

# A novel type of formation of zwitterionic compounds, containing two phosphorus atoms of opposite charge and different coordination number

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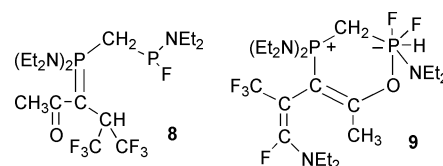
The oxidation of bis[bis(dialkylamino)phosphinyl]methane **1** with 5,5,5-trifluoro-4-(trifluoromethyl)penta-3-en-2-one **2** unexpectedly gave zwitterionic compound **7** which according to X-ray analysis contains two phosphorus atoms of opposite charge and different coordination number ( $\lambda^4\text{P}^{+}$ ;  $\lambda^6\text{P}^{-}$ ) with a direct P–H bond at the hexacoordinated phosphorus.

Here we report on an unusual reaction of methylenediphosphine **1** with 5,5,5-trifluoro-4-(trifluoromethyl)penta-3-ene-2-one **2** in which the C=C double bond is activated by one acyl and two trifluoromethyl groups. This reaction is of interest from three points of view. First, it leads to the formation of the unusual zwitterionic compound **7** which contains two oppositely charged phosphorus atoms with different coordination numbers ( $\lambda^4\text{P}^{+}$ ;  $\lambda^6\text{P}^{-}$ ); zwitterionic compounds of this type are a rarity.<sup>1–3</sup> Secondly, the hexacoordinated phosphorus of **7** has a direct P–H bond which has not been reported previously for zwitterionic compounds. Finally, this reaction is remarkable since  $\text{CF}_3$  groups act as a fluorinating agent for one of the phosphorus atoms substituting the dialkylamino groups by fluorine. Amazingly, one of the dialkyl amino groups thus substituted was found in reaction product **7** attached to the carbon atom of the former  $\text{CF}_3$  group.

The reaction proceeds readily at  $-15\text{ }^\circ\text{C}$  in diethyl ether solution.<sup>†</sup> The proposed mechanism of this reaction (Scheme 1) includes an electrophilic attack of the  $\text{sp}^2$ -carbon atom of **2** at the trivalent phosphorus atom to give the intermediate betaine **3**. Usually such betaines undergo prototropic migration from the  $\alpha$ -position forming ylides.<sup>4,5</sup> However, the presence of  $\text{CF}_3$  groups close to the negative charge in compound **3** leads to the

elimination of HF to give ylide **4** (*cf.* ref. 6). Hydrogen fluoride immediately cleaves P–N bonds at the trivalent phosphorus atom forming  $-\text{PF}(\text{NR}_2)$  and  $-\text{PF}_2$  units. Then, the dialkylamine released, adds to the  $\text{C}=\text{CF}_2$  double bond giving the intermediate product **5**. The next step yielding compound **6** is not quite clear. Formally, elimination of HF from one part of the molecule of **5** and its subsequent addition to the  $\text{PF}_2$  unit takes place to give the phosphorane center with a P–H bond. Further transformation of **6**, with the negative charge of the ylidic carbon atom delocalized on the adjacent carbonyl group, is quite clear. Intramolecular cyclization occurs with the charge transfer to the pentacoordinated phosphorus resulting in the thermodynamically stable reaction product **7**. Because of its zwitterionic character compound **7** has reduced solubility and crystallized from the reaction mixture as colorless crystals.

NMR spectroscopic analysis of the mother-liquor after crystallization of **7** supported the proposed mechanism. It contained diethylammonium fluoride, the monofluoro derivative **8** and zwitterionic compound **9**. The formation of **9** which



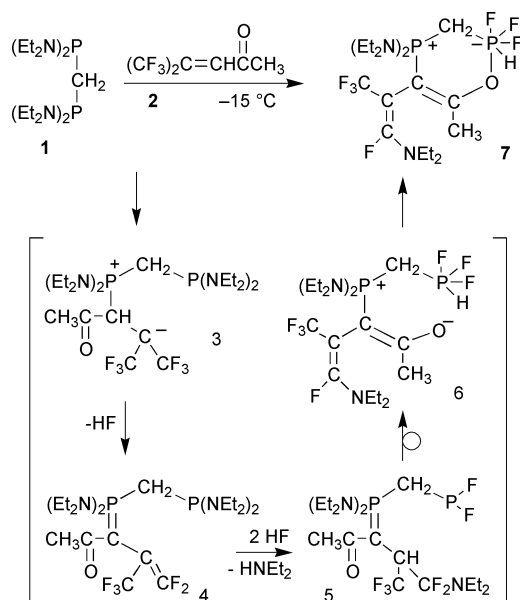
is a structural isomer of **3** indicates, that some steps of the proposed mechanism may be concerted. For example, elimination of HF from **3** and its subsequent interaction with **4**, followed by the addition of the  $\text{HNEt}_2$  released, may occur as a concerted intramolecular rearrangement of **3** into **9**.

