Journal of Organometallic Chemistry 695 (2010) 974–980

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

A fluoroaryl substituent with spectator function: Reactivity and structures of cyclic and acyclic HF_4C_6-substituted phosphanes

Andreas Orthaber, Ferdinand Belaj, Rudolf Pietschnig *

Karl-Franzens-Universität, Institut für Chemie, Schubertstraße 1, A-8010 Graz, Austria

ARTICLE INFO

Article history:
Received 25 September 2009
Received in revised form 21 October 2009
Accepted 22 October 2009
Available online 27 October 2009

Keywords:
Organo fluorine compounds
Phosphorus
Diphosphene
Inorganic rings
Ab initio calculations

ABSTRACT

The reactivity of a series of phosphanes with a fluoroaryl group (HF_4C_6-) carrying a spectator function in para position has been explored with respect to the formation of low coordinated and phosphorus rich phosphanes. An asymmetric diphosphene has been indentified as an intermediate in the synthesis of a linear 1,3-dihydrophosphane, while the symmetric diphosphene undergoes 2 + 2 cycloaddition under formation of the corresponding cyclotetraphosphetane for which a crystal structure could be obtained. Attempts to synthesize HF_4C_6-substituted iminophosphanes generally failed, which is attributed to the electronic nature of the corresponding precursors as suggested by quantum chemical calculations.

1. Introduction

Phosphorus containing compounds with electron withdrawing moieties attracted considerable attention in the last decade [1,2]. Electron deficient groups are known to influence both electronic and optical properties of phosphorus containing compounds [3–7]. Pentafluorophenyl and trifluoro methyl substituted phenyl groups are the most frequently used substituents in the synthesis of fluorinated phosphorus containing materials and complexes [8–10]. Very recently perfluorinated phosphanoboranes have been in the focus of interest for the synthesis of "frustrated" Lewis acid/base pairs looking at applications as e.g. hydrogen storage or activation [11,12]. Tuning of different phosphorus based ligands has been studied with respect to hydroformylation reactions [13]. Electron deficient units are essential for the synthesis of molecular n-type conducting materials and different attempts have been made to incorporate C_6F_5 groups into the backbone of phosphorus derived oligomers and polymers [1]. Diphosphenes bearing electron withdrawing groups are known to have reduced reactivity [14]. The steric situation alone cannot explain this behavior, because the size of CF_3 is comparable to that of the isoelectronic *t*-butyl group. Consequently, electronic deactivation of the P=P group is likely to be the crucial factor. Recently, we and others observed the formation of P-rich compounds from diphosphenes [15–17]. Phosphorus rich compounds are of growing interest as stable activated products of white phosphorus [18,19]. In the underlying study we explore the influence of a fluorinated aryl group with an additional spectator function on the electronic activation or deactivation of low coordinated phosphanes and their conversion to linear and cyclic phosphanes.

2. Results and discussion

Pentafluorophenyl groups are well established as electron withdrawing groups in chemistry [10,20]. We have chosen the tetra fluorophenyl group (2,3,5,6-F_4C_6H-), which carries a hydrogen atom in *para* position providing the possibility to follow reactions easily by ^1H spectroscopy. In addition, 2D ^1H–^{13}C coupled spectra give the opportunity to detect the aromatic carbon atoms more conveniently. We were able to synthesize the diethylaminophosphane (**1**) in good overall yields starting from the corresponding lithiated fluoroaryl compound. Lithiation is carried out strictly below −80 °C and the lithium compound is used without further purification. During the addition of the chlorophosphane the temperature is not allowed to rise above −60 °C. This procedure is beneficial over literature procedures, where R^F–MgBr is reacted with Cl–$P(NEt_2)_2$, owing to the strikingly lower costs of the starting materials R^F–H compared with R^F–Br. The synthesis of the dichlorophosphane **3** (R^F–PCl_2) must by accomplished by the use of diethylamino groups as protecting groups to prevent multiple substitution at the phosphorus atom. This is in contrast to the synthesis of $MesPCl_2$ where multiple substitution hardly occurs. The diethylaminophosphane derivative **1** is obtained as viscous oil in spectroscopically pure form after distillation. It shows a broad singlet in the phosphorus NMR spectra at 84.9 ppm and neither cou-

* Corresponding author. Tel.: +43 316 380 5285; fax: +43 316 380 9835.
E-mail address: rudolf.pietschnig@uni-graz.at (R. Pietschnig).

0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2009.10.025

pling to the fluorine nor to the hydrogen atoms could be resolved. Also the ^{19}F NMR spectra show only a single multiplet at −141.6 ppm. Furthermore ^{13}C NMR data and MS data are in agreement with the proposed structure of **1**. In order to explore the reactivity of this compound we oxidized **1** with an excess of gray selenium to the corresponding selenophosphorane **2** which proceeds in almost quantitative yields after 12 h. The constitution of compound **2** was determined by X-ray crystallography revealing an almost planar central phenyl ring which is nearly coplanar with one of the P–N bonds (angle between ring plane and P1–N2 0.49(5)°) (Fig. 1). The P═Se bond is 2.1074(3) Å, which is in the normal range for this class of compounds and encloses an angle with the least-squares (l.s.) plane of the phenyl ring of 60.77(4)°. The phosphorus atom is slightly shifted out of the l.s. plane of the phenyl ring by an angle of 7.14(5)° resulting in a slight elongation of the P–C bond. Owing to this unsymmetrical orientation of the –P(═Se)N_2-fragment (with respect to the phenyl ring) quite different bond angles [N1–P1–C1 103.37(5)°, N2–P1–C1 111.25(5)°, N1–P1–Se1 117.84(4)°, N2–P1–Se1 110.57(4)°] are observed. On the other hand the observed P–N distances are all almost equal [P1–N1 1.647(1) Å, P1–N2 1.648(1) Å]. In the crystal structure the tetrafluorophenyl rings of two molecules related by an inversion center are packed with a distance of 3.310(8) Å between their ring l.s. planes showing weak π−π interaction.

