, $^3J_{P,C}$ = 2.9 Hz, 4C, NCH_2CH_3), 13.87 (dm, $J_{P,C}$ = 195.05 Hz, 1C, $PCCN$), 27.74 (dd, $^1J_{P,C}$ = 28.8, $^1J_{P,C}$ = 90.7 Hz, PCP), 39.51 (d, $^2J_{P,C}$ = 2.9 Hz, 4C, NCH_2CH_3), 40.07 (d, $^2J_{P,C}$ = 4.9 Hz, 4C, NCH_2CH_3), 46.27 [sept. d, $^2J_{P,C}$ = 14.6 Hz, $^2J_{F,C}$ = 29.3 Hz, 1C, $CH(CF_3)_2$], 124.23 [q, $^1J_{F,C}$ = 284.8 Hz, 2(CF_3)], 124.70 (d, $^2J_{P,C}$ = 13.7 Hz, CN) ppm. ^{19}F NMR ($CDCl_3$): δ = −66.70 (d, $^3J_{H,F}$ = 8.0 Hz, 6F) ppm. ^{31}P NMR ($CDCl_3$): δ = 63.71 (d, $^2J_{P,P}$ = 7.3 Hz), 69.77 (d, $^2J_{P,P}$ = 7.3 Hz) ppm. $C_{22}H_{43}F_6N_5P_2S$ (585.62): calcd. C 45.12, H 7.40, N 11.96; found C 44.89, H 6.96, N 11.23.

Compound 13b: Compound **8** (170 mg, 0.90 mmol) was added to a solution of **10b** (400 mg, 0.72 mmol) in toluene (2 mL) and the reaction mixture was left at room temperature for 7 days. If the ^{31}P NMR spectrum showed the residual starting material **10b** the reaction mixture was heated at 70 °C for about 15 min. (NB The reaction can be carried out at elevated temperature, although the yield is then lower.) The solvent was removed in vacuo and the remaining thick dark-brown oil was thoroughly washed with cold hexane (2 × 1 mL) at −15 °C. The product was then extracted with boiling hexane (5 × 3 mL) and the obtained solution was left overnight at −15 °C. Light yellow crystalline product, yield 184 mg (51%), after re-crystallization from hexane 137 mg (38%). M.p. 90−91 °C. ^{1}H NMR ($CDCl_3$): δ = 1.14 (t, $^3J_{H,H}$ = 7.03 Hz, 6 H, NCH_2CH_3), 1.16 (t, $^3J_{H,H}$ = 7.03 Hz, 12 H, NCH_2CH_3), 2.3−2.7 (m, 2 H, P−CH_2−P), 2.9−3.4 [m, 12 H, NCH_2CH_3, 1 H, $CH(CF_3)_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 12.68 (dm, $J_{P,C}$ = 238.9 Hz, 1C, $PCCN$), 13.48 (m, 4C, NCH_2CH_3), 15.13 (m, 2C, NCH_2CH_3), 34.26 (ddd, $^1J_{P,C}$ = 19.5, $^1J_{P,C}$ = 87.8, $^2J_{F,C}$ = 48.8 Hz, PCP), 39.36 (m, 4C, NCH_2CH_3), 42.89 (d, $^3J_{F,C}$ = 18.5 Hz, 2C, NCH_2CH_3), 47.44 [m, 1C, $CH(CF_3)_2$], 124.16 [q, $^1J_{F,C}$ = 281.8 Hz, 2(CF_3)], 124.90 (d, $^2J_{P,C}$ = 12.6 Hz, CN) ppm. ^{19}F NMR ($CDCl_3$): δ = −67.04 (dd, $^3J_{H,F}$ = 7.8, $^3J_{P,F}$ = 3.6 Hz, 6F), −106 (d, $^1J_{P,F}$ = 958 Hz, 1F) ppm. ^{31}P NMR ($CDCl_3$): δ = 62.23 (dd, $^2J_{P,P}$ = 68.2, $^3J_{P,F}$ = 17.1 Hz,), 155.05 (dd, $^2J_{P,P}$ = 68.2, $^1J_{F,P}$ = 958 Hz) ppm. $C_{18}H_{33}F_7N_4P_2$ (500.42): calcd. C 43.20, H 6.64, N 11.20; found C 44.39, H 6.98, N 12.20.