The detailed structure of **7** was solved by X-ray analysis (Fig. 1).<sup>‡</sup> The results obtained confirm the unusual structure of **7**. To the best of our knowledge the molecular structures of only two compounds containing a P–H bond at hexacoordinated phosphorus have been published previously.<sup>7,8</sup>

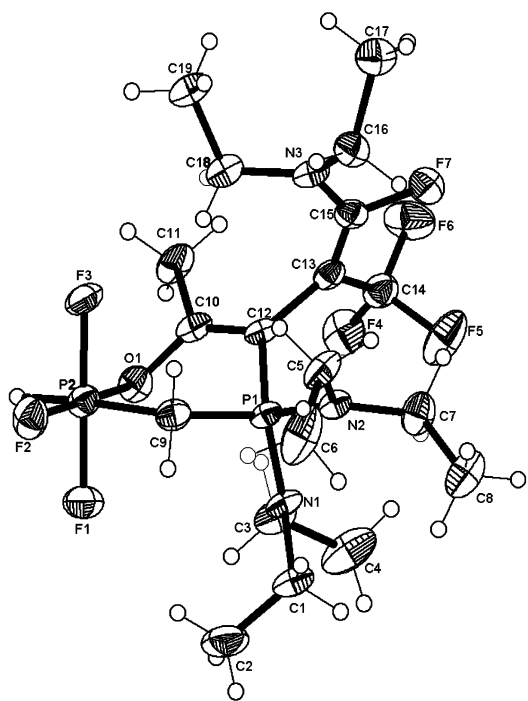
The negatively charged hexacoordinated phosphorus atom P2 has a slightly distorted tetragonal bipyramidal structure. Almost all angles at P2 are very close to  $90^\circ$ . Only one angle,  $\text{O}(1)\text{--P}(2)\text{--C}(9)$ , which is a part of the six membered ring is somewhat larger ( $95.70(18)^\circ$ ). With this value the ring cannot be flat and has a distorted boat conformation with atoms  $\text{O}(1)$  and  $\text{P}(1)$  in the out-of-plane positions.

Theoretically, in solution compound **7** can exist in an equilibrium with betaine **6** or ylide **10** (Scheme 2) However, thorough  $^{31}\text{P}$  NMR investigations of **7** did not show any signal attributable to pentacoordinated phosphorus. Thus the equilibrium is completely shifted to the zwitterionic form **7** in which the distribution of the negative charge is much more effective than in **6** or **10**.

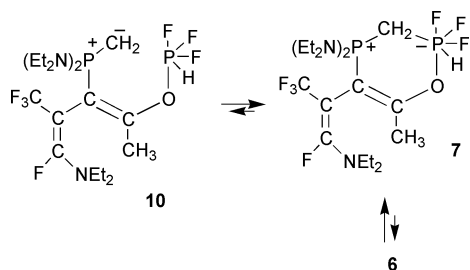
The  $\{^1\text{H}\}^{31}\text{P}$  NMR spectrum of compound **7** (Fig. 2) displayed a sharp high field doublet of triplets at  $\delta_{\text{P}} -134.2$  which is characteristic for hexacoordinated phosphorus  $\text{P}(2)$ . Without proton decoupling each line of this multiplet showed a triplet because of the coupling to  $\text{CH}_2$  protons in  $\alpha$  position.