The amino groups can be replaced by halogen atoms with either PX_3 or anhydrous HX. For the scrambling reaction with PCl_3 the boiling point of the resulting product is only marginally different from that of the second product $(Et_2N)PCl_2$. Therefore, it is preferable to cleave the protecting groups with HCl. Additionally we observed the formation of the mixed species $R^FPClNEt_2$ (**3**) under distillation conditions if $(Et_2N)PCl_2$ was present. This might be reasoned by reverse scrambling reactions at higher temperatures. Compound **3** is obtained in pure form from the distillation residue as high viscous oil with a ^{31}P NMR resonance at 112.7 ppm. Furthermore the cleavage of the diethylamino groups by anhydrous HCl proceeds rather slowly compared to other analogous reactions. The formed ammonium salt can be easily removed by filtration and the product $HC_6F_4PCl_2$ (**4**) is collected by distillation under reduced pressure.

The reductive coupling of **4** with elemental magnesium resulted in the formation of cyclotetraphosphetane **5** (Scheme 1). A potential symmetric diphosphene is expected to be unstable because the steric bulk of the fluorinated aryl moiety is comparable to that of $MesPCl_2$ and thus 2 + 2 cycloaddition of the intermediate diphosphene may take place. Ring sizes other than four have not been observed in this reaction. The crystal structure analysis of **5** proves the identity of tetrakis-(2,3,5,6-tetrafluorophenyl)tetraphosphetane, whose molecular structure is depicted in Fig. 2. The molecules are lying around two-fold rotation axes and have almost *mm2* symmetry (C_{2v}). The P–P and P–C distances are not significantly different for each ring position despite the different orientations of the phenyl rings: whereas the two phenyl rings at P2 and P2′ are almost co-planar with a torsion angle P2′···P2–C21–C22 of 2.9(4)°, the two phenyl rings at P1 and P1′ have a torsion angle P1′···P1–C11–C12 of 96.0(3)°. These structural parameters are in good agreement with the published structure of the pentafluorophenyl substituted cyclotetraphosphetane [21]. The packing of the molecules shows remarkable tubular voids of ca. 3.8 Å in diameter parallel to the *a*-axis confined by the F atoms F13, F23 and F26.

In order to stabilize a potential diphosphene moiety we coupled Mes^*PH_2 (Mes^* = 2,4,6-tris-^{t}butyl phenyl) with **4** which resulted in the formation of the desired diphosphene (**6**) based on the ^{31}P NMR spectra (Fig. 3). Unfortunately the steric demand and the electronic situation do not allow to stabilize the P═P moiety sufficiently and **6** undergoes subsequent diphosphene metathesis under formation of the symmetric $Mes^*P{=}PMes^*$ and tetraphosphetane **5**. Besides unreacted Mes^*PH_2 and the symmetric diphosphene $Mes^*P{=}PMes^*$ further products are also formed during this reaction. Attempts to elucidate their structure by means of ^{31}P–^{31}P-correlated spectroscopy showed the presence of R′PH–P(R′)–PHR for R = C_6F_4H and R′ = Mes^* (**7**) (Fig. 4). Triphosphane **7** shows three ^{31}P NMR signals at P_A −49.5 ppm, P_B −55.1 ppm and P_C −75.8 ppm with a characteristic coupling pattern. Formation of **7** can be reasonably explained by addition of unreacted Mes^*-PH_2 to the diphosphene **6**, which is formed as an intermediate. Such a P–H addition to a diphosphene was recently also observed for ferrocenyl mono- and bisdiphosphenes [16,17].

Interestingly, cyclotetraphosphetane **5** is also obtained by reduction with other phosphanes. The "Phospha-Wittig" route to phosphaalkenes as established by Protasiewicz and coworkers involves the reaction of dichlorophosphanes with PMe_3 in the presence of Zn dust and aldehydes [22]. Reaction of **4** with PMe_3 in the presence of ferrocenyl aldehyde gave only the cyclotetrapho-

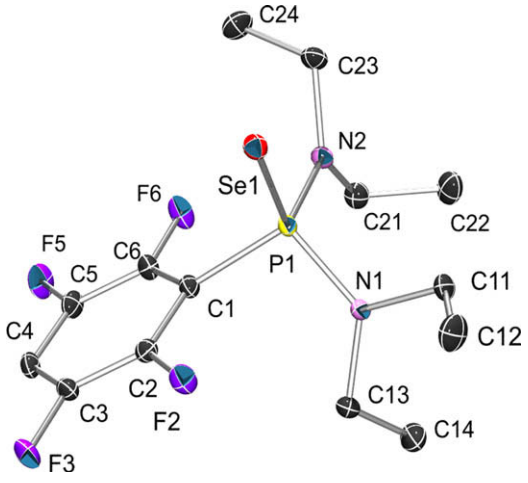


Fig. 1. Molecular structure of **2**. Ortep plot at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths, distances [Å] and angles [°]: Se1–P1 2.1073(3), P1–N1 1.647(1), P1–N2 1.648(1), P1–C1 1.845(1), N1–P1–N2 106.0(1), N1–P1–C1 103.4(1), N2–P1–C1 111.3(1), N1–P1–Se1 117.84(4), N2–P1–Se1 110.57(4), C1–P1–Se1 107.66(4), N1–P1–C1–C6 −121.0(1), N2–P1–C1–C6–7.7(1), Se1–P1–C1–C6 113.58(1).

