ACCOUNTS OF CHEMICAL RESEARCH

VOLUME 2 NUMBER 12 DECEMBER, 1969

Chemical Consequences of Fluorocarbon Phosphines

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Received April 7, 1969

Many classes of phosphorus compounds have been extensively studied, but the chemistry of the 3-covalent compounds, all of which may be regarded as substitution derivatives of phosphine (PH_3), has developed more slowly—only recently showing any wide variety of new types. For example, aminophosphines of the R_2NPCl_2 type had been known for 80 years before anyone noticed how easily they can be converted to substances of the R_2NPR_2 type.[2] Also, little was known of P–P-linked polyphosphines until recent times. More understandably, phosphine derivatives of the R_2POR and R_2PSR types were not isolated until it became possible to avoid their Arbuzov-like rearrangements to R_3PO and R_3PS types.

A large expansion of phosphine chemistry was made possible by the discovery of an easy way to attach the CF_3 group to phosphorus. One simply heats $AgCO_2CF_3$ with iodine to get CF_3I,[3] which reacts with phosphorus and iodine at 190° (optimally, 4 days) to form $(CF_3)_3P$, $(CF_3)_2PI$, and CF_3PI_2.[4] From these three compounds it is possible to make many others, some of which represent new phosphine types, foreign to classical organophosphorus chemistry. The very electronegative CF_3 group (between Cl and F on most scales) strongly affects the chemical character of phosphorus. Moreover, such compounds are conveniently stable because CF_3 does not easily move from one atom to another as halogens do. Accordingly, one easily discovers new patterns of chemical behavior and seeks to understand them through new applications of modern valence theory.

Because of the strong electron-withdrawing power of CF_3, the phosphorus lone-pair electrons interact poorly with Lewis acids, in contrast to the strong basicity of hydrocarbon phosphines. For the same reason, the phosphorus 3d, 4s, and 4p orbitals have relatively low energy levels, so that their various hybrids can be used for bonding to electron-donor (basic) atoms. Accordingly, some CF_3 phosphines form observable 1:1 adducts with strong bases, or such adducts may reasonably be assumed for explaining the mechanisms of reactions such as the analytically useful basic hydrolysis to form HCF_3.

Also the π-acceptor action of phosphorus (mostly involving its 3d orbitals) is strongly enhanced by CF_3, which itself cannot offer π electrons to compete with π-donor ligands. This π bonding modifies the chemical behavior of the donor atom and often correlates with intense ultraviolet absorption.

The high volatility of most $P–CF_3$ compounds facilitates their study by the quantitative Stock high-vacuum methods. Presumably they represent the larger field of $P–C_nF_{2n+1}$ compounds, and the main principles should be applicable even to the modification of fluorocarbon plastics.

P–P-Bonded Polyphosphines

Syntheses. The conversion of P–I to P–P bonds occurs very easily; indeed, both CF_3PI_2 and $(CF_3)_2PI$ liberate iodine on standing in sealed tubes, tending to equilibrate with $(CF_3P)_n$ ring compounds or $(CF_3)_2P-P(CF_3)_2$, respectively. For complete conversion, the original method was to shake the iodophosphine with mercury,[4a] but it is more convenient to heat the iodophosphines with powdered antimony in a sealed tube. At 100° the by-product SbI_3 remains in solution, not interfering with the process as the mercury iodides did. In one easy step, then, one obtains the diphosphine $P_2(CF_3)_4$ or a mixture of crystalline $(CF_3P)_4$ and liquid $(CF_3P)_5$—the homocyclic polyphosphines.[5]

Another way to make these homocycles is by heating $P_2(CF_3)_4$ or $(CF_3)_2PH$ (made by alcoholysis of the diphosphine, or by other X–H exchanges) to 350°, with continuous removal of the quenched-out products. The two pyrolyses are described by the equations

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[1] Recipient of the 1969 American Chemical Society Award for Distinguished Service in the Advancement of Inorganic Chemistry, sponsored by Mallinckrodt Chemical Works.

[2] A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80,** 1107 (1958).

[3] A. L. Henne and W. G. Finnegan, *ibid.*, **72,** 3806 (1950).

[4] (a) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1568 (1953); (b) A. B. Burg, W. Mahler, A. J. Bilbo, C. P. Haber, and D. L. Herring, *J. Am. Chem. Soc.*, **79,** 247 (1957).

[5] W. Mahler and A. B. Burg, *ibid.*, **80,** 6161 (1958).

$$nP_2(CF_3)_4 \longrightarrow n(CF_3)_3P + (CF_3P)_n$$
$$n(CF_3)_2PH \longrightarrow nHCF_3 + (CF_3P)_n$$

Here the $(CF_3P)_n$ product includes some pentamer, much tetramer, and substantial yields of higher polymers. These seem to be larger homocycles, wholly convertible to a tetramer–pentamer mixture by catalysts at lower temperatures.

The $P_2(CF_3)_4$ pyrolysis was the first example of a general reaction which occurs far more easily with other open-chain polyphosphines. For example, the tetraphosphine $H(CF_3P)_4H$ (made from the pentamer by reaction with lauryl alcohol under a high-vacuum reflux column) very easily loses a CF_3P unit (as tetramer or pentamer) to form the somewhat more stable triphosphine $H(CF_3P)_3H$. This in turn decomposes to $(CF_3P)_4$, $(CF_3P)_5$, and the diphosphine $(CF_3PH)_2$, which with far greater difficulty goes to $(CF_3P)_4$, $(CF_3P)_5$, and CF_3PH_2.[6]

Similarly, the open-chain triphosphine $CF_3P[P(CF_3)_2]_2$, made by slowly introducing trimethylamine vapor into the bottom of a chamber containing $(CF_3)_2PCl$ and CF_3PH_2 vapors at −40°, decomposes very easily (especially if catalyzed by bases or even mercury) to $(CF_3P)_4$, $(CF_3P)_5$, and $P_2(CF_3)_4$.[7] The main driving force in all such decompositions must be the high stability of the $(CF_3P)_n$ rings.

