Heteroatom Chemistry
Volume 10, Number 7, 1999

Molecules That We Made: An Essay on Phosphorus Chemistry

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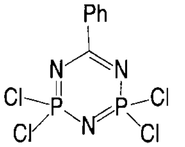
In 1963, I was looking for a reagent that could convert a nitrosamine to a triazene, and I thought that a phosphazene in a Wittig-type reaction might do so. What I had intended never came true, but it caused me to look more closely at phosphorus chemistry. This look made me stay there for the rest of my days in research.

At that time, there was much discussion about the bonding in cyclophosphazenes. Irritatingly, we write the formula of a cyclotriphosphazene like that of an aromatic six-membered ring. Would fragments of these two ring types in praxi fit together? By different multistep syntheses [1–6], and by subsequent substitution reactions [7–9], we prepared many triazaphosphinines and triazadiphosphinines, such as **1**. X-ray analyses [10,11] documented the clean merger of the two parts.



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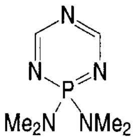

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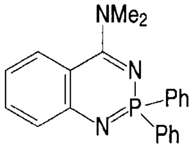

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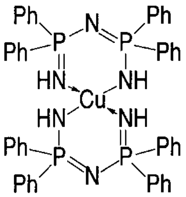
Other positive answers to the above question were the syntheses of **2** and of the corresponding triazadiphosphinine, just by warming triazine with the respective aminophosphazene [12], and the thermal rearrangement of a 2-cyanophenyl phosphazene leading to **3** [13]. Recently, these so-called cyclocarbaphosphazenes were reviewed [14].

We used the functionalized phosphazenes, which we had in hand also as chelating ligands [15–17], as in **4**, and, in 1964, we wrote a half-page note about these chelates. Meanwhile, metal imidodiphosphinates and metallacyclophosphazenes have established wide fields of their own, with a large and still increasing number of representatives.



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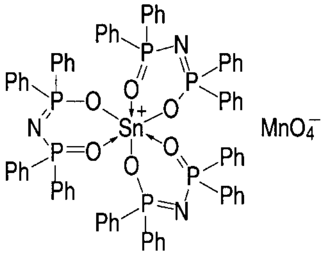

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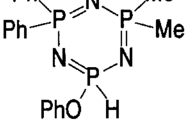
Of the tin derivatives [18–20], I remember, in particular, a tris(imidodiphosphinato)tin chloride. It completely decolorizes an aqueous $KMnO_4$ solution and becomes the permanganate **5**, which can be isolated as purple crystals. When we tried to introduce P(III) in a cyclophosphazene, we obtained the first examples of hydridophosphazenes, such as **6** [21–23], and, from them we obtained metal derivatives, such as **7** [24,25]. Somewhat later, another access to such compounds was found [26], and recently even a trishydridocyclotriphosphazene could be made [27].



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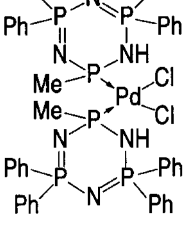

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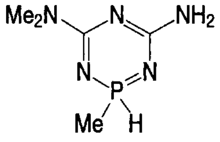
From a study of the prototropic equilibrium between aminophosphines $R_2P\text{-}NHR$ and hydridophosphazenes $R_2PH{=}NR$, we obtained additional cyclic and acyclic examples of the latter, such as **8** and **9** [18–30].



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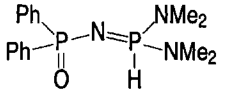

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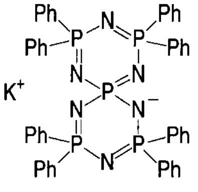
^{31}P NMR spectroscopy was very new at that time, and we tried to learn more about the chemical shifts from systematic investigations [31–36]. Often, we had to prepare the necessary compounds for the first time. One of them was a tetrachlorophosphonium perchlorate, a compound with the puzzling formula PCl_5O_4.