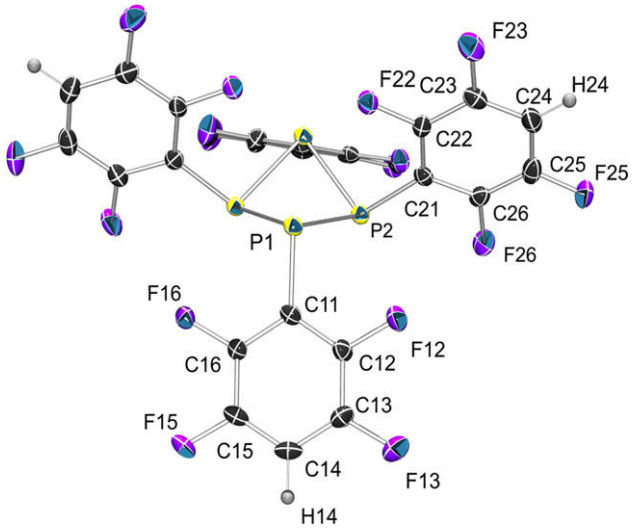
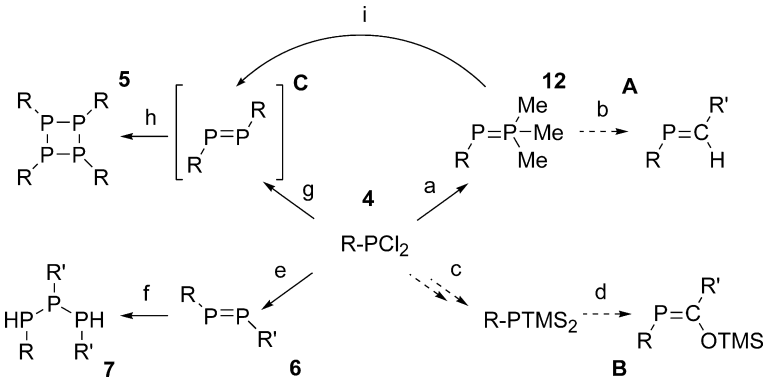


Fig. 2. Molecular structure of **5**. Ortep plot at 50% probability level. Selected bond lengths, distances [Å] and angles [°]: P1–P2 2.237(1), P1–P2′ 2.238(1), 1.833(3), P2–C2 1 1.829(3), P2–P1–P2′ 79.87(5), P1–P2–P1′ 83.34(5), P2′–P1–P2–P1′ 41.82(5).



Scheme 1. Synthetic routes to phosphaalkenes and diphosphenes including follow up reactions. (a) PMe_3; (b) Zn, R′-CHO (c) (1) LAH; (2) *n*-BuLi; (3) TMS-Cl; (d) R′-COCl (*Becker* route); (e) (1) R-PHLi; (2) DBU; (f) +R′PH_2; (g) Mg; (h) [2 + 2]-cycloaddition; (i) + R-PCl_2 (**4**).

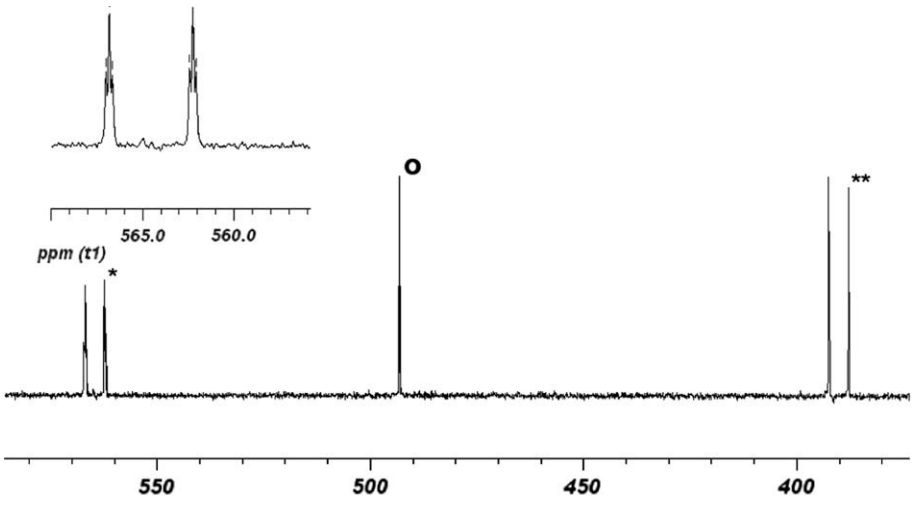


Fig. 3. ^{31}P NMR of the low field region of the diphosphene **6** (*Ar^{F}-*P*; **2,4,6-^{t}Bu–C_6H_2–*P*). Formation of the symmetric diphosphene Mes*-P=P-Mes* (○) is already observed.

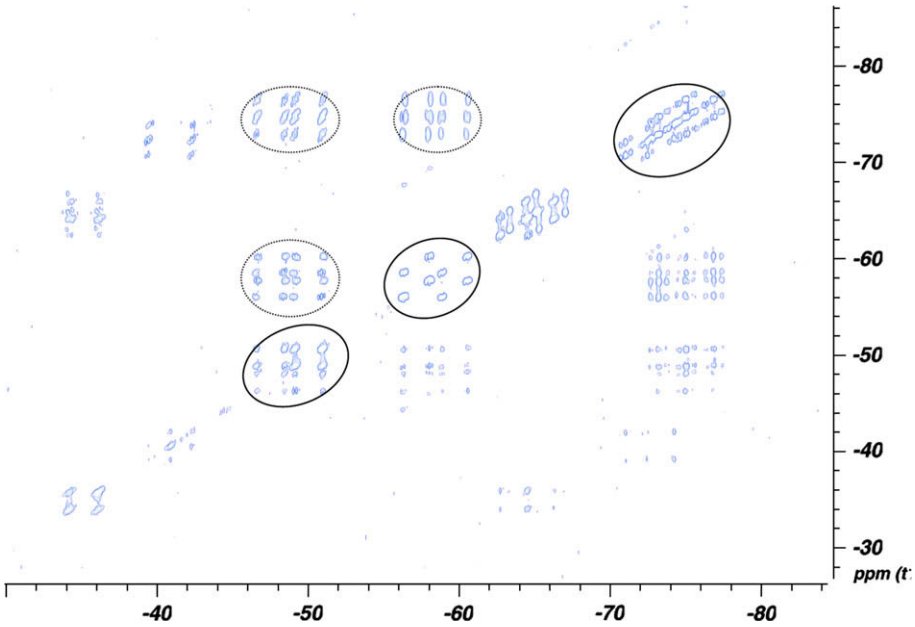


Fig. 4. ^{31}P NMR of the high field region of the PP-COSY spectrum showing the triphosphane **7**, besides other unidentified side products. Dotted circles indicate the corresponding cross peaks.

