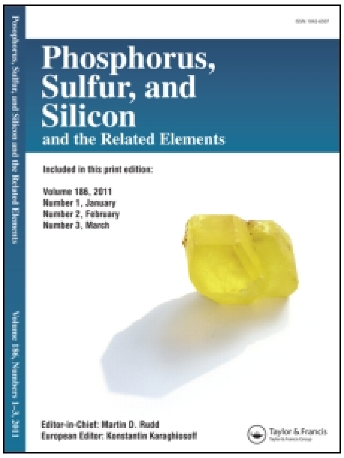

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Synthesis and Reactivity of Cyclic 4-π Electron Ylides: Non-Antiaromatic Inorganic Ring Systems

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SYNTHESIS AND REACTIVITY OF CYCLIC 4-π ELECTRON YLIDES : NON-ANTIAROMATIC INORGANIC RING SYSTEMS

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Abstract The synthesis, structure and reactivity of 2,2,4,4-tetrakis(diisopropylamino)-1,3,2λ^5,4λ^5-diazadiphosphete **3**, 2,2-bis(diisopropylamino)-1,2λ^5-azaphosphete **9**, and 2,2-bis(diisopropylamino)-1,3,2λ^5-diazaphosphete **14** are presented.

INTRODUCTION

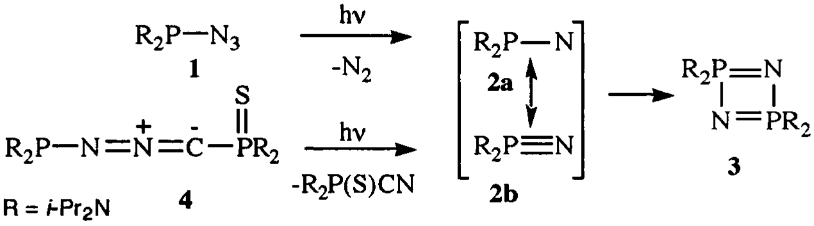
For more than a century, the synthesis and bonding description of 6-π electron 6-membered rings and 4-π-electron 4-membered rings have attracted considerable attention.[1] The former are often associated with aromaticity and stability, the latter with antiaromaticity and high reactivity. Whereas benzene was discovered in 1825 by Faraday,[2] for a long time all efforts to obtain stable cyclobutadienes failed.[3] The crucial breakthrough was achieved in 1965, when Petit stabilized the parent cyclobutadiene with the organometallic fragment $Fe(CO)_3$.[4] Since then, a very few substituted cyclobutadienes, stabilized by push-pull effects or bulky substituents, have been isolated.[5]

The aromatic and antiaromatic character of these systems is perturbated when one or more second row heteroatoms are present in the ring.[6] With a third row element (or heavier), possessing available p-orbitals to build the π-system, the comparison is even more striking :[6] for example, neither silabenzene[7] or germabenzene[8] are stable. When the heteroatom has no p-orbital available for the π-system, the 6-membered ring is no longer a Hückel aromatic system and, of course, the 4-membered ring should not be antiaromatic.[9] Starting from this hypothesis, it becomes clear that cyclic 4-π-electron systems featuring a third row element should be stable.

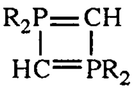
Here, we summarize our results concerning the synthesis, structure and reactivity of three non-antiaromatic cyclic 4-π-electron systems, namely the 1,3,2λ^5,4λ^5-diazadiphosphetes (cyclodiphosphazenes),[10] 1,2λ^5-azaphosphetes[11] and 1,3,2λ^5-diazaphosphetes.[12]

SYNTHESIS

Although several hundred cyclo tri-, tetra-, and polyphosphazenes were known,[13] it was only in 1984 that we reported the synthesis and X-ray crystal structure of the first cyclodiphosphazene 3.[10a] The starting point of this story was based on calculations by Trinquier[14] which predicted that the structure of a phosphinonitrene 2a can be formulated as a phosphonitrile 2b, due to delocalization of the lone pairs $n_\pi(P) \rightarrow p_\pi(N)$ and to some extent $n_\pi(N) \rightarrow d_\pi(P)$. We initially proved this hypothesis by irradiating the bis(diisopropylamino)phosphanyl azide 1 in the presence of a variety of trapping agents;[15] indeed, the products obtained resulted from simple addition across the phosphorus-nitrogen triple bond. In the absence of trapping agents, photolysis of 1 led to the desired head-to-tail cyclic dimer of 2, namely the 2,2,4,4-tetrakis(diisopropylamino)-1,3,2λ5,4λ5-diazadiphosphete 3, in 42% yield.[10] More recently we have found that the photolysis of the stable phosphorus-substituted nitrilimine 4 also led to 3 in 35 % yield;[16] this second method also involves the dimerization of transient phosphonitrile 2.