A more stable triphosphine results when $(CF_3)_2PCl$ is phosphinolyzed by CH_3PH_2 to the fairly stable $CH_3HPP(CF_3)_2$, which reacts further to make $CH_3P[P(CF_3)_2]_2$. Here the central CH_3P group seems to block the decomposition.[8]

Related to this is the diphosphine $(CH_3)_2PP(CF_3)_2$, which is easily made from $(CF_3)_2PCl$ and $(CH_3)_2PH$.[9] It is clear that one phosphorus atom should exhibit good base action whereas the other may act as a fairly good Lewis acid. Hence the $(CH_3)_2P$ part of one molecule attacks the $(CF_3)_2P$ part of the other, initiating condensation to a nonvolatile oil. This occurs near 100°, whereas $P_2(CH_3)_4$[10] and $P_2(CF_3)_4$ are stable up to 300°.

Another aspect of the acid–base chemistry of $(CH_3)_2PP(CF_3)_2$ concerns its cleavage by protic acids. Hydrogen chloride would be expected to attack it at the more basic phosphorus atom and so form $(CH_3)_2PH$ and $(CF_3)_2PCl$, but these would form stronger bonds by exchange of H for Cl; in fact, the only products found are $(CH_3)_2PCl$ and $(CF_3)_2PH$. Equally interesting is the addition of methyl iodide. Here again, it seems that the acidic group (CH_3^+) attaches to the more basic phosphorus atom; but the initially formed $(CH_3)_3PP(CF_3)_2{}^+I^-$ exchanges rapidly with another $(CH_3)_2PP(CF_3)_2$ at the P–P bond, so that the only observed products are $P_2(CF_3)_4$ and the methiodide $(CH_3)_2PP(CH_3)_3{}^+I^-$.

Ring Stability. There is a remarkable contrast between the unstable open-chain trifluoromethylpolyphosphines and the stable $(CF_3P)_4$ and $(CF_3P)_5$. These two ring compounds are interconvertible by base catalysis, with the pentamer (mp −33°) favored in the liquid phase or the tetramer favored by crystallization,[11] but no other species is found in the equilibrium mixtures; higher polymers are thermodynamically unstable relative to the tetramer and pentamer. The $(C_6H_5P)_n$ system is different; the existence of $(C_6H_5P)_4$ has become doubtful, but the easy reaction of $C_6H_5PH_2$ with $C_6H_5PCl_2$ directly yields $(C_6H_5P)_5$, $(C_6H_5P)_6$, and possibly higher polymers.[12]

It may be instructive that the $(CF_3P)_4$ and $(CF_3P)_5$ rings are far from the expected planar-polygon configurations,[13] whereas $(C_6H_5P)_5$ is reported to have a regular P_5 pentagonal ring.[12] The bent-square pattern of $(CF_3P)_4$ is definitely not due to repulsions by cross-ring CF_3 groups, and the cross-ring P–P distance (2.980 Å) is too long to account for more than 8% of single P–P bond character. For ring stabilization, then, we are left to consider the delocalization of the phosphorus lone-pair electrons entirely around each ring by means of orbitals above the normal valence tetrad of phosphorus. The required full-ring molecular orbitals would be constructed of phosphorus 3d, 4s, and 4p atomic orbitals, with some $P–CF_3$ σ^* antibonding orbitals also included because the polarity of the P–C bond would give them bonding strength near the P atoms. On this basis, the primary theoretical problem would be to explain why the delocalization stabilizes the P_4 and P_5 rings much more than it seems to do for the larger rings.

This proposed circumannular delocalization correlates with the very intense ultraviolet absorption by the tetramer and pentamer[5] and is supported even more convincingly by the high diamagnetic susceptibility of $(CF_3P)_5$, the ring current of which seems to exceed even that of benzene.[14]

A more subtle evidence of the value of this hypothesis was the discovery of the "inorganic thiophene" $(CF_3P)_4S$.[15] My colleague Jürgen Heners had made some open $CF_3P–N$ hetero chains[16] which were expected to close up to P_xN_y heterocycles, but could not be forced to do so. Also, earlier attempts by Mahler to form a $CF_3P–O$ heterocycle, by very slow access of oxygen to $(CF_3P)_4$, led only to the phosphonic anhydride polymers $(CF_3PO_2)_n$.[5] It could be understood that neither oxygen nor nitrogen, lacking effective orbitals above the valence octet, could participate in circumannular delocalization, but sulfur could do so. Indeed, the direct addition of S_8 to $(CF_3P)_4$ at 150–200° gave high yields of the heterocycle

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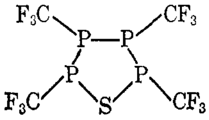
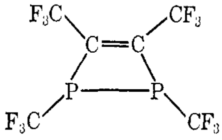
(6) A. B. Burg and L. K. Peterson, *Inorg. Chem.*, **5**, 943 (1966).
(7) A. B. Burg and J. F. Nixon. *J. Am. Chem. Soc.*, **86**, 356 (1964).
(8) A. B. Burg and K. K. Joshi, *ibid.*, **86**, 353 (1964).
(9) L. R. Grant, Jr., and A. B. Burg, *ibid.*, **84**, 1834 (1962)
(10) A. B. Burg, *ibid.*, **83**, 2226 (1961).
(11) A. B. Burg and W. Mahler, *ibid.*, **83**, 2388 (1961).
(12) L. Maier, *Helv. Chim. Acta*, **49**, 1119 (1965).
(13) J. Donohue, *Acta Cryst.*, **15**, 708 (1962), and earlier papers.
(14) J. L. Laity (working with the late H. Dauben at the University of Washington), private communication.
(15) A. B. Burg, *J. Am. Chem. Soc.*, **88**, 4298 (1966).
(16) J. Heners and A. B. Burg, *ibid.*, **88**, 1677 (1966).



This in itself implies a challenging theoretical problem, for many patient attempts by my colleague Dr. D. M. Parker to form $(CF_3P)_xS_y$ rings of any other size served only to show that the P_4S ring is almost uniquely preferred. For example, when sulfur adds to $(CF_3P)_5$ one gets no $(CF_3P)_5S$, but only $(CF_3P)_4S$ and a slight by-product which may be $(CF_3P)_3S$, according to its nmr and mass spectra. Even this easily converts to $(CF_3P)_4S$.