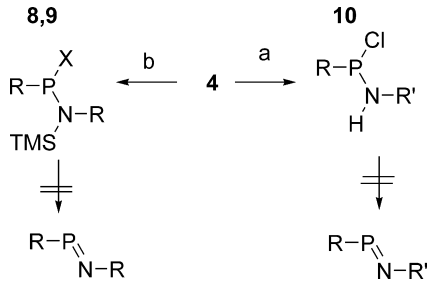
sphetane and unreacted aldehyde but not the intended phosphaalkene. The electron withdrawing fluoroaryl substituent may lead to an increased electrophilicity at phosphorus which could favor the competing reaction of **4** with the corresponding "Phospha-Wittig" reagent **(12)** once it is formed. The resulting products are then the kinetically unstable symmetric diphosphene $(HF_4C_6)_2P_2$ which may undergo 2 + 2 cycloaddition to **5** and PMe_3Cl_2. In our studies we were able to form the "Phospha-Wittig" reagent already in the absence of Zn dust. Compound **12** could be detected by ^{31}P spectroscopy from the crude reaction mixture (28.2 ppm, d, $^1J_{PP}$ 403 Hz and −55.8 ppm, d, $^1J_{PP}$ 403 Hz). In this mixture tetraphosphetane **5** and PMe_3Cl_2 are the only observed products after 1 day.

Formal replacement of one phosphorus atom in diphosphenes by nitrogen leads to the class of iminophosphanes. The synthetic strategy towards iminophosphanes usually involves the elimination of LiCl in the first step forming an aminophosphane [23]. If a lithium amide of a primary amine is used (route a, Scheme 2), the second step proceeds either via lithiation of RPCl–NHR′ followed by further LiCl elimination or via dehydrohalogenation with non-nucleophilic bases. Similarly, in the reaction of dichlorophosphane **4** with $LiNTMS_2$ the first step also involves LiCl elimination, the second step however is driven by the elimination of TMSCl. In many cases the latter step proceeds only at elevated temperatures which may require heating. To lower the required temperature for the silyl elimination, chlorine may be replaced by fluorine minimizing the possibility of thermally induced dimerization or polymerization. By contrast, the trend is just the opposite for lithium halide elimination ($T_{Br} < T_{Cl} < T_F$) [23].

To achieve P–N bond formation, we reacted one equivalent of Wannagat's base [24] with **4** at a low temperature. LiCl is filtered off and after removal of the solvent product **8** is obtained as a colorless oil. It shows phosphorus spectra similar to **3** (br. s, 119.8 ppm), where couplings to fluorine and hydrogen could not be resolved either. Further attempts to convert aminophosphane **8** into an iminophosphane failed in our hands. Even at elevated temperatures (up to 165 °C) the elimination of TMS-Cl did not occur indicating unusual thermal stability of this chlorophosphane (*vide infra*). As already mentioned before, the elimination might be facilitated by fluorine exchange owing to the strength of the Si–F bond. Therefore, we tried to exchange Cl by F using different fluorinating reagents like AgF, SbF_3. Unfortunately, none of them led to the envisaged fluorophosphane in a clean reaction. Different activators like [18]-crown-[6] or silver triflate were employed but did not trigger any conversion. Some conversion could be achieved using SbF_3 in a toluene/diethyl ether mixture. The reaction proceeds slowly and is accompanied by by-products. For the reaction of **8** with SbF_3 two new resonances are detected in the ^{31}P NMR spectra at 160.9 ppm (d, $^1J_{PF}$ 1044 Hz) **(9)** and 135.0 ppm (d, $^1J_{PF}$ 1007 Hz) besides those of the starting material. Also in the MS spectra the formation of the desired product **9** could be confirmed. The second product which was formed in about 20% could not be identified unambiguously, but an addition/oxidation product with antimony can be expected. The reaction of the **8** with KF in chloroform-d_1 turned out to be the most successful approach. Complete conversion into the fluorine derivative is achieved after 4 h at slightly elevated temperatures (i.e. 50 °C). This reaction seems to be quite solvent dependent since no conversion was obtained if dichloromethane was used as solvent instead of chloroform. Compound **9** shows a phosphorus NMR resonance at 160.9 ppm. In the ^{19}F NMR spectra a typical doublet at −123.9 ppm ($^1J_{PF}$ 1043.6 Hz) was observed. To our surprise also in this case the envisaged elimination of TMS-F could not be achieved. The series of unsuccessful attempts to induce halosilane eliminations ($AlCl_3$, TMS-N_3, Ag-triflate) for these fluoroaryl substituted halophosphanes suggests a very strong affinity of the phosphorus atom towards the adjacent halogen. This behavior may be reasonably explained by the electron withdrawing character of the aryl group, which increases the electrophilicity of the phosphorus atoms thus strengthening the P–X bond.

Calculations of free energies for these reactions indicate that the formation of the iminophosphane from **8** is slightly more favorable than from **9**, but the energy differences are very small and solvation effects might alter these findings drastically. The energy balance of the calculations shows that in principle the reactions are thermodynamically favored. Naturally, the energy barrier of the transition state will be relevant as well, but is hard to estimate and even harder to locate on the PES, owing to intermolecular processes involved. In conclusion, the calculations suggest that introduction of a fluorine atom at phosphorus does not affect the elimination reaction for the HF_4C_6-substituted compounds significantly. Elimination to the corresponding iminophosphanes is thermodynamically feasible but no appropriate reaction conditions have been found in our hands. Table 1 summarizes the energy differences for reactions: (i) **8** → R–P═N-TMS + TMS-Cl and (ii) **9** → R–P═N-TMS + TMS-F [25].