Compound 14b: Sulfur (10 mg) was added to a solution of **13b** (100 mg, 0.2 mmol) in $CHCl_3$ (1 mL) and the mixture was heated at 60 °C for 3.5 h. The solvent was removed in vacuo and the residue was extracted with diethyl ether (1.5 mL) at −10 °C in order to separate the product from the remaining sulfur. Evaporation of diethyl ether in vacuo yielded 77 mg (72%) of **14b**. M.p. 51−53 °C. ^{1}H NMR ($CDCl_3$): δ = 1.17 (t, $^3J_{H,H}$ = 7.03 Hz, 6 H, NCH_2CH_3), 1.20 (t, $^3J_{H,H}$ = 7.03 Hz, 12 H, NCH_2CH_3), 2.8−3.5 [m, 2 H, P−CH_2−P, 12 H, NCH_2CH_3, 1 H, $CH(CF_3)_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 13.05 (dm, $J_{P,C}$ = 195.03 Hz, 1C, $PCCN$), 13.39 (m, 4C, NCH_2CH_3), 14.17 (m, 2C, NCH_2CH_3), 33.87 (ddd, $^1J_{P,C}$ = 34.1, $^1J_{P,C}$ = 95.6, $^2J_{F,C}$ = 85.8 Hz, PCP), 39.77 (d, 2C, $^2J_{P,C}$ = 4.9 Hz, NCH_2CH_3), 39.99 (d, 2C, $^2J_{P,C}$ = 4.9 Hz, NCH_2CH_3), 40.53 (dd, $^2J_{P,C}$ = 3.9, $^3J_{F,C}$ = 1.9 Hz, 2C, NCH_2CH_3), 47.10 [m, 1C, $CH(CF_3)_2$], 124.33 [q, $^1J_{C,F}$ = 283.8 Hz, 2(CF_3)], 124.52 (d, $^2J_{P,C}$ = 13.7 Hz, CN) ppm. ^{19}F NMR ($CDCl_3$): δ = −66.52 (q, $^4J_{FF}$ = 8.5 Hz, 3F), −67.04 (q, $^4J_{FF}$ = 8.5 Hz, 3F), −41.80 (dd, $^1J_{P,F}$ = 1063, $^2J_{H,F}$ = 9.8 Hz) ppm. ^{31}P NMR ($CDCl_3$): δ = 59.75 (d, $^2J_{P,P}$ = 4.9 Hz), 84.90 (dd, $^2J_{P,P}$ = 4.9, $^1J_{F,P}$ = 1060.7 Hz) ppm. $C_{18}H_{33}F_7N_4P_2S$ (532.48): calcd. C 40.60, H 6.24, S 6.02; found C 39.86, H 6.21, S 6.24.

Compound 16a: Compound **8** (200 mg, 1.06 mmol) was added to a solution of **10a** (360 mg, 0.82 mmol) in dichloromethane (4 mL) and the reaction mixture was maintained at 20 °C for 16 h. The solvent was then removed in vacuo and compound **13a** was extracted from the residue with diethyl ether (2 × 2.5 mL). The remaining product was dried in vacuo, dissolved in the minimum amount of dichloromethane, diluted with diethyl ether until the solution became turbid and the solution was left at −15 °C. After 2 days colorless crystals of **16a** were separated and dried in vacuo (280 mg, 54%), m.p. 185−186 °C. ^{1}H NMR ($CDCl_3$): δ = 2.66 [m, 2 H, $CH(CF_3)_2$], 2.77 (d, $^3J_{PH}$ = 10.0 Hz, 24 H, NCH_3), 3.18 (t, $^2J_{PH}$ = 16.1 Hz, 2 H, P−CH_2−P) ppm. ^{13}C NMR (CD_3COCD_3): δ = 12.00 (dm, $J_{P,C}$ = 196.8 Hz, 2C, $PCCN$), 26.4 (t, $J_{P,C}$ = 93.0 Hz, PCP), 36.75 (s, 8C, NCH_3), 47.03 [sept. t, $^2J_{P,C}$ = 29.3, $J_{P,C}$ = 6.8 Hz, $CH(CF_3)_2$], 123.0 (t, $^2J_{P,C}$ = 7.1 Hz, 2 C, CN), 124.8 [q, $^1J_{F,C}$ = 279.8 Hz, 2(CF_3)] ppm. ^{19}F NMR ($CDCl_3$): δ = −67.1 (d, $^3J_{H,F}$ = 7.8 Hz, 6F) ppm. ^{31}P NMR ($CDCl_3$): δ = 59.9 (s, 2P) ppm. $C_{19}H_{28}F_{12}N_6P_2$ (630.39): calcd. C 36.20, H 4.48; found C 35.81, H 4.12.

Compounds 19a, 19b: A solution of **10a** or **10b** (0.2 mmol) in toluene (1.5 mL) was placed in a 10 mL flask. The flask was then evacuated slightly and gaseous hexafluoroacetone (4.8 mL, 0.21 mmol) was introduced with a syringe. The mixture was left for 24 h at room temperature, then the solvent was removed in vacuo. The remaining oil was dissolved in minimum amount of diethyl ether (about 2 mL), diluted with hexane and left for two days at −15 °C. Colorless crystals were separated and dried in vacuo.