Phosphazenes are generally prepared from PCl_5, or some other chlorophosphorane, and ammonia. The reaction involves both substitution and condensation, and it has often been studied since the time of Liebig and Wöhler [37]. Its most prominent products are the cyclophosphazenes $(NPCl_2)_n$. We found out how to confine the reaction to substitution alone and thus obtain the tetraaminophosphonium chloride $P(NH_2)_4^+\ Cl^-$ [38,39]. The corresponding iodide nicely demonstrates how new achievements depend on those of the preceding generation; in 1954, Robert Klement in the Munich laboratory [40] prepared $PS(NH_2)_3$, which, in our hands, gave $P(NH_2)_4^+\ I^-$ [41,42]. Recently, Wolfgang Schnick, who is now also at this university, obtained P_3N_5 in crystals suitable for structure analysis by thermolysis of the latter [43].

Of phosphazenes with alternating P and N members, cationic acyclic and neutral cyclic examples, $N_{n-1}P_nX_{2n+2}^+$ and $N_nP_nX_{2n}$, have long been known. Consequently, anionic bicyclic phosphazenes were to be anticipated with a formula $N_{n+1}P_nX_{2n-2}^-$. The spirocycle **10** became their first representative [44–46]. The variations, **11** and **12**, of monocyclic phosphazenes contain an O in place of an N atom or an additional N atom in the ring [47,48].



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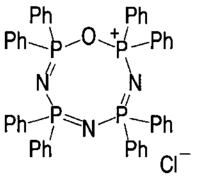

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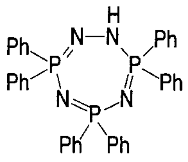

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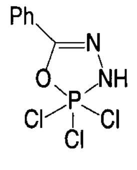
As we had done in **12**, we made the hydrazine unit also a part of the ring in some other types of cyclic phosphazenes. After we had earlier used amidines to provide building blocks, we now utilized amidrazones and acyl hydrazines. The reaction of the latter with PCl_5 had earlier been used to obtain nitrile imines. In repeating the reaction [49], we isolated intermediates such as **13**. They may be viewed as cycloadducts of phosphine oxides and nitrile imines, and in fact, they decompose to give such products.



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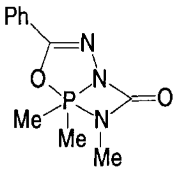

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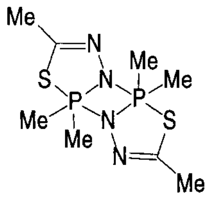

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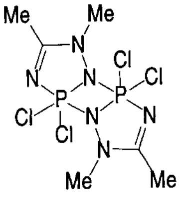
The nonionic structure of **13** taught us that the five-membered ring effectively favors the pentacoordination of phosphorus [50]. The phosphazene (1,3,4,2λ^5-oxadiazaphosphole), of which **13** is the hydrochloride, consequently forms a dimer if it is not trapped [51] in a cycloadduct of type **14**. We found most of the other five-membered cyclic phosphazenes, which have a heteroatom adjacent to phosphorus, to be dimeric as well; see, for example, thia- and selenadiazaphospholes such as **15** [52,53], or the derivatives **16** and **17** of the isomeric triazaphospholes [54–56]. Amino substituents can sufficiently counteract the tendency toward dimerization, and thus the phosphazene **18** remains monomeric.



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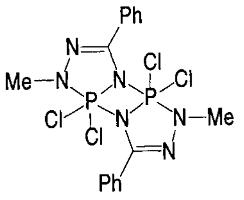

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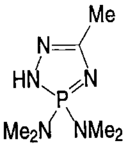

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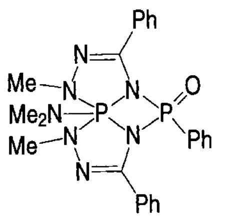
Compound **19** is remarkable inasmuch as PN_5 coordination is otherwise very rare. It stands as an example of the many variations of how triazaphosphole rings can combine to form more complex molecules [57–60], some of which will be mentioned subsequently. Spirocyclic structures such as **20** also turned out to be the correct ones [61,62] for some known compounds to which, however, open chain and eight-membered monocyclic structures were ascribed earlier.