Alternatively we tried to synthesize iminophosphanes via the second route (Scheme 2), by the reaction of a primary lithium amide with **3**. At a low temperature *t*-Bu–NHLi gives a clean reaction with **3** and the desired amino phosphane (**10**) is obtained quantitatively as colorless oil. The phosphorus NMR signal is in the expected region (89.0 ppm) showing the expected coupling pattern of a doublet of triplets arising from $^3J_{PF}$ and $^3J_{PH}$, respectively. The constitution of this compound is further corroborated by 2D-NMR experiments. Addition of a base to this compound should lead to the abstraction of the NH proton, but likewise care must be taken to avoid Ar-H activation. In an initial attempt *n*-BuLi was used at low temperatures (−80 °C), but instead of acting as a base it turned out to undergo substitution of the chlorine atom resulting in the formation of $HC_6F_4P(n\text{-Bu})\text{–}NH(t\text{-Bu})$ (**11**). The ^{31}P signal is shifted to higher field (18.5 ppm) and constitution of



Scheme 2. Formation of **8**, **9**, **10** and possible ways to iminophosphanes, (a) R′ = *t*-Bu, R′-NHLi, (b) $LiN(TMS)_2{\cdot}Et_2O$ for **8** X = Cl and **9** X = F and R = TMS.

Table 1
Absolute energies of TMS-X (X = Cl, F), **8**, **9**, and R–P═N-TMS in [hartree]. Reaction energies for reactions (i) and (ii) in [kcal/mol].

	TMS-Cl	TMS-F	**8**	**9**	R–P═N-TMS	(i)	(ii)
ΔE_{elec}	−869.6156	−509.2745	−2303.8559	−1943.5116	−1434.2251	9.6	7.5
$\Delta E_{elec + ZPE}$	−869.5034	−509.1529	−2303.5662	−1943.2207	−1434.0509	7.5	10.6
ΔG_{298}	−869.5350	−509.1928	−2303.6229	−1943.2770	−1434.0987	−6.7	−9.1

11 was confirmed by 2D-NMR spectroscopy. Further attempts to induce HCl elimination of **10** with Wannagat's base or LDA did not give any satisfactory results. Reaction of **10** with DBU gave so far unidentified products, but formation of the iminophosphane or the corresponding 2 + 2 cycloaddition product can be excluded by comparison of ^{31}P NMR shifts with literature data [26].

3. Conclusion

In summary we have explored the reactivity of a series of phosphanes with a new fluoroaryl group (HF_4C_6-), which carries a spectator function in *para* position. An asymmetric diphosphene is obtained as an intermediate in the synthesis of a linear 1,3-dihydrophosphane, while the symmetric diphosphene undergoes 2 + 2 cycloaddition under the formation of the corresponding cyclotetraphosphetane for which a crystal structure could be obtained. Attempts to synthesize HF_4C_6-substituted iminophosphanes generally failed, which could be attributed to the electronic nature of the corresponding precursors as suggested by quantum chemical calculations. Further studies are necessary to understand the reactivity of these phosphanes in order to develop strategies to incorporate this substituent into phosphorus rich materials with interesting bonding situations and reactivity.

4. Experimental

All reactions are carried out with a modified Schlenk technique. Solvents are degassed and dried over alumina using the PureSolv system. All reagents are obtained from ABCR (1,2,4,5-tetrafluorobenzene) or Sigma–Aldrich (*n*-BuLi, *t*-BuNH$_2$, LDA) and used without further purification. DBU was dried and degassed prior to use. LiNTMS$_2$·Et$_2$O is prepared according to a published procedure [24]. NMR measurements are carried out on a Varian Unity INOVA400 and a Bruker AvanceIII 300 operating at 400 MHz an 300 MHz proton frequencies, respectively. X-ray studies were performed on a STOE four-circle diffractometer or a Bruker SMART-APEX II diffractometer with a CCD detector. Mass spectra were recorded with an Agilent 5975C mass spectrometer equipped with a direct injection unit (DI-EI) at current of 70 eV.

4.1. Synthesis of **1**

To a solution of 1,2,4,5-tetrafluorobenzene (13.46 g, 89.7 mmol) in THF one equivalent of *n*-BuLi (hexane solution 1.6 M, 56 ml, 89.6 mmol) is added in ca. 80 ml THF at −100 °C over a period of 1 h. Stirring is continued for 1/2 h before ClP(NEt$_2$)$_2$ (19.30 g, 91.6 mmol) is added very slowly. The reaction mixture is stirred for 1 h at −100 °C then 1 h at −60 °C and subsequently allowed to warm to room temperature over night with continued stirring. The resulting precipitate is removed by filtration and from the solution the solvent is stripped off in vacuum yielding 23.48 g spectroscopically pure product (81%) which can be distilled b.p.: 54 °C (0.05 mbar). ^{1}H NMR (C_6D_6, 400 MHz): 6.88 (m, 1H, aryl-H), 3.04 (m, 8H, CH_2), 1.02 (t, $^3J_{HH}$, 12H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz), 14.73 (d, $^3J_{PC}$ 3.5 Hz, CH_3), 44.27 (d, $^2J_{PC}$ 18.6 Hz, CH_2), 104.89 (t, $^3J_{CF}$ 23.1 Hz, C_{aryl}-H), 123.14 (m, C_{aryl}-P), ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ = 84.2 (br.s). EI-MS [*m*/*z*]: M$^+$ 324.1 (5%), M$^+$-NEt$_2$ 252.1 (23%), P(NEt$_2$)$^+$ 175.2 (44%), NEt$_2^+$ 73.0 (62%), NEt$^+$ 44.0 (77%) Et$^+$ 28.1 (100%).