19a: Yield 80 mg (66%), m.p. 88−90 °C. ^{1}H NMR ($CDCl_3$): δ = 0.64 (dd, $^2J_{P,H}$ = 5.6, $^2J_{P,H}$ = 8.1 Hz, 1 H, P−C*H*−P), 2.56 [d, $^3J_{P,H}$ = 10.0 Hz, 12 H, N(CH_3)$_2$], 2.63 [d, $^3J_{P,H}$ = 10.0 Hz, 12 H, N(CH_3)$_2$], 2.95 [sept. d, $^3J_{H,F}$ = 8.5, $^3J_{PH}$ = 8.5 Hz, 1 H, C*H*(CF$_3$)$_2$], 5.08 [sept. d, $^3J_{H,F}$ = 5.8, $^3J_{P,H}$ = 11.9 Hz, 1 H, C*H*(CF$_3$)$_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 7.67 (dd, $^1J_{P,C}$ = 168.7, $^1J_{P,C}$ = 205.8 Hz, P*C*P), 15.86 (dm, $J_{P,C}$ = 136.5 Hz, 1C, P*C*CN), 36.97 (d, $^2J_{P,C}$ = 3.9 Hz, 4C, NMe$_2$), 37.17 (d, $^2J_{P,C}$ = 4.9 Hz, 4C, NMe$_2$), 48.20 [sept. d, $^2J_{P,C}$ = 12.7, $^2J_{F,C}$ = 29.3 Hz, 1C, *C*H(CF$_3$)$_2$], 70.11 [sept. d, $^2J_{P,C}$ = 2.9, $^2J_{F,C}$ = 34.1 Hz, 1C, *C*H(CF$_3$)$_2$], 120.20 (q, $^1J_{F,C}$ = 285.7 Hz, 2C, CF$_3$), 124.68 (q, $^1J_{F,C}$ = 279.9 Hz, 2C, CF$_3$), 127.63 (d, $^2J_{P,C}$ = 14.7 Hz, CN) ppm. ^{19}F NMR ($CDCl_3$): δ = −67.29 (d, $^3J_{H,F}$ = 8.5 Hz, 6F), −73.15 (d, $^2J_{H,F}$ = 5.8 Hz, 6F) ppm. ^{31}P NMR ($CDCl_3$): δ = 60.65 ($^2J_{P,P}$ = 39.0 Hz), 63.81 ($^2J_{P,P}$ = 39.0 Hz) ppm. $C_{17}H_{27}F_{12}N_5OP_2$ (607.36): calcd. C 33.61, H 4.48, N 11.53; found C 33.24, H 4.31, N 11.80.

19b: Yield 139 mg (97%), m.p. 79−82 °C. ^{1}H NMR ($CDCl_3$): δ = 0.67 (dd, $^2J_{P,H}$ = 9.7, $^2J_{P,H}$ = 12.3 Hz, 1 H, P−C*H*−P), 1.10 (t, $^3J_{H,H}$ = 7.1 Hz, 24 H, CH_2CH_3), 2.8−3.5 [m, 16 H, CH_2CH_3, 1 H, C*H*(CF$_3$)$_2$], 5.36 [sept, $^3J_{H,F}$ = 5.9 Hz, 1 H, C*H*(CF$_3$)$_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 12.2 (dd, $^1J_{P,C}$ = 173, $^1J_{P,C}$ = 199 Hz, P*C*P), 13.1 (d, $^3J_{P,C}$ = 2.9 Hz, 4 C, NCH$_2$*C*H$_3$), 13.8 (d, $^3J_{P,C}$ = 1.9 Hz, 4 C, NCH$_2$*C*H$_3$), 38.8 (d, $^2J_{P,C}$ = 4.9 Hz, 4 C, N*C*H$_2$CH$_3$), 40.4 (d, $^2J_{P,C}$ = 4.9 Hz, 4 C, N*C*H$_2$CH$_3$), 48.7 [sept. d, $^2J_{P,C}$ = 12.7, $^2J_{F,C}$ = 28.3 Hz, 1 C, *C*H(CF$_3$)$_2$], 70.4 [sept. d, $^2J_{P,C}$ = 2, $^2J_{F,C}$ = 37 Hz, 1C, *C*H(CF$_3$)$_2$], 121.0 (q, $^1J_{F,C}$ = 279 Hz, 2C, CF$_3$), 124.7 (q, $^1J_{F,C}$ = 285 Hz, 2C, CF$_3$), 128.1 (d, $^2J_{P,C}$ = 14.7 Hz, CN) ppm. ^{19}F NMR ($CDCl_3$): δ = −66.5 (d, $^3J_{H,F}$ = 8.3 Hz, 6 F), −72.6 (d, $^3J_{H,F}$ = 5.8 Hz, 6 F) ppm. ^{31}P NMR ($CDCl_3$): δ = 61.9 (d, $^2J_{P,P}$ = 41 Hz), 64.2 (d, $^2J_{P,P}$ = 41 Hz) ppm. $C_{25}H_{43}F_{12}N_5OP_2$ (719.58): C 41.73, H 6.02, N 9.73; found C 40.89, H 6.56, N 10.23.