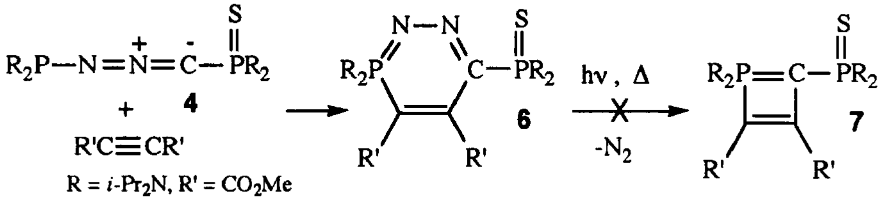


The year after the discovery of the stable cyclodiphosphazene, Fluck et al. reported the synthesis and reactivity of a 1λ5,3λ5- diphosphete 5.[17]

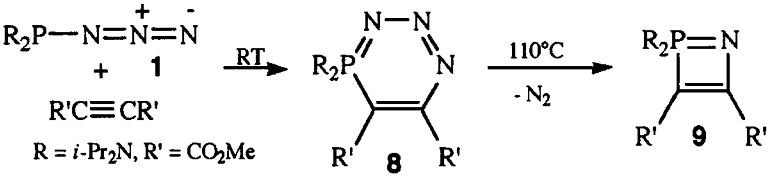
R = Me₂N  5

As both compounds 3 and 5 featured two third row elements, the next question was whether the presence of only one of these elements would be sufficient to stabilize a 4-π-electron 4-membered ring. We first tried to prepare a λ5-phosphete such as 7. Since the thermal and photochemical elimination of dinitrogen from cyclic azoalkanes is an efficient method for the preparation of strained, or even antiaromatic species,[18] it was tempting to study the thermal behavior of 1,2,3λ5-diazaphosphinine 6, which is easily available from *N*-phosphanyl nitrilimine 4 and dimethyl acetylenedicarboxylate.[19] However, all attempts to eliminate dinitrogen from the 6-membered heterocycle

6 by photolysis or thermolysis failed.

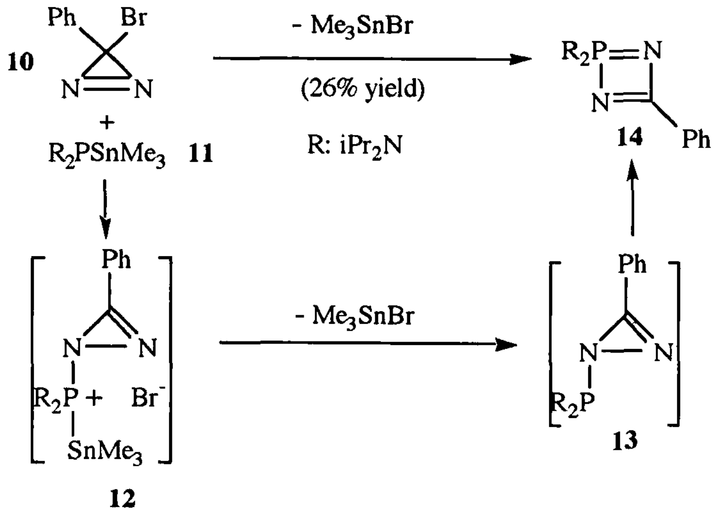


The reluctance of 6 to lose N_2 is consistent with the high stability of phosphazo derivatives. Indeed, 6 features the same $R_3P{=}N{-}N{=}C{<}$ sequence as observed in Staudinger-Meyer adducts (phosphines + diazo derivatives), which are not precursors of phosphorus ylides.[20] In marked contrast, it is well known that the phosphazides (the Staudinger adducts of phosphanes with azido derivatives, $R_3P{=}N{-}N{=}N{-}$), easily decompose into dinitrogen and iminophosphoranes.[21] Therefore, it was of interest to prepare 1,2,3,4λ^5-triazaphosphinines 8, as potential precursors of 1,2λ^5-azaphosphetes 9. As a synthetic route, we extended the formal 1,4-dipolar reactivity of phosphanyl-substituted 1,3-dipoles[19,22] to phosphanyl azides. Bis(diisopropylamino)phosphanyl azide 1 cleanly reacted with dimethyl acetylenedicarboxylate, affording the desired 6-membered ring 8 in 75% yield. As expected, extrusion of dinitrogen occured in refluxing toluene giving 1,2λ^5-azaphosphete 9 in 80% yield.[11]



The synthetic route used for the preparation of the 1,3,2λ^5-diazaphosphete 14[12] is totally different. It involves a ring expansion reaction starting from a bromodiazirine. Recently, independent works by Creary[23] and Dailey[24] demonstrated that the first step of exchange reactions of halodiazirines 10 with nucleophiles proceeds via an S_N2' mechanism. Hence, we were able to transiently obtain the N-phosphoniodiazirine 12, which using nucleophilic bis(diisopropylamino)trimethylstannylphosphane 11, could be transformed, via elimination of bromotrimethylstannane, into the transient N-phosphanyldiazirine 13. The three membered heterocycle 13 is antiaromatic and undergoes a ring expansion reaction affording the corresponding 1,3,2λ^5-diazaphosphete