4.2. Synthesis of **2**

To a solution of **1** (65 mg, 0.2 mmol) in dichloromethane (2 ml) an excess of gray selenium (158 mg, 2.0 mmol) is added and the resulting mixture is stirred over night at slightly elevated temperature (30 °C). The excess of metal is removed by filtration and washed with dichloromethane. The filtrate is dried in vacuum yielding almost quantitatively **2** as a white crystalline solid (76 mg, 94%). Crystals suitable for X-ray diffraction were obtained by recrystallization from chloroform-d^1. M.p.: 183 °C; ^{1}H NMR (C_6D_6, 400 MHz): (m, 1H, aryl-H), (m, 8H), (t, 12H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz), 14.10 (d, $^3J_{PC}$ 2.3 Hz), 41.43 (d, $^2J_{PC}$ 5.3 Hz), 108.32 (t, $^3J_{CF}$ 21.5 Hz), 118.68 (d, $^1J_{PC}$ 89.5 Hz), 145.30 (d, $^1J_{PF}$ 251.0 Hz), 146.1 (d, $^1J_{PF}$ 254.0 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ = 55.3 (br.s. $^1J_{PSe}$ 798 Hz). EI-MS [*m*/*z*]: M$^+$ 404.1 (7%), M$^+$−Se 323.1 (9%), M$^+$−Se−NEt$_2$ 252.1 (100%), P(=Se)NEt$^+$ 181.0 (10%), NEt$_2^+$ 72.1 (24%).

4.3. Synthesis of **3**

Distillation of the crude mixture of **3** and Cl_2PNEt_2 (ca. 15 g) gives at higher temperatures scrambling reactions yielding **2** as the distillation residue. Extraction of the residue with Et$_2$O gives **2** besides small amounts of **3**. Yield: ca. 0.7 g, 2.4 mmol. ^{1}H NMR (C_6D_6, 400 MHz): 1.11 (6H, t, $^3J_{HH}$ 7.10 Hz, CH_3), 3.21 (4H, dq, $^3J_{PH}$ 3.2 Hz, $^3J_{HH}$ 7.5 Hz, CH_2), 7.13 (1H, m, aryl-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 14.02 (d, $^3J_{PC}$ 6.3 Hz, CH_3), 45.20 (d, $^2J_{PC}$ 17.2 Hz), 108.33 (t, $^3J_{CF}$ 22.7 Hz), 119.21 (dt, $^1J_{PC}$ 62.2 Hz, $^3J_{CF}$ 17.9 Hz), 145.95 (dm, $^1J_{CF}$ 247.8 Hz), 146.33 (dm, $^1J_{CF}$ 248.9 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): 112.7 (ttm, $^3J_{PF}$ 55.2 Hz, $^4J_{PF}$ 11.9 Hz). EI-MS [*m*/*z*]: M$^+$ 287.0 (57%, Cl pattern), M$^+$−CH$_3$ 272.0 (100%), M$^+$−Cl 252.1 (61%), M$^+$−NEt$_2$ 214.9 (63%), ClPNEt$_2^+$ 138.0 (23%), PNEt$_2$Cl$^+$–CH$_3$ 127.0 (23%).

4.4. Synthesis of **4**

Compound **1** (18.2 g, 56.1 mmol) was dissolved in Et$_2$O (300 ml) and cooled with an ice bath, while anhydrous HCl is bubbled over the solution. A white voluminous precipitate is formed immediately. Stirring is continued for 60 min under continued HCl stream. The precipitate is removed by filtration and washed with diethylether. The solvent is removed under reduced pressure (100 mbar) and the product is collected by fractional distillation (4 mbar, 54 °C, 8.1 g, 58%). ^{1}H NMR (C_6D_6, 400 MHz): 6.31 (m, 1H, aryl-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 110.60 (tt, $^3J_{CF}$ 22.7 Hz, $^4J_{CF}$ 1.5 Hz), 119.17 (dt, $^1J_{PC}$ 80.7 Hz, $^2J_{CF}$ 17.4 Hz), 145.54 (dm, $^1J_{CF}$ 250.9 Hz), 146.43 (dm, $^1J_{CF}$ 253.9 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): 135.9 (t, $^3J_{PF}$ 63.7 Hz) ^{19}F{^{1}H} −131.2 (dm., $^3J_{PF}$ 63.0 Hz, *o*-aryl-F) −136.4 (m, *m*-aryl-F). EI-MS [*m*/*z*]: M$^+$ 349.9 (3%), M$^+$−Cl 214.0 (100%), M$^+$−PCl$_2$ 99.0 (55%), 150.0 (98%), PCl$^+$ 65.0 (61%).

4.5. Synthesis of (tetrakis(2,3,5,6-tetrafluorophenyl)-tetraphosphetane), **5**

Compound **4** (154 mg, 0.6 mmol) is dissolved in 3 ml Et$_2$O and 3 ml dichloromethane and magnesium powder (100 mg, 4.1 mmol) is added. The resulting mixture is stirred for 3 days at 30 °C. All volatiles are removed in vacuum and the remaining residue is extracted with diethylether. After recrystallization from chloroform colorless crystals suitable for X-ray diffraction are obtained (50 mg, 47%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.03 (m, 1H, aryl-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 108.15 (t, $^3J_{PF}$ 23 Hz, aryl-H), 145.82 (dm, $^1J_{PF}$ 253 Hz), 146.91 (dm, $^1J_{PF}$ 244 Hz), C_{aryl}-P n.d. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): −63.3 (m); ^{19}F{^{1}H} −126.2 (m, *o*-aryl-F), −137.0 (m, *m*-aryl-F).

Compound **5** is also obtained by reaction of **4** (237 mg, 0.9 mmol) with PMe$_3$ (1.5 ml, 1 M in hexane) in the presence of Zn dust (ca. 100 mg, 1.5 mmol) in 3 ml $CDCl_3$. The mixture is stirred for 24 h at ambient temperatures. After removal of all volatiles

the residue is extracted with chloroform-d_1 and benzene yielding pure **5** in quantitative yield (160 mg, >99%).