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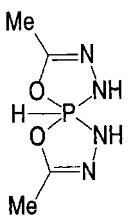

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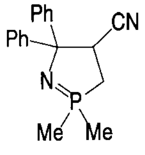
With Rolf Huisgen's laboratory next door to ours we were, of course, familiar with 1,3-dipoles and their reactivities. Methyleneaminophosphines $R_2P\text{-}N=CR_2$ [63,64] are not immediately recognized as dipoles; however, they readily give 3 + 2 cycloaddition products with alkenes and alkynes. The cycloadducts, such as **21**, are five-membered cyclic phosphazenes that stay monomeric but which add almost any other unsaturated system to their P=N bond. With ketones, we observed the occurrence of an aza-Wittig reaction, of which the intermediate **22** can be isolated [65,66]. We also obtained adducts with CO_2 and CS_2 [67], isocyanates [68], isothiocyanates [69], ketenes [70], iminophosphines and iminophosphoranes [71], epoxides [72], nitrones, nitrile oxides, and nitrile imines [73,74]. A one-pot combination of the two mentioned types of cycloaddition was found in the reaction of the methyleneaminophosphite $(MeO)_2P\text{-}N=CPh_2$ with *p*-nitrobenzaldehyde [75]; four acyclic molecules combine to form the tricyclic structure **23**.



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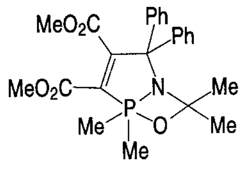

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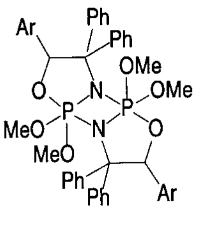
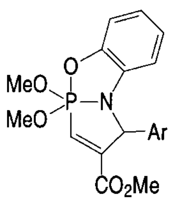


23

Where the demands of its parts are in accord, the whole will be stable. A molecule of this kind will be of low energy and will form selectively. On the basis of this rule, we prepared many more compounds with a five-coordinate phosphorus atom as the bridgehead of two or three five-membered rings [76–82]. Two of them stand out in my mind: the two rings of compound **24** form in one step when a propiolate ester adds to an *o*-(methyleneamino)phenyl phosphite [79], and the two rings of the dark red compound **25** result when a chlorophosphine is chelated with TAN, a reagent otherwise used in metal analysis [80]. The stereochemistry of these phosphoranes was elucidated and reviewed by Bill Sheldrick [83–85].



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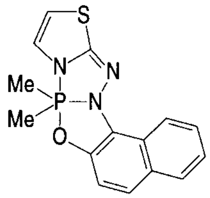

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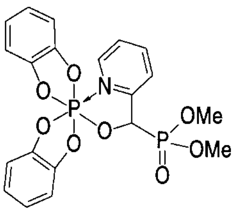

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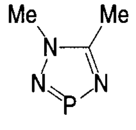
Though it had not been articulated, the fact that five-membered rings were beneficial to phosphorus pentacoordination had long been utilized; in 1927 Ludwig Anschütz had prepared the *o*-phenylene ester of the hypothetical orthophosphoric acid $P(OH)_5$ [86]. Later, its identity was much debated, but we were able to confirm it [87]. With the help of pyrocatechol substituents, we also achieved cations and neutral compounds of six-coordinate phosphorus [88–90], of which **26** provides an example.

It certainly seems to be a break in continuity when most of what follows involves phosphorus in a low-coordination state. What appears to be a contrast nevertheless stems from the same root and was developed side by side with the above results: reduction of compounds **16** and **17** gave the 1,2,4,3λ^3-triazaphospholes **27** and **28** [54]. By a different route, they had been obtained previously in Toulouse [91]. The 6π-system of these heterocycles requires a two-coordinate phosphorus. This leads to a paradox which, however, is well founded. While acyclic λ^5-phosphazenes are mostly monomeric, λ^5-triazaphospholes form dimers. While, on the other hand, acyclic λ^3-phosphazenes (or iminophosphines as they are usually called) mostly form dimers, λ^3-triazaphospholes are monomeric.