Related to this subject was the synthesis of the heterocycles



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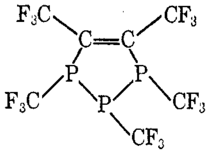


from $(CF_3P)_{4,5}$ and $CF_3C{\equiv}CCF_3$ at 170°.[17] As Mahler points out, the olefinic π electrons can delocalize around the ring, much in the manner of the phosphorus lone pairs. Further confirmation of the main hypothesis is found in the negative results from many attempts by my former colleague, Dr. Keith Gosling, to make heterocycles by introducing $(CF_3P)_n$ ring fragments into olefins. In contrast, the halogen-like addition of $(CF_3)_2PP(CF_3)_2$ to ethylene (easy at 25°) forms $(CF_3)_2PC_2H_4P(CF_3)_2$,[18] and the similar reaction of $P_2(CH_3)_4$ (at 300°) gives a good yield of $(CH_3)_2PC_2H_4P(CH_3)_2$.[10] Thus the failure of the ring P–P bond to insert ethylene must mean that a saturated C–C ring segment would have a destabilizing effect, such as the prevention of circumannular delocalization.

Monomer Complex Chemistry. Direct evidence of the electron-acceptor character of the CF_3 phosphines is found in the action of the strong tertiary base $(CH_3)_3P$ upon $(CF_3P)_4$ or $(CF_3P)_5$ to make the solid monomer complex, $(CH_3)_3P\text{–}PCF_3$.[11] This reversible process accounts for the action of tertiary bases as catalysts for the destruction of the open-chain polyphosphines or for the equilibration of mixtures of $(CF_3P)_4$ and $(CF_3P)_5$. Such mixtures also form when $(CH_3)_3P$ removes sulfur from the heterocyclic $(CF_3P)_4S$ to make $(CH_3)_3PS$.

It was hoped that the easy dissociation of $(CH_3)_3P\text{–}PCF_3$ *in vacuo* at 25° would provide a source of the CF_3P fragment for many interesting chemical reactions, but it now seems that this complex is a less effective source of the CF_3P unit than the $(CF_3P)_4$ and $(CF_3P)_5$ rings themselves; the reversion to these ring compounds does not imply a free CF_3P unit but rather $(CH_3)_3P\text{–}PCF_3PCF_3\cdots$ chain building, leading to cyclization. Such chain formation would require base action by the complex-bonded PCF_3 unit, and indeed this does use its lone-pair electrons to attach Lewis acids such as BH_3 or B_5H_9 fragments, although the products are not yet fully understood.

A useful result of this base action is the addition of methyl iodide to make $(CH_3)_3P\text{–}PCH_3CF_3{}^+I^-$. Then HCl cleaves the P–P bond to afford almost quantitative yields of $(CH_3)_3PH^+I^-$ and CH_3CF_3PCl, thereby providing an easy entry to the extensive chemistry of the CH_3CF_3 phosphines.[19]

The existence of the monomer complex $(CH_3)_3P\text{–}PCF_3$ leads one to ask what would happen if the base were CH_3PH_2 or $(CH_3)_2PH$ instead of $(CH_3)_3P$. In fact, CH_3PH_2 attacks $(CF_3P)_4$ in a quantitative process at room temperature[20]

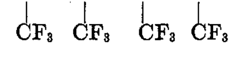
$$5(CF_3P)_4 + 20CH_3PH_2 \longrightarrow 20CF_3PH_2 + 4(CH_3P)_5$$

Closely related but more complex is the attack by $(CH_3)_2PH$ upon $(CF_3P)_4$, first forming mostly CF_3PH_2 and $P_2(CH_3)_4$. The latter reacts with more $(CF_3P)_4$ to give a high yield of the triphosphine $CF_3P[P(CH_3)_2]_2$.[20] In both processes, the first step may well be the formation of a PCF_3 complex in which the PCF_3 unit is basic enough to seize protons from the four-coordinate phosphorus.

Alcoholytic P–P Cleavages. The base acceptor action of the CF_3 phosphines probably initiates the facile cleavage of their P–P bonds by alcohols. The action of methanol to convert $(CF_3)_2PP(CF_3)_2$ to $(CF_3)_2PH$ and $CH_3OP(CF_3)_2$ is the prototype of many alcoholyses leading to a wide variety of alkoxyphosphines.[21] All of these seem permanently stable against rearrangement to phosphine oxides because the base action of the phosphorus lone-pair electrons here is too weak to take an R group from oxygen, except by heat and catalysis.

In the alcoholyses of longer chain polyphosphines there should be directive effects: presumably the RO group will go mostly to the P atom having the best σ-electron-acceptor strength. A clear example is provided by the triphosphine $CF_3P[P(CF_3)_2]_2$, for which it can be argued that the end P atoms should be more electron deficient than the central P atom. In fact, its alcoholysis (at 25° or lower) detaches one $P(CF_3)_2$ group as $ROP(CF_3)_2$; this and the diphosphine $CF_3HPP(CF_3)_2$ are the exclusive products.[22]

Another approach to P_n open chains is through alcoholysis of $(CF_3P)_n$ rings.[6] For example, the first-stage methanolysis product of $(CF_3P)_4$ must be



$$CH_3O\text{—}\underset{CF_3}{P}\text{—}\underset{CF_3}{P}\text{—}\underset{CF_3}{P}\text{—}\underset{CF_3}{P}\text{—}H$$

Here it can be argued that the CH_3OP unit should be the next point of attack by the oxygen of the alcohol and that this attack could be as effective as the cleavage

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[17] W. Mahler, *J. Am. Chem. Soc.*, **86**, 2306 (1964).

[18] L. R. Grant, Jr., Ph.D. Dissertation, University of Southern California, 1961, p 29.

[19] A. B. Burg, K. K. Joshi, and J. F. Nixon, *J. Am. Chem. Soc.*, **88**, 31 (1966).

[20] A. H. Cowley, *ibid.*, **89**, 5990 (1967).

[21] J. E. Griffiths and A. B. Burg, *ibid.*, **84**, 3442 (1962).