4.6. Attempted synthesis of diphosphenes **6** and resulting side products **7**

2,4,6-Tris-*t*-butyl-phenylphosphane (Mes^*PH_2, 163 mg, 0.6 mmol) is dissolved in ca. 10 ml Et_2O and cooled to −10 °C and one equivalent (370 μl) *n*-BuLi is added very slowly. The slurry is allowed to warm to room temperature and stirred over night. Mes^*-PHLi is added to a cooled solution (−80 °C, 10 ml Et_2O) of **4** (125 mg, 0.5 mmol). The solution is allowed to warm to room temperature within 2 h. This intermediate was not isolated, but directly reacted with one equivalent DBU at −80 °C. The precipitate is removed and the filtrate is dried in vacuum yielding the crude product as the above described mixture. After recrystallization from pentane/C_6D_6 the product was obtained as a mixture of the diphosphene and other side products. Owing to the crude mixture of products only ^{31}P resonances are reported. Compound **6**: ^{31}P NMR (C_6D_6, 121.5 MHz): 565.7 (dt, $^1J_{PP}$ 555 Hz, $^3J_{PF}$ 21.3 Hz, HF_4C_6-*P*), 391.3 (d, $^1J_{PP}$ 555 Hz, Mes^*-*P*). Compound **7** $Mes^*P_A(H)$–$P_B(Mes^*)$–$P_C(H)R^F$: −49.5 (ddt $^1J_{PP}$ 307 Hz, $^1J_{PP}$ 223 Hz, P_B) −55.1 (dd $^1J_{PP}$ 307 Hz, $^2J_{PP}$ 17 Hz, P_A), −75.8 (dtd, $^1J_{PP}$ 223 Hz, $^3J_{PF}$ 63.1 Hz, $^2J_{PP}$ 17 Hz, P_C).

4.7. Synthesis of **8**

To a cooled solution of $LiNTMS_2{\cdot}Et_2O$ (120 mg, 0.5 mmol) in 15 ml toluene one equivalent of **4** (124 mg, 0.5 mmol) is added slowly. The mixture is warmed to room temperature and the initial clear solution becomes a cloudy and slightly yellow suspension. The reaction progress was monitored by ^{31}P NMR spectroscopy. Complete consumption of the **4** was observed after one day where the formation of a single reaction product with a phosphorus resonance at 119.8 ppm could be observed. After removal of the solvent, **8** is obtained as a colorless oil (b.p. > 300 °C). ^1H NMR (C_6D_6, 300 MHz): 0.23 (d, $^3J_{PH}$ 1.5 Hz, 18H, CH_3), 6.16 (m, 1H, aryl-H); ^{13}C NMR (by HMBC/HSQC measurements): 3.13 (9C, $SiMe_3$), 107.00 (1C C_{aryl}-H) 146.04 (dm, $^1J_{CF}$ 261.9 Hz, *o*,*m*-aryl); ^{19}F NMR (C_6D_6, 282.4 MHz): −133.2 (m, *o*-aryl-F), −138.4 (m, *m*-aryl-F); ^{31}P NMR (C_6D_6, 121.5 MHz): 119.8 (br s); EI-MS [*m*/*z*]: M^+ 375.0 (Cl pattern 5%), M^+-CH_3 360.0 (22%), M^+−Cl 340 (98%), M^+−TMSCl 267.1 (25%), 248.0 (33%), 122.0 (37%), TMS^+ 73.1 (100%).

4.8. Synthesis of **9**

To a solution of **8** in $CDCl_3$ (41 mg in 650 μl $CDCl_3$) a large excess of strictly anhydrous KF was added. The mixture was stirred for 1 day at slightly elevated temperatures (65 °C) and complete conversion was monitored by ^{31}P NMR spectroscopy. After removal of the solvent the residue is extracted with Et_2O giving pure product after evaporation of the solvent (40 mg, 91%). ^1H NMR ($CDCl_3$, 300 MHz): 0.26 (br. s, 18H, CH_3), 7.05 (m, 1H, C_{aryl}-H); ^{31}P NMR ($CDCl_3$, 121.5 MHz): 160.9 ($^1J_{PF}$ 1045.6 Hz); ^{19}F NMR ($CDCl_3$, 282.4 MHz): −123.9 ($^1J_{PF}$ 1043.4, $^4J_{PF}$ 26.3 Hz), −136.3 (m, *m*-aryl-F), −138.4 (m, *o*-aryl-F). EI-MS [*m*/*z*]: M^+ 359.1 (29%), M^+−F 340.0 (60%), M^+−TMS 286.1 (40%), M^+-NTMS_2−F 192.9 (100%), $PNTMS_2^+$ 191.1 (76%), $TMSF^+$ 92.0 (31%).

4.9. Synthesis of **10**

To *t*-butyl amine (250 mg, 3.42 mmol) in heptane/Et_2O (25 ml, 1:1) one equivalent of *n*-BuLi (2.14 ml, 3.42 mmol) is added at 0 °C. The mixture is stirred for 1 h and warmed to room temperature. The addition of the dichlorophosphane **3** is then carried out at −80 °C. After stirring over night, the solvent is removed and the residue extracted with pentane yielding the crude product (725 mg, 74%). ^1H NMR (C_6D_6, 300 MHz): 1.35 (d, $^4J_{PH}$ 1.5 Hz, 9H, *t*-Bu), 3.38 (d, $^2J_{PH}$ 4.4 Hz, 1H, NH), 7.12 (m, 1H, Ar-H); ^{13}C NMR (C_6D_6, 100.6 MHz): 31.31 (d, $^3J_{PC}$ 11.5 Hz, CH_3), 53.90 (d, $^2J_{PC}$ 16.3 Hz, CCH_3), 108.37 (t, $^2J_{CF}$ 22.6 Hz, C_{aryl}-H), 121.45 (dt, $^1J_{PC}$ 48.2 Hz, $^2J_{CF}$ 68.0 Hz, C_{aryl}-P), 145.97 (br d, $^1J_{CF}$ 250.1 Hz, *o*,*m*-C_{aryl}-F); ^{19}F NMR (C_6D_6, 282.4 MHz): −134.4 (dm, $^3J_{PF}$ 59.2 Hz, *o*-aryl-F), −137.33 (m, *m*-aryl-F); $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): 89.0 (t, $^3J_{PF}$ 59.2 Hz), ^{31}P NMR (C_6D_6, 121.5 MHz): 89.0 (td, $^3J_{PF}$ 59.2 Hz, $^2J_{PH}$ 8.9 Hz). EI-MS [*m*/*z*]: M^+ 287.1 (22%, Cl pattern), M^+-CH_3 272.1 (100%), M^+−Cl 252.0 (37%), M^+−Bu 231.1 (55%), M^+−NHBu 215.0 (65%), M^+−BuCl 196.0 (99%), 127.0 (25%), Bu^+ 57.1 (54%).