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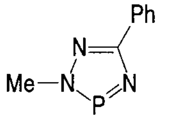

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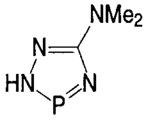

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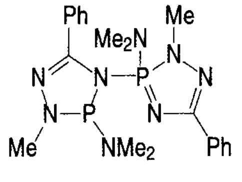
We obtained additional triazaphospholes (and among them the *N*-functional example **29**) readily by reaction of amidrazones or aminoguanidines with PCl_3 or $P(NMe_2)_3$ [92–94]. Their reactivity resides primarily in the P=N bond. Oxidation by bromine [60] or sulfur [95] or complex formation [96,97] initiates its self-addition. Bicyclic or polycyclic oligomers are the result. The dimers **30** and **31** exemplify them.



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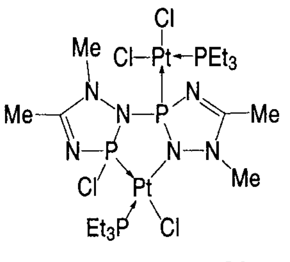

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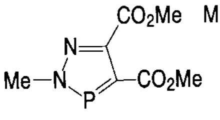
We found that, in **28**, a benzonitrile fragment can be exchanged for an acetylene yielding the diazaphosphole **32** [98]. Dialkyl-1*H*- and -2*H*-1,2,3-diazaphospholes such as **33** and **34**, became available from ketone hydrazones and PCl_3 [99–101]. The first 2*H*-isomer had been prepared this way in Moscow [102]. Substitution at the reactive diazaphosphole 4-position gave various derivatives [100,103–105]. The pathway to them often involves an addition to the P=C bond, as in **35**.



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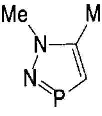

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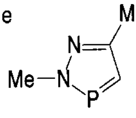

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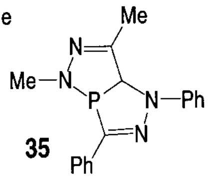

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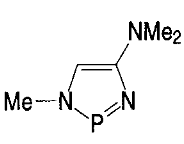
Many more azaphospholes seemed to be possible, and we looked for syntheses of them, primarily ones that are based on PCl_3 or other chorophosphines. As such, chloromethyl dichlorophosphine $ClCH_2PCl_2$ turned out to be useful, and also methylene bis(dichlorophosphine) $CH_2(PCl_2)_2$. Azaphospholes **36–39** were synthesized [106–110], including anelated ones for which the 2-phosphaindolizines **40** and their aza-analogs **41–43** stand as examples [94,110–114].



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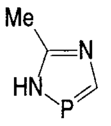

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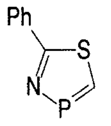

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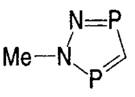

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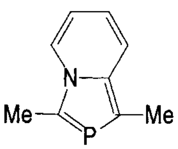

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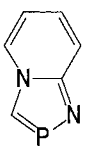

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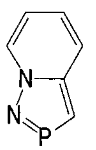

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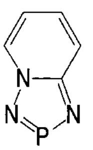

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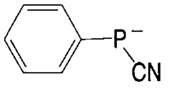
Thus azaphospholes proved to be rich, readily accessible and stable compounds, and I know no good answer to the question why they had not been developed earlier, that is, together with the other azoles in the first half of this century. In one of our reviews [115–120], we therefore called the azaphospholes a postscript chapter to heterocyclic chemistry.

In azaphospholes, a two-coordination of phosphorus and a 6π system are interdependent. Next we looked for acyclic conjugated systems that contain and stabilize two-coordinate phosphorus. Its character can range from phosphide to phosphenium, and its bonding partner consequently should be an electron-withdrawing or donating moiety, respectively. We expected that cyano substituents would take on much of the charge of a phosphide. The dicyanophosphide ion anticipated in this way would extend the pseudohalide series: Cl^-, SCN^-, $P(CN)_2^-$. We found two preparative routes based in essence on the reduction of phosphorus tricyanide [121,122] and on the disproportionation of white phosphorus [123,124].

$$P(CN)_3 + 2e^- \rightarrow P(CN)_2^- + CN^-$$

$$P_4 + 8CN^- \rightarrow 4\ P(CN)_2^- + 4e^-$$

Both equations identify the dicyanophosphide ion as a P(I) compound. It may be viewed as a cyanide complex of P^+. Ligand exchange reactions in a first step gave the cyanophosphinidene derivatives **44–46** [124–127].