Scheme 1

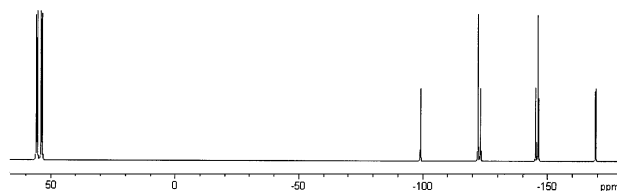


**Fig. 1** Perspective view and labeling scheme for compound **7**. Selected bond lengths (pm) and angles ( $^{\circ}$ ): P(1)–N(1) 164.0(4), P(1)–C(9) 179.6(5), P(1)–C(12) 179.2(4), C(9)–P(2) 186.3(5), P(2)–F(1) 164.2(3), P(2)–F(2) 164.9(3), P(2)–F(3) 165.1(3), P(2)–O(1) 177.4(3), C(10)–C(12) 133.9(7), C(12)–C(13) 148.2(6), C(13)–C(15) 135.4(7), C(15)–N(3) 134.4(6); C(12)–P(1)–C(9) 106.2(2), P(1)–C(9)–P(2) 116.5(3), O(1)–P(2)–C(9) 95.70(18), C(12)–C(10)–O(1) 122.1(4), C(10)–C(12)–P(1) 114.8(4).



**Scheme 2**

Such a multiplet is accounted for by the equivalence of two of the three fluorine atoms attached to phosphorus. Remarkably, one of these equivalent fluorine atoms does not interact with the other phosphorus P(1) which displays a doublet of doublets. The



**Fig. 2**  $\{^1\text{H}\}^{31}\text{P}$  NMR spectrum of compound **7**.

$^2J_{\text{PP}}$  coupling constant is very small ( $<1$  Hz) and was not resolved.<sup>9</sup>

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## Notes and references

† A solution of **2** (400 mg, 1.94 mmol) in diethyl ether (2 mL) was added to a solution of **1** (320 mg, 0.62 mmol) in diethyl ether (3 mL) at  $-20$   $^{\circ}\text{C}$  and the reaction mixture was left at this temperature for 2 h. Then the reaction solution was separated from a small amount of  $\text{Et}_2\text{NH}_2\text{F}$  formed during this time and diluted with hexane (2 mL). The colourless crystalline product formed in 3 days at  $-20$   $^{\circ}\text{C}$  was separated and dried *in vacuo*. Yield 27%, mp 115–118  $^{\circ}\text{C}$ . *Spectral data for 7*:  $\delta_{\text{H}}$  (89.56 MHz,  $\text{CDCl}_3$ ) 1.13 (t,  $J$  7.0 Hz, 12 H), 1.18 (t,  $J$  7.0 Hz, 6 H), 2.05 (s, 3 H), 1.8–2.8 (m, 2 H,  $\text{PCH}_2\text{P}$ ), 2.8–3.2 (m, 8 H), 3.2–3.7 (m, 4 H), 6.12 (dddd,  $J$  121.0, 127.0, 130.3, 1017 Hz, 1 H).  $\delta_{\text{F}}$  (84.26 MHz,  $\text{CDCl}_3$ )  $-36.0$  (dm,  $J$  868 Hz, 3 F),  $-54.6$  (d,  $J$  21 Hz, 3 F),  $-70.7$  (qm,  $J$  21 Hz, 1 F).  $\delta_{\text{P}}$  (36.2 MHz,  $\text{CDCl}_3$ ) 55.7 (dd,  $J$  9, 56.5 Hz, 1 P),  $-134.2$  (dt,  $J$  845, 868 Hz, 1 P).

‡ *Crystal data for 7*:  $\text{C}_{19}\text{H}_{36}\text{F}_7\text{N}_3\text{OP}_2$ ,  $M = 517.45$ , triclinic, space group  $P\bar{1}$ ,  $a = 898.7(3)$ ,  $b = 1198.1(3)$ ,  $c = 1243.6(2)$  pm,  $\alpha = 99.44(10)$ ,  $\beta = 91.68(2)$ ,  $\gamma = 110.99(2)^{\circ}$ ,  $V = 1.2276(5)$   $\text{nm}^3$ ,  $T = 173(2)$  K,  $Z = 2$ ,  $\lambda(\text{Mo-K}\alpha) = 71.073$  pm,  $\mu = 0.246$   $\text{mm}^{-1}$ . The structure was solved by direct methods and refined by full-matrix least squares on  $F^2$ . Independent reflections = 3605 ( $R_{\text{int}} = 0.0586$ ). Goodness-of-fit on  $F^2 = 0.977$ . Final  $R$  indices [ $I > 2\sigma(I)$ ]:  $R1 = 0.0688$ ,  $wR2 = 0.1560$ .

CCDC reference number 163090.

See <http://www.rsc.org/suppdata/cc/b1/b109484j/> for crystallographic data in CIF or other electronic format.

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- 9 The  $^2J_{\text{PP}}$  coupling constant of the P–C–P system can vary in the range 0–240 Hz.