X-ray Crystallographic Study: The single-crystal X-ray structure determination was performed at 173(2) K on a Siemens P4 diffractometer using graphite monochromated Mo-K_α radiation (λ = 71.073 pm) and a low temperature LT2 device. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program suite.[24] Crystal data for **10b** ($C_{14}H_{27}F_6N_5P_2$): M_w = 441.35, monoclinic, space group $P2_1/c$, a = 1195.0(2), b = 1348.9(2), c = 1397.7(4) pm, β = 110.400(10)°, V = 2.1117(8) nm^3, Z = 4, D_c = 1.388 Mg/m^3, μ = 0.266 mm^{-1}; 6078 reflections collected, 256 parameters refined using 4850 unique reflections (R_{int} = 0.0463) to final indices $R1$ [$I > 2\sigma(I)$] = 0.0651 and wR_2 (all data) = 0.1652 [$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2 + P]$ where $P = (2F_c^2 + F_o^2)/3$. All non-hydrogen atoms were refined anisotropically and the position of the hydrogen atoms was calculated as a riding model. The final residual Fourier positive and negative peaks were equal to 0.401 and −0.480 e Å^{-3}.

CCDC-164430 contains the supplementary crystallographic data (for **10a**). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[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; pp. 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, *Chem. Commun.* **1998**, 1203−1204.
[6] I. V. Shevchenko, R. Mikolenko, S. Loss, H. Grützmacher, *Eur. J. Inorg. Chem.* **1999**, 1665−1671.
[7] I. Yavari, M. R. Islami, H. R. Bijanzadeh, *Tetrahedron* **1999**, *55*, 5547−5554.
[8] I. Yavari, M. T. Maghsoodlou, *Tetrahedron Lett.* **1998**, 4579−4580.
[9] I. Yavari, N. N. Arasi, H. R. Bijanzadeh, *J. Fluor. Chem.* **2000**, *103*, 155−157.
[10] Y. G. Gololobov, V. A. Pinchuk, H. Thönnessen, P. G. Jones, R. Schmutzler, *Phosphorus, Sulfur and Silicon* **1996**, *115*, 19−37.
[11] R. F. Stockel, F. Megson, H. T. Beachem, *J. Org. Chem.* **1968**, *33*, 4395−4397.
[12] M. A. Howells, R. D. Howells, N. C. Baenziger, D. J. Burton, *J. Am. Chem. Soc.* **1973**, *95*, 5366−5370.
[13] I. T. Hennawy, *Collect. Czech. Chem. Commun.* **1994**, *59*, 2109−2115.
[14] P. J. Goldman, *Biol. Chem.* **1973**, *93*, 5366−5370.
[15] D. Peters, R. Miethchen, "Loss of Fluorine To Form C=C Bonds", in Houben-Weyl, *Organo-Fluorine Compounds* (Eds.: B. Baasner, H. Hagemann, J. C. Tatlov), Georg Thieme Verlag, Stuttgart, New York, 2000, vol. E10b, Part 2; pp. 345−381.
[16] W. H. Gumprecht, "Hydrolysis of Trifluoromethyl Groups", in *Chemistry of Organic Fluorine Compounds II; A Critical Review* (Ed.: M. Hudlický and A. E. Pavlath), ACS Monograph 187; American Chemical Society: Washington DC, **1995**, pp. 433−436.
[17] V. Martin, H. Molines, C. Wakselman, *J. Org. Chem.* **1992**, *57*, 5530−5532.
[18] M. A. Show, J. C. Tebby, R. S. Ward, D. H. Williams, *J. Chem. Soc. (C)* **1970**, 504−507.
[19] O. I. Kolodiazhnyi, in *Phosphorus Ylides*, Wiley-VCH; Weinheim, New York, Chichester, Brisbane, Singapore, Toronto, **1999**.
[20] I. Kawamoto, T. Hata, Y. Kishida, C. Tamura, *Tetrahedron Lett.* **1971**, 2417.
[21] H. J. Hecht, G. Ruban, *Cryst. Struct. Commun.* **1981**, 495.
[22] H. Grützmacher, H. Pritzkow, *Chem. Ber.* **1989**, 1411−1416.
[23] I. Shevchenko, V. Andrushko, E. Lork, G.-V. Röschenthaler, *Eur. J. Inorg. Chem.*, submitted.
[24] SHELX-97, G. M. Sheldrick, University of Göttingen, 1997.

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