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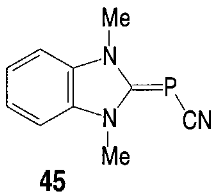

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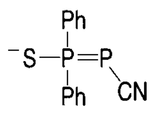
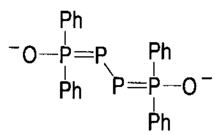


46

The breakdown of PP bonds under the attack of a nucleophile (which was successful in the preparation of $P(CN)_2^-$) attracted our further attention. This way P_4 could even be split in half to give the anion **47** [128]. The two-coordinate phosphorus atoms in the pentaphospholanide **48** [129] and in the diazahexaphosphocine **49** (a cyclotetraphosphazene homolog) [130,131] also originate from P_4.



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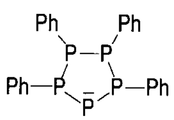

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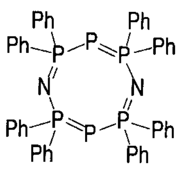
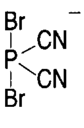


49

Delicate equilibria were found to be derived from the nucleophilic degradation of $(PhP)_5$ [124,126, 132,133]. Such equilibria often allow the transfer of one or more phenylphosphinidene units to another reagent, and there is certainly a lot of unused potential in them. The cyanophenylphosphide **44** is a simple product of such a reaction.

When we added halogens to $P(CN)_2^-$, we entered the novel field of monomeric and dimeric tetra(pseudo)halophosphites (or phosphoranides) and united our work with the work of Keith Dillon [134–137]. The structures of the monomers, such as **50**, provide snapshots along the pathway of a substitution reaction at a halophosphine. In one of these experiments, we accidentally obtained an anion with the puzzling composition $P(CN)_5^-$, the structure of which turned out to be **52** [138].



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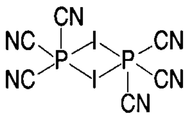

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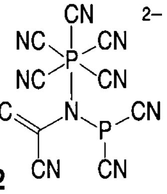
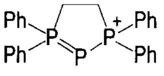


52

As we considered $P(CN)_2^-$ to be a cyanide complex of P^+, it made sense to look also for phosphine complexes of the latter, that is, for triphosphenium ions. The first one was **53** [139]. We obtained the triphenylphosphine complex from PCl_3 simply by adding $AlCl_3$ as a third component [140]:

$$PCl_3 + 2\ PPh_3 + 2e^- \rightarrow (Ph_3P)_2P^+ + 3\ Cl^-$$

Although part of a cation, its central phosphorus atom has phosphide character. Alkylation gave dications of triphosphines [141] and of tetraphosphines **54** [142]. The hexakis(dimethylamino) triphosphenium ion **55** proved to be particularly useful as a source of P^+ [143,144]. Recently, a planar phosphonium derivative has been made from it [145]. In our hands, it gave phosphaallylic cations from the insertion of P^+ into a C = C double bond [143].



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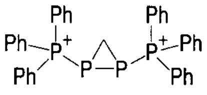

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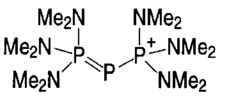
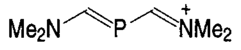


55

By a different route, phosphaallylic ions such as **56**, became generally accessible [146,147]. A heterocyclic version reported in 1964 by Karl Dimroth [148] was one of the first examples of two-coordinate phosphorus. The phosphaallylic ions are reactive both at the phosphorus and at the adjacent carbon atoms [149]. Most important are their reactions with hydrazines and hydroxylamine, yielding diazaphospholes, such as the prototypical **57**, and oxazaphospholes, such as **58** [146,149].



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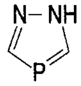

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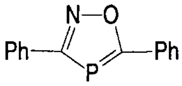
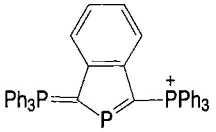


58

In the same issue that we published the synthesis of **57**, Gottfried Märkl [150] and Manfred Regitz [151] also published their syntheses of 1,2,4-diazaphospholes. Because of their chemistry and structure [152], these compounds proved to be perfect analogs to pyrazoles.

To conceive of another conjugated chain with a central two-coordinate phosphorus atom, we thought of a CR unit inserted in each PP bond of a triphosphenium ion. By such an arrangement, the center should switch from phosphide to phosphenium character. We first verified this type of compound in the diphosphonio isophosphindole cation **59** [153] (from which meanwhile a chemistry of its own was developed [154]), but found later on that even the acyclic system **61** is sufficient for the PCl bond to become ionic [155,156]. In accord with its syntheses and its behavior, we named it a bis(ylidyl) phosphenium ion. Less pronounced but more differentiated was the ylide effect to be seen in the structures of the halophosphanyl ylides, such as **60** [157–160], and later on also in those of chloroarsanyl ylides [161].



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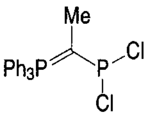

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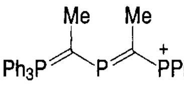
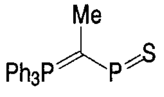


61

The chlorophosphanyl ylides became the starting point to many more ylidyl phosphorus compounds [162–167]. Most of them reflect the influence of the ylide substituent by having a pronounced increase or decrease in stability. Positive examples are the thioxophosphines **62** and dithioxophosphoranes **63** [168–172], negative ones are the hydridophosphines [166].



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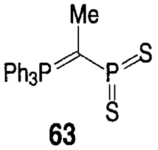
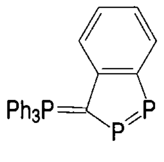


63

When we were reacting phosphonium benzylides with chorophosphines, we experienced the first electrophilic aromatic substitution of ylides [176]. Intramolecular versions of this substitution resulted in the diphosphaindene **64** [173] and the diphosphanaphthalene cation **65** [174].



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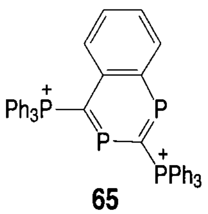
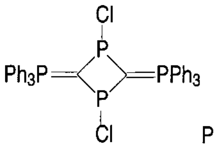


65

The dimer **66**, trimer **67**, and tetramer **68** of the ylidediyl chlorophosphine Ph_3PCPCl constitute another, rather multiform family of heterocycles [175–178], and the choroarsine oligomers parallel them perfectly [161].



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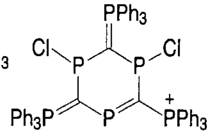

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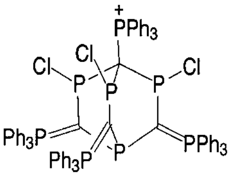
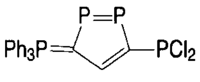


68

Ylidediyl units furthermore proved to be fine building elements for di- and triphosphole and for diaza- and triazaphosphole rings **69–73** [179–183].



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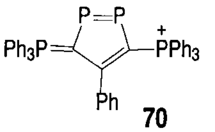

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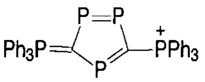

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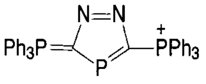

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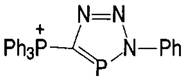
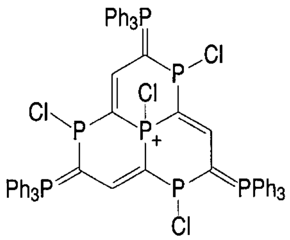


73

For the synthesis of **69**, we started with an allylide. In its reaction with PCl_3, it used all of its functions and gave, besides **69**, the triphosphaphenalene ion **74**. Two of these bowl-shaped cations can encapsulate a choride anion. Maybe someone sometime can make use of this observation.



74

All of these molecules became landmarks to me. They remind me of days and years of activity and of those who in this time combined their efforts with mine. They are named in the references. For a while, we joined our expertise and shared the fun of applying it to synthesize and to identify these molecules. We enjoyed the success when the result was as planned, and we enjoyed the surprise when it was unexpected and caused us to correct our view. Although our motifs were just few, the response was rich and justified my enchantment with phosphorus chemistry. I am pleased by the interest some of our molecules attracted, especially when they initiated further investigations.

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