14 in 26 % isolated yield.[12]



STRUCTURE

The non existence of the cyclodiphosphazenes has been explained in terms of ring strain and contraction of the N-P-N bond angles below 115-120° which could cause serious interpenetration of the nitrogen van der Waals boundaries.[13a] Therefore, the results of the X-ray crystal diffraction study of **3** were of particular interest. The ORTEP view and selected geometric parameters of the molecule are in Figure 1. It appeared that the value of the N(1)-P(1)-N'(1) angle was 95.0(6)°, therefore much smaller than the value considered as a limit for the stability of the ring! The four-membered ring is organized around a symmetry center implying the absolute planarity of the ring. All endo- and exocyclic phosphorus-nitrogen bond lengths are equal (1.64 Å) and each nitrogen center is trigonal planar. In agreement with high-level calculations,[25] cyclodiphosphazenes have a strong zwitterionic character, although some back bonding from N to P occurs. In other words, the phosphorus-nitrogen bond order is between 1 and 2, but this compound is certainly best represented as indicated in Figure 1.

The surprising stability of the first isolated "heterocyclobutadiene" **3** was explained by its zwitterionic character, but also by the high thermodynamic energy of the corresponding monomer **2**, preventing dissociation, and to steric factors which hinder polymerization. Indeed, according to theoretical calculations[25] the cyclodimerization of

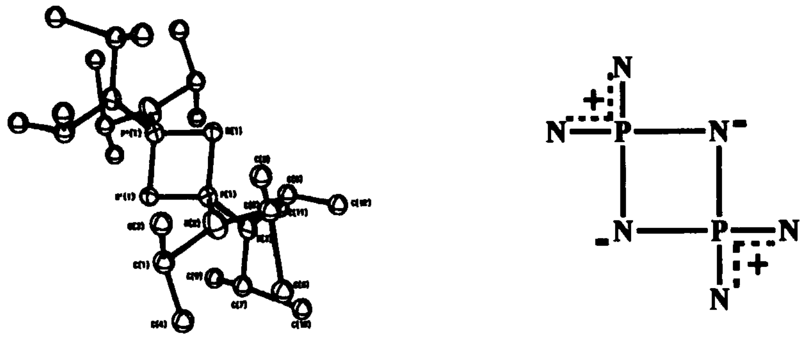
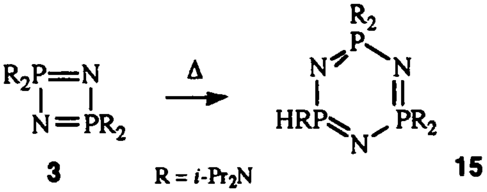


Figure 1. ORTEP view and bonding description of 3

two $R_2P=N$ units results in a large energy benefit, especially with amino substituents ($E = -100$ kcal/mol), but the trimerization is even more thermodynamically favored ($E > -200$ kcal/mol). Note that so far, all attempts to prepare other cyclodiphosphazenes bearing smaller substituents failed;[26] moreover heating the tetrakis(diisopropylamino)cyclodiphosphazene 3 leads to a trimer 15.[10]



These results should shed new light on questions of equilibria among monomers, rings, and chains in phosphazenes.

The structure of $1,2\lambda^5$-azaphosphetes 9 has also been clearly established by a single crystal X-ray diffraction study. The thermal ellipsoid plot and the pertinent structural parameters of the molecule are shown in Figure 2. As in the case of the cyclodiphosphazene 3, the four-membered ring has a planar arrangement (maximum deviation from planarity 0.003 (4)Å). Although the C-P-N angle is small [81.2 (2)°], the large N-C-C angle [109.7 (3)°] induces a short diagonal P---C distance [2.109 (4) Å]. This short distance between 1,3-centers seems to be a characteristic feature of polarized 4-π-electron 4-membered rings such as 1,3-push-2,4-pull cyclobutadienes,[5a] azete[27], diphosphete,[17] and cyclodiphosphazene. The exocyclic phosphorus-nitrogen bond lengths [1.629 (3), 1.626 (3) Å] are shorter than the endocyclic P-N bond length [1.702

(3) Å], and are comparable to those observed in bis(diisopropylamino)-phosphenium salts (1.61 Å)[28]. This is an indication that, here also, there is a positive charge delocalization on the exocyclic N-P-N fragment, which is confirmed by the planarity of the nitrogen atom. The N-C [1.352 (5) Å] and C-C [1.406 (6) Å] bond lengths are intermediate between those of single and double bonds, indicating that the N-C-C part of the ring can be regarded as an anionic allylic system. Thus, the 4-π-electron 4-membered ring 9 is best described by the "non-anti-aromatic" structure indicated in Figure 2.