[22] N. W. Otterness, M.S. Thesis, University of Southern California, 1967.

of the original ring. The second step actually does seem to occur about as fast as the first, so that $(CH_3O)_2PCF_3$ soon appears, and the unstable $H(CF_3P)_3H$ can be isolated in yields as high as 50%. However, it is difficult to prove an exclusive directive effect, for fractions believed to contain moderate yields of CH_3OCF_2PH and $CH_3O(PCF_3)_2H$ also appear, and these cannot be ascribed solely to the alcoholysis of $H(CF_3P)_3H$.

Oxyphosphine Chemistry

The $ROP(CF_3)_2$ type so effectively resists conversion to the $R(CF_3)_2PO$ type that stability is retained when R varies over a wide range of organic and even inorganic groups. Many more element–$OP(CF_3)_2$ compounds seem possible than have yet been discovered; the present examples, most of which have no parallel in hydrocarbon phosphine chemistry, can only be regarded as a beginning.

Alkoxyphosphine Rearrangements. The conversion of $CH_3OP(CF_3)_2$ to $CH_3(CF_3)_2PO$ in the presence of CH_3I (equimolar) was only 12% complete after 6 days in the liquid phase at 148°.[21] Phosphorus here must have very poor nucleophilic reactivity, for even this small progress could be ascribed mostly to high pressure and the irreversibility of P–CH_3 bond formation. Far easier is the rearrangement of $(CH_3)_3COP(CF_3)_2$: with CH_3I during 2 hr at 70–80°, it was almost 80% converted to $(CH_3)_3C(CF_3)_2PO$.[21] This was not a classical Arbuzov reaction (R going from I to P and R′ from O to I), for no CH_3 was attached to P, and no $(CH_3)_3CI$ could be found. The definitely catalytic role of CH_3I might be explained by supposing that it exchanges CH_3 for $(CH_3)_3C$ on O and that the resulting $(CH_3)_3CI$ very easily offers the planar $(CH_3)_3C^+$ group (like the planar trimethylboron) for attachment to P. Then the O-bonded CH_3 would go back to I, and the catalytic cycle would be complete. This special process only emphasizes the normal stability of $ROP(CF_3)_2$ compounds against such rearrangements.

The Diphosphoxane. The compound $(CF_3)_2POP(CF_3)_2$ is easily made by the action of $(CF_3)_2PCl$ or $(CF_3)_2PI$ on Ag_2CO_3 at 25°, and is stable to 250°.[21] Its volatility (24 mm at 0°) is about 10% higher than that of $P_2(CF_3)_4$, suggesting a nearly linear POP chain with strong two-way $O \rightarrow P$ π bonding; confirmatory is the absence of any infrared band assignable to POP symmetric stretching. There is no analogous alkyl- or aryldiphosphoxane; all attempts to make even $(CH_3)_2POP(CF_3)_2$ led only to $P_2(CF_3)_4$ and the diphosphine dioxide $[(CH_3)_2PO]_2$,[21] and the quest for $(CH_3CF_3P)_2O$ fared no better.[23] On the other hand, the dioxide of $P_2(CF_3)_4$ apparently cannot exist: POP bonding takes priority.

The diphosphoxane $(CF_3)_2POP(CF_3)_2$ may be regarded as the anhydride of the phosphinous acid $(CF_3)_2POH$, and indeed its only known basic property is formation of transition-metal complexes wherein P receives π electrons effectively. Its electron-acceptor character is demonstrated by its formation of a 1:1 adduct with trimethylamine, presumably with some suppression of $O \rightarrow P$ π bonding. Its POP bond cleavages by protic and Lewis acids need not depend upon base action by the POP oxygen.

The Phosphinous Acid. The compound $(CF_3)_2POH$ can be made by HCl cleavage of $(CF_3)_2POP(CF_3)_2$ at 80°;[21] the similar cleavage by water is harder to control. A more interesting synthesis occurs when $(CF_3)_2PH$ (low-pressure vapor) passes over HgO: presumably $(CF_3)_2HPO$ is formed first, but much of it converts rapidly to $(CF_3)_2POH$ in a process reversing the sense of the Arbuzov rearrangement. This illustrates especially well the antithetical character of the CF_3 phosphine chemistry *vs.* the hydrocarbon phosphine chemistry.

The "Phosphonous" Acid. Esters of the type $CF_3P(OR)_2$ are easily made from CF_3PCl_2, but the free acid $CF_3P(OH)_2$ does not exist as such. Attempts to make it lead instead to a phosphinic acid, CF_3HPOOH (dimeric, with 8 kcal per hydrogen bond, like a carboxylic acid),[24] just as the phosphonic acid $HPO(OH)_2$ is obtained instead of phosphorous acid, $P(OH)_3$. In such cases it seems that the oxygen atoms lose basicity by π bonding to phosphorus, which then has enough base strength to take a proton from oxygen. Another indication of poor base action by such oxygen atoms is the difficulty of acid cleavage of $CF_3P(OCH_3)_2$: HCl is virtually ineffective, but the stronger acid HBr works slowly at 25°.

Acetoxyphosphines. The types $(CF_3)_2POR$ and $CF_3P(OR)_2$ include four volatile compounds with R = acetyl or trifluoroacetyl, again with no known parallel in conventional organophosphorus chemistry. The initial synthesis was by the action of $(CF_3)_2PI$ on $AgCO_2CF_3$ to form $(CF_3)_2POOCCF_3$. This proved to be moderately unstable, equilibrating with minor proportions of $(CF_3)_2POP(CF_3)_2$ and $(CF_3CO)_2O$, demonstrating that these could be used for a cleaner synthesis. Now it was argued that the C–CF_3 group withdraws π electrons from the P–O bond, so that $O \rightarrow P$ π bonding is less than in the corresponding compound $(CF_3)_2POOCCH_3$. Accordingly, this acetoxyphosphine was made quantitatively from acetic anhydride and $(CF_3)_2POP(CF_3)_2$ and proved to be quite stable.[25] Its 1:1 trimethylamine adduct (presumably with an $N \rightarrow P$ dative σ bond) proved to be slightly less stable than that of the diphosphoxane.

The bis(acetoxy)phosphines $CF_3P(OOCCH_3)_2$ and $CF_3P(OOCCF_3)_2$ are so unstable as to require flow methods for efficient synthesis: one passes CF_3PCl_2 vapor over $AgCO_2CH_3$ or $AgCO_2CF_3$. They condense with loss of the corresponding acetic anhydrides to form open POP chains with acetyl end groups. No $(CF_3PO)_n$ rings ever were formed, and the infrared

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(23) D. K. Kang, Ph.D. Dissertation, University of Southern California, 1969.

(24) A. B. Burg and J. E. Griffiths, *J. Am. Chem. Soc.*, **83**, 4833 (1961).

(25) L. K. Peterson and A. B. Burg, *ibid.*, **86**, 2587 (1964).

spectra showed no P=O stretching bands, meaning that there was no Arbuzov-like rearrangement to a phosphine oxide.[25]

Stability of Oxyphosphines: the ROQ Rule. The principle illustrated by the acetoxyphosphines can be generalized to include many mixed acid anhydrides, formed by group exchange between two different acid anhydrides. Since acid anhydrides normally have some π bonding between oxygen and the atoms which it connects, it can be argued that the stability of the mixed anhydride is improved by a difference in π-acceptor strength of those two atoms: the process ROR + QOQ → 2ROQ becomes irreversible if the π-acceptor strength of R is significantly greater than that of Q. The reason is that the three-atom π bonding in ROR will amount to less than the two O→R π bonds in 2ROQ, while the energetics of O→Q π bonding cannot restore equality unless Q accepts π bonding as strongly as R does.

By this argument, we recognize that $(CF_3)_2POOCCH_3$ is stable because P has better π-acceptor strength than C in the POC bond; but in $(CF_3)_2POOCCF_3$ the difference is smaller, leading to moderate reversion to the two acid anhydrides. In the bis(acetoxy)phosphines, the CF_3P unit has less π-acceptor power and must employ it in two directions, so that stability suffers.

The possibility of a stable $(CF_3)_2POP(O)(CF_3)_2$ relates to the same principle: the phosphinate part should be a stronger π acceptor than the phosphinite moiety. The general study of element oxyphosphines on this basis should be interesting.

Siloxyphosphines. The π-acceptor action of phosphorus in $(CF_3)_2POP(CF_3)_2$ should be considerably more effective than that of silicon in $R_3SiOSiR_3$ compounds. Accordingly, the ROQ rule predicts stability for the $R_3SiOP(CF_3)_2$ type. In fact, the volatile $(CH_3)_3SiOP(CF_3)_2$, made by three different quantitative processes, seems permanently stable at 100°.[26] Its failure to combine with BF_3 supports the assumption of strong π bonding by the oxygen electrons. The analogous compound $H_3SiOP(CF_3)_2$ is less stable, but only because the Si–H bond cleaves the P–O bond.

The main principle extends also to the polyphosphinoxysilanes, initial examples of which are $HSi[OP(CF_3)_2]_3$ and $Si[OP(CF_3)_2]_4$. Both are stable at 100° and volatile in the high-vacuum line at 25°. Compounds in this class could serve as interesting polyfunctional ligands for metal complexes.

Boroxyphosphines.[27] The three volatile boron phosphinites $(CH_3)_2BOP(CF_3)_2$, $CH_3B[OP(CF_3)_2]_2$, and $B[OP(CF_3)_2]_3$, made by using the corresponding boron chlorides to cleave $(CF_3)_2POP(CF_3)_2$, further illustrate three-atom π bonding by oxygen 2p electrons. At 100° the monophosphinite is quite stable but the diphosphinite forms a trace of $(CF_3)_2POP(CF_3)_2$, presumably because the other product, $(CH_3BO)_3$, has ring π stabilization. Similarly, the irreversible decomposition of the triphosphinite (slow at 25°, but fairly rapid at 60°) may be ascribed to the stability of the product B_2O_3 or its predecessors. The different driving forces for decomposition make it difficult to judge π stabilization in these boroxyphosphines in terms of the ROQ π theory; indeed, one cannot even decide whether B or P is the stronger π acceptor in each compound.

However, it is interesting that the ether complex $(CH_3)_2O \cdot B[OP(CF_3)_2]_3$ is quite undissociated in the liquid phase, whereas no such complex of $B(OCH_3)_3$ exists even in solution in dimethyl ether at low temperatures. It appears that the electron-withdrawing power of the three $P(CF_3)_2$ groups is enough to make $B[OP(CF_3)_2]_3$ almost as strong a Lewis acid as boron trifluoride.

Arbuzov Effects of a Methyl Group.[23] The phosphinous ester $CH_3OPCH_3CF_3$ can be made by methanolysis of CH_3CF_3PCl in the presence of trimethylamine, and seems stable, although CH_3I catalysis converts it in the Arbuzov manner to the phosphine oxide $(CH_3)_2CF_3PO$ easily at 65°. Similarly, the kinetically stable $CH_3SPCH_3CF_3$ readily undergoes, with catalysis, an Arbuzov-like rearrangement.

Of special interest is an Arbuzov-like action of HCl on $(CH_3)_3COPCH_3CF_3$, forming $(CH_3)_3CCl$ and the stable CH_3CF_3HPO. All attempts to make the analogous $(CH_3)_2HPO$ have failed: it seemed that the desired product disproportionated completely to $(CH_3)_2PH$ and $(CH_3)_2POOH$.[28] Also $(CF_3)_2HPO$ could not be obtained: its conversion to $(CF_3)_2OPH$ (an "anti-Arbuzov" reaction) was too fast.[28] It seems that CH_3CF_3HPO lacks whatever structural or mechanistic character may be required for either process, and so remains stable. Some diaryl–HPO compounds also are reported to be stable, presumably for the same reason.

Phosphinoamines. The ammonia chemistry of the $P(CH_3)_2$, PCH_3CF_3, and $P(CF_3)_2$ groups offers interesting trends and contrasts which correlate with (but are not fully explained by) an increase of phosphorus π-acceptor character in the indicated order. For example, all attempts to make $H_2NP(CH_3)_2$ have led only to $NH[P(CH_3)_2]_2$, which itself easily equilibrates with NH_3 and $N[P(CH_3)_2]_3$ on mild heating;[29] in contrast, $H_2NP(CF_3)_2$ is the only phosphinoamine directly obtainable by ammonolysis of a $(CF_3)_2PX$ compound.[30] To obtain $HN[P(CF_3)_2]_2$ one uses more $(CF_3)_2PX$ with $(CH_3)_3N$ present to remove the HX, and $N[P(CH_3)_2]_3$ has been made only from the salt $NaN[P(CF_3)_2]_2$.[31] Presumably the N–$P(CH_3)_2$ system is governed more by the effect of the $P(CH_3)_2$ group upon nitrogen hybridization than by the π-bond

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(29) A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).

(30) G. S. Harris, *J. Chem. Soc.*, 512 (1958).

(31) A. B. Burg and J. Heners *J. Am. Chem. Soc.*, **87**, 3092 (1965).

relationships which are so much stronger in the N–P-$(CF_3)_2$ system. The N-PCH_3CF_3 chemistry is intermediate: $H_2NPCH_3CF_3$ and $HN(PCH_3CF_3)_2$ are easily made and interconverted by NH_3 or HCl,[19] and $N(PCH_3CF_3)_3$ probably will not be difficult to make.

The compound $HN[P(CF_3)_2]_2$ (stable at 250°) represents an extreme example of N→P π bonding: the nitrogen lone-pair electrons are so fully employed that HCl cannot cleave the N–P bond even at 100°, while the σ-acceptor character of the phosphorus is so diminished that ammonia fails to cleave that bond either in the liquid phase or in the gas phase at 200°. In $N[P(CF_3)_2]_3$ the NP_3 pattern may be nearly planar, with even less N-base action, so that its quantitative cleavage back to $HN[P(CF_3)_2]_2$ by HCl (at 100°), H_2O, $H_2NP(CF_3)_2$, or NH_3 seems attributable to the residual σ-acceptor strength of phosphorus.

Close analogs of such chemistry are provided by the $As(CF_3)_2$ group, for which there is considerable evidence of weaker π-acceptor action.[32] The compound $HN[As(CF_3)_2]_2$ is easily acid cleaved, and $(CF_3)_2PCl$ attacks it to form $(CF_3)_2AsCl$ and successively $(CF_3)_2AsNHP(CF_3)_2$ and $HN[P(CF_3)_2]_2$—all in the direction of increasing π-bond energy. Also, when HCl cleaves either $(CF_3)_2AsNHP(CF_3)_2$ or $(CF_3)_2AsN[P(CF_3)_2]_2$, the liberation of $(CF_3)_2AsCl$ is quantitative, but no $(CF_3)_2PCl$ is formed. An improvement of π-bond energy again is recognized when $(CF_3)_2AsOAs(CF_3)_2$ reacts with $2(CF_3)_2PCl$ to form $2(CF_3)_2AsCl$ and $(CF_3)_2POP(CF_3)_2$.[32]

Phosphinoboron Hydride Chemistry

Dative Bonded Rings. A fuller understanding of the bonding principles represented by the prototype $(PB)_3$ ring compound $[(CH_3)_2PBH_2]_3$ (stable to 400°)[33] required some variation of the groups on phosphorus, but it could not have been predicted that $[(CF_3)_2PBH_2]_3$ would even exist. The actual discovery of this 200°-stable trimer was based upon the hope that heating the equilibrium mixture of $(CF_3)_2PF$, B_2H_6, and $(CF_3)_2PF\cdot BH_3$ would lead to an interesting result.[34] A more effective synthesis was from $(CF_3)_2PI$ and B_2H_6, going through the formation of $(CF_3)_2PH$ and BI_3 at 100°.[35]

The stability of $[(CF_3)_2PBH_2]_3$ cannot be ascribed to good P→B dative σ bonding, for the $(CF_3)_2P$ group is remarkably weak in that respect: $(CF_3)_2PF\cdot BH_3$ is extremely unstable, and neither $(CF_3)_2PH$ nor $P_2(CF_3)_4$ can hold either BF_3 or BH_3 in a demonstrable manner. It seems necessary to assume that the B–H bonding electrons delocalize toward the phosphorus π-acceptor orbitals, strengthening the P→B σ-dative bonding by relief of its adverse polarity.

By this hypothesis, replacement of CH_3 by CF_3 on P would enhance this π effect, widening the HBH bond angle. In fact, such an increase in the HBH bond angle is detectable by a comparison of infrared spectra. As the angle widens, the BH_2 out-of-plane rocking mode must decrease its radius of gyration, sharply increasing the frequency. The BH_2 in-plane rocking frequency also must increase, because greater electronegativity strengthens the B–H bonding, but this effect is small. The list of frequencies (cm^{-1}) given in Table I seems confirmatory.

Table I

	In-plane ρ		Out-of-plane ρ	
	BH_2	BD_2	BH_2	BD_2
$[(CH_3)_2PBH_2]_3$	665	515	812	603
$(CH_3CF_3PBH_2)_3$	693		903	
$[(CF_3)_2PBH_2]_3$	715	566	995	755
$[(CF_3)_2AsBH_2]_3$	636?		960	
$[(CH_3)_2NBH_2]_3$[36]	826?		850	

The intermediate compound $(CH_3CF_3PBH_2)_3$ is interesting on account of the atypical polymerization of its unit: whereas the other trimers seem to be the most stable of the possible polymers, the $CH_3CF_3PBH_2$ unit goes wholly to the high-polymer form when one heats the adduct $CH_3CF_3PH\cdot BH_3$ in a very small container; the trimer could be made only in the gas phase, in yields not higher than 35%. Also interesting is the isomerism which occurs because the CH_3 and CF_3 groups occupy axial or equatorial positions of a cyclohexane-like $(PB)_3$ ring. However, the mixture seemed to convert to one species during long storage at moderately elevated temperatures.

Also quite interesting is the existence of $[(CF_3)_2AsBH_2]_3$,[37] for arsenic should be weaker than phosphorus in regard to both σ-dative and π-acceptor bonding. In fact, its synthesis did require condensation from a circulating gas system, for it is unstable at 25°.

Phosphinopentaboranes. Compounds of the $R_2PB_5H_8$ type have been made fairly easily from LiB_5H_8[38] and R_2PCl, and also show interesting differences as R goes from CH_3 to CF_3.[39] The slightly volatile $(CH_3)_2PB_5H_8$ gives H and B nmr spectra proving that a BPB bridge has replaced one BHB bridge in the base of the B_5H_9 structure. It is somewhat unstable, changing to a resin in which the basic $(CH_3)_2P$ unit acts as a stabilizer. The less basic CH_3CF_3P group also bridges boron in the B_5H_9 basal square, but now isomerism is possible. The initially formed $CH_3CF_3PB_5H_8$ is associated and slightly volatile, but converts completely to the far more volatile isomer, with the positions of CH_3 and CF_3 reversed; this isomer is permanently stable. Finally, the $(CF_3)_2P$ group does not form a BPB bridge, apparently because stronger basicity by phosphorus would be needed for that; instead, it goes to the pyramid-peak position where the high electron density doubtless is somewhat shared with phosphorus. Here again is a permanently stable compound, 1-$(CF_3)_2PB_5H_8$. These compounds

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(32) J. Singh and A. B. Burg, *J. Am. Chem. Soc.*, **88**, 718 (1966).

(33) A. B. Burg and R. I. Wagner, *ibid.*, **75**, 3872 (1953).

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(36) A. B. Burg and J. S. Sandhu, *J. Am. Chem. Soc.*, **89**, 1626 (1967).

(37) A. P. Lane and A. B. Burg, *ibid.*, **89**, 1040 (1967).

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suggest an extensive chemistry of phosphinopolyboranes.

Alkene and Alkyne Chemistry

Dr. Louis R. Grant, Jr., has thoroughly explored the addition of the diphosphine $(CF_3)_2PP(CF_3)_2$ in a halogen-like manner to C_2H_4, C_2F_4, and C_2H_2. New C–C connected multiple phosphines in considerable variety arise from the transfer of CF_3 groups from one phosphorus to another, or even from phosphorus to carbon; such effects occur especially when iodine is used as a catalyst. Some of the acetylene products were ethylene derivatives, subject to hydroboration. For fuller details, the original dissertation is recommended.[18]

Transition Metal Complexes

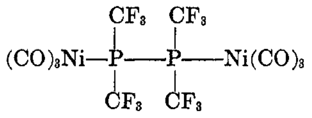
Ligands having both σ-donor and π-acceptor bonding power (phosphines, arsines, stibines, organic sulfides, CO, or CN^-) often attach very strongly to transition elements, for such bonds reinforce each other: either a σ or a π bond alone would have unfavorable polarity, but a σ bond from the ligand and a π bond from the d-electron system of the metal can mutually neutralize these bond-weakening polarities. All types of fluorocarbon phosphines are potentially useful for studies of such bonding and a few of them have been so employed, with interesting results. Our own work on the subject has been concerned primarily with substances made by displacing CO from nickel tetracarbonyl.

Monophosphine Ligands. Early in the year 1957, Mahler sought to make a $Ni[(CF_3P)_4]_2$ sandwich compound (before the P_4 ring was proved not to be flat) and obtained such a mixture of polymers that a study of simpler systems obviously was needed. It was soon found that $(CF_3)_3P$ would displace one or two CO from $Ni(CO)_4$,[40] but no third $(CF_3)_3P$ unit could be sterically accommodated.[41]

A more thorough study of such substances[42] showed that ligand–nickel bond strength increases in the order PF_3, CF_3PF_2, $(CF_3)_2PF$, $(CF_3)_3P$, but steric interference becomes noticeable for $[(CF_3)_2PF]_3NiCO$, and in $[(CF_3)_2PF]_4Ni$ the nickel(0) atom is so well covered that air fails to attack it at 85°. The effect of CF_3 on the bonding power of phosphorus is attributed to better $Ni \rightarrow P$ π bonding, since the P–CF_3 bond would not compete with that as P–F could. In fact, the infrared spectra (extending the broad study by Bigorgne)[43] show that the P–F bond does offer a small π-bonding competition against $Ni_{3d} \rightarrow P$ π bonds, causing a slightly weaker C═O bond than when CF_3 replaces F on P.

The compound $[(CF_3)_3P]_2Ni(CO)_2$ is not quite stable: the colorless liquid slowly turns intensely red, with infrared absorption at 1878 and 1897 cm^{-1} showing Ni–(CO)–Ni bridging in a stable nonvolatile and an unstable volatile species;[44] the ^{19}F nmr spectrum also shows these products. At elevated temperatures the analogous $[(CF_3)_3P]_2CoNOCO$ also decomposes partially, giving a nonvolatile product which seems to be a CO-bridged tricobalt species.[45] For cobalt, of course, CO bridging is common, but for nickel it has been quite rare.

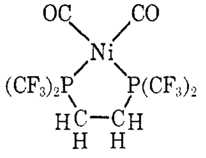
Polyphosphines and Chelation. The action of $P_2(CF_3)_4$ on $Ni(CO)_4$ led to an extension of the $(CF_3)_3PNi(CO)_3$ type,[40] namely



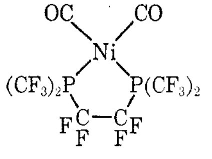
$$(CO)_3Ni—\underset{CF_3}{\overset{CF_3}{P}}—\underset{CF_3}{\overset{CF_3}{P}}—Ni(CO)_3$$

simply designated as "NiPPNi."[41] Its dark red color is strongly visible even for the vapor at 0.5 mm (20°) and is attributed to π-electron delocalization over the chain. Presumably a P_4Ni_2 ring or a polymeric $(P–P–Ni)_n$ chain could be made by using more $P_2(CF_3)_4$, but this aspect requires further attention.

The bifunctional phosphines $(CF_3)_2PC_2H_4P(CF_3)_2$ and $(CF_3)_2PC_2F_4P(CF_3)_4$[18] have been applied to nickel carbonyl to form the two colorless, volatile nickel chelate ring compounds

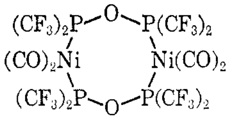


and



and polymeric by-products.[42,46] The C_2H_4-connected ring compound is more stable (and less volatile); a second molecule of the bisphosphine can displace one more CO, but for steric reasons cannot form a spiran. The C_2F_4-connected ring compound slowly turns pink on standing, presumably forming a CO bridge in the manner of $[(CF_3)_3P]_2Ni(CO)_2$.

Nickel Sesquicarbonyls. Bisphosphines of the general type $(CF_3)_2PXP(CF_3)_2$ obviously are eligible as ligands for transition elements, but not for chelation if only because the PXP bond angles are too wide. For example, $(CF_3)_2POP(CF_3)_2$ probably has almost linear POP bonding (like disiloxane but with stronger π bonding); hence the main product of its reaction with nickel carbonyl is the somewhat unstable eight-atom-ring compound[47]



Having no π delocalization of P lone pairs across oxygen, this compound is colorless, like the nickel complexes of monophosphine ligands.

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(40) H. J. Emeléus and J. D. Smith, *J. Chem. Soc.*, 527 (1958).

(41) A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, **80**, 2334 (1958).

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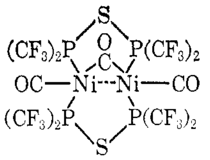
In contrast, the ligand $(CF_3)_2PSP(CF_3)_2$[48,49] has less effective central π bonding, as shown by comparing the reactions

$$(CF_3)_2POP(CF_3)_2 + HOH \longrightarrow 2(CF_3)_2POH$$

and

$$(CF_3)_2PSP(CF_3)_2 + HSH \rightleftarrows 2(CF_3)_2PSH^{49}$$

By the ROQ rule the latter is reversible only because the PSP π bonding is fairly weak. Accordingly, the PSP bond is not so wide, and it is deformable enough to permit the structure



which is like the $(POPNi)_2$ ring compound except for the CO bridge across the middle.

This bicyclononane-like structure has been proved by X-ray crystallography.[50] The six-atom rings have the cyclohexane chair form, so that a one-atom connection between the sulfur atoms would complete an adamantane-like pattern of connectivity.

Presumably the similar sesquicarbonyls made from the PNP bisphosphines, namely $\{HN[P(CF_3)_2]_2\}_2Ni_2(CO)_3$ and $\{CH_3N[P(CF_3)_2]_2\}_2Ni(CO)_3$, would have a similar structure. They are appreciably more stable than the sulfur compound, probably because the PNP angle in the free ligand is not too far from that in the complex. Moreover, the HN compound is slightly more stable than the CH_3N compound, possibly because nitrogen can have a more suitable hybridization in the HNP_2 unit than in the CH_3NP_2 unit.[51]

All of these sesquicarbonyls are yellow solids, apparently stable in air and sublimable by heat under high vacuum. The infrared spectra of both nitrogen compounds could be recorded for the vapors at 110°, and some volatility measurements (*e.g.*, 1.36 mm at 116.5°) were possible for the HN compound.

Such examples indicate that the CF_3 phosphine ligands can contribute very well to the chemical variety of metal carbonyl analogs, with much yet to be learned.

Phosphorus(V) Chemistry

The CF_3 chemistry of phosphorus in oxidation state 5 is another diverse area of research, approachable by various routes from the CF_3 phosphines.

Oxygen Compounds. The very strong acids $CF_3PO(OH)_3$ and $(CF_3)_2POOH$ originated at Cambridge,[52,53] and the related sulfur compounds (acids, halides, amides, and esters) also come fairly easily from the phosphines.[54,55] Oxidation of a CF_3 phosphine by mercuric oxide is very effective, often with interesting side effects; for example, the action of $(CF_3)_3P$ on HgO gives no $(CF_3)_3PO$, for one-third of the CF_3 groups go to make the slightly volatile $Hg(CF_3)_2$,[56] while the remaining $(CF_3)_2P$ groups form a mercury phosphinate.[57] This product reacts with methyl iodide at 100° to form the ester $CH_3OPO(CF_3)_2$, which can be made also (in 80% yield) by passing $CH_3OP(CF_3)_2$ over HgO at 100°.

The easy oxidation of $(CF_3)_3P$ by NO_2 provides a quantitative synthesis of the highly volatile phosphine oxide $(CF_3)_3PO$, which undergoes a quantitative one-stage aminolysis to $(CH_3)_2NPO(CF_3)_2$; this is convertible by high-pressure HCl to $(CF_3)_2POCl$, from which an extensive phosphinic acid chemistry can be developed.[58] The NO_2 oxidation of CF_3PCl_2[59] also is quantitative, but the action of NO_2 on $(CF_3)_2PCl$ is far more complex, yielding $(CF_3)_2PCl_3$ (23%), $(CF_3)_2POCl$ (33%), $[(CF_3)_2PO]_2O$ (33%), and apparently NO^+-$(CF_3)_2PO_2^-$ (11%).

Nitrilophosphoric Polymers. The highly electronegative CF_3 group also contributes unique effects to $(NPX_2)_n$ chemistry. It does not seem possible to make the $[NP(CF_3)_2]_n$ polymers by conventional ammonolytic processes using $(CF_3)_2PCl_3$, for the CF_3 group is removed or destroyed. However, they are formed easily enough by the decomposition of $(CF_3)_2PN_3$,[60] or more safely by adding chlorine to $(CF_3)_2PNH_2$ and removing 2HCl by use of trimethylamine.[61] High polymers predominate and seem to be more stable than the trimer or tetramer, for an open-chain pattern allows each nitrogen atom to use freely both of its lone electron pairs for the very strong three-atom π bonding which the CF_3 groups induce. However, phosphorus in $[NP(CF_3)_2]_n$ still has some σ-acceptor strength, for these otherwise very promising thermally stable plastics are easily destroyed by water.

Based as it is upon a 1-hr lecture at the 157th National Meeting of the American Chemical Society, this brief review has necessarily omitted a considerable number of results obtained in other laboratories, although an effort has been made to include whatever would contribute to the main theme of chemical understanding and to illustrate further the wide scope of applicability of CF₃ phosphines to other fields of chemistry. I am indeed grateful for the excellent work done by my present and former colleagues, and happy about good work done elsewhere. In such a large field, there is ample room for entry by other creative minds and hands. It is a pleasure to acknowledge generous support by the U. S. Air Force during the first 8 years of our research and subsequently for 7 years by the National Science Foundation, as well as parallel interest and support by the Office of Naval Research for aspects concerning boron.

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