4.10. Reaction of **10** with n-BuLi (**11**)

Reaction of **10** (170 mg, 0.6 mmol) with one equivalent *n*-BuLi (380 μL, 0.6 mmol) is carried out in Et_2O at low temperatures (−80 °C). The precipitate is filtered off and an oily residue is obtained after removal of the solvent in 60% yield (111 mg). ^1H NMR ($CDCl_3$, 400 MHz): 0.74 (3H, t, $^3J_{HH}$ 7.0 Hz, CH_3), 1.01 (s, 9H, *t*-Bu CH_3), 1.22 (m, 2H, CH_2–CH_3), 1.60 (m, 2H, CH_2–P), 1.80 (m, 2H, $CH_2CH_2CH_2$) 2.25 (1H, d, $^2J_{PH}$ 12.4 Hz, NH), 6.23 (m, 1H, C_{aryl}-H); ^{13}C NMR (100.6 MHz): 13.6 (s, CH_2CH_3) 27.40 (d, J_{PC} 17.2 Hz), 31.52 (d, $^3J_{PC}$ 9.4 Hz $C(CH_3)_3$) 31.82 (m, PCH_2), 51.08 ($^2J_{PC}$ 16.4 Hz $C(CH_3)_3$). EI-MS [*m*/*z*]: M^+ 309.1 (7%, Cl pattern), M^+-CH_3 293.2 (27%), M^+−Bu 251.1 (14%), M^+−NHBu 237.1 (38%), 210.1(42%), M^+−2*x*Bu 196.0 (100%), $P(NH)Bu^+$ 127.1 (12%).

Acknowledgements

Financial support by the Austrian Science Fund (FWF) (Grants P18591-03 and P20575-N19) and the EU-COST Action CM0802 "PhoSciNet" is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 748985 and 748984 contain the supplementary crystallographic data for **2** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.025.

References

[1] Y. Ren, Y. Dienes, S. Hettel, M. Parvez, B. Hoge, T. Baumgartner, Organometallics 28 (2009) 734–740.
[2] B. Hoge, W. Wiebe, Angew. Chem., Int. Ed. 47 (2008) 8116–8119.
[3] P. Le Floch, Coord. Chem. Rev. 250 (2006) 627–681.
[4] M. Hissler, C. Lescop, R. Réau, C.R. Chim. 11 (2008) 628–640.
[5] M.G. Hobbs, T. Baumgartner, Eur. J. Inorg. Chem. (2007) 3611–3628.
[6] T. Baumgartner, R. Reau, Chem. Rev. 106 (2006) 4681–4727.
[7] C. Lescop, M. Hissler, in: B. Pignataro (Ed.), Tomorrow's Chemistry Today, 2009, pp. 295–319.
[8] J. Grobe, D. Le Van, B. Broschk, M. Hegemann, B. Luth, G. Becker, M. Bohringer, E.-U. Würthwein, J. Organomet. Chem. 529 (1997) 177–187.
[9] P. Espinet, A.C. Albéniz, J.A. Casares, J.M. Martínez-Ilarduya, Coord. Chem. Rev. 252 (2008) 2180–2208.
[10] B. Hoge, J. Bader, J. Fluorine Chem. 128 (2007) 857–861.
[11] P.A. Chase, D.W. Stephan, Angew. Chem., Int. Ed. 47 (2008) 7433–7437.
[12] P.A. Chase, G.C. Welch, T. Jurca, D.W. Stephan, Angew. Chem., Int. Ed. 119 (2007) 8196–8199.
[13] M.L. Clarke, D. Ellis, K.L. Mason, A.G. Orpen, P.G. Pringle, R.L. Wingad, D.A. Zaher, R.T. Baker, Dalton Trans. (2005) 1294–1300.
[14] M. Scholz, H.W. Roesky, D. Stalke, K. Keller, F.T. Edelmann, J. Organomet. Chem. 366 (1989) 73–85.
[15] C. Moser, F. Belaj, R. Pietschnig, Chem. Eur. J. (2009), in press, doi:10.1002/chem.200902255.
[16] C. Moser, M. Nieger, R. Pietschnig, Organometallics 25 (2006) 2667–2672.

[17] N. Nagahora, T. Sasamori, N. Takeda, N. Tokitoh, Organometallics 24 (2005) 3074–3080.
[18] P. Barbaro, M. Di Vaira, M. Peruzzini, S.S. Costantini, P. Stoppioni, Angew. Chem., Int. Ed. 47 (2008) 4425–4427.
[19] J.M. Lynam, Angew. Chem., Int. Ed. 47 (2008) 831–833.
[20] A.G. Massey, A.J. Park, J. Organomet. Chem. 5 (1966) 218–225.
[21] F. Sanz, J.J. Daly, J. Chem. Soc., Chem. Commun. (1971) 1083–1086.
[22] R.C. Smith, X. Chen, J.D. Protasiewicz, Inorg. Chem. 42 (2003) 5468–5470.
[23] E. Niecke, D. Gudat, Angew. Chem., Int. Ed. 30 (1991) 217–237.
[24] U. Wannagat, H. Niederprüm, Chem. Ber. 94 (1961) 1540–1547.
[25] Calculations on the corresponding non-fluorinated congeners showed that the reactions energies are of the same order of magnitude. Thus influence of the the perfluorinated groups seems equal on both asymptotes of the eliminiation reaction and the energy barrier due to the transistion state is crucial for this reactivity (further information in the supplementary material).
[26] K. Miqueu, J.-M. Sotiropoulos, G. Pfister-Guillouzo, V.L. Rudzevich, H. Gornitzka, V. Lavallo, V.D. Romanenko, Eur. J. Inorg. Chem. (2004) 2289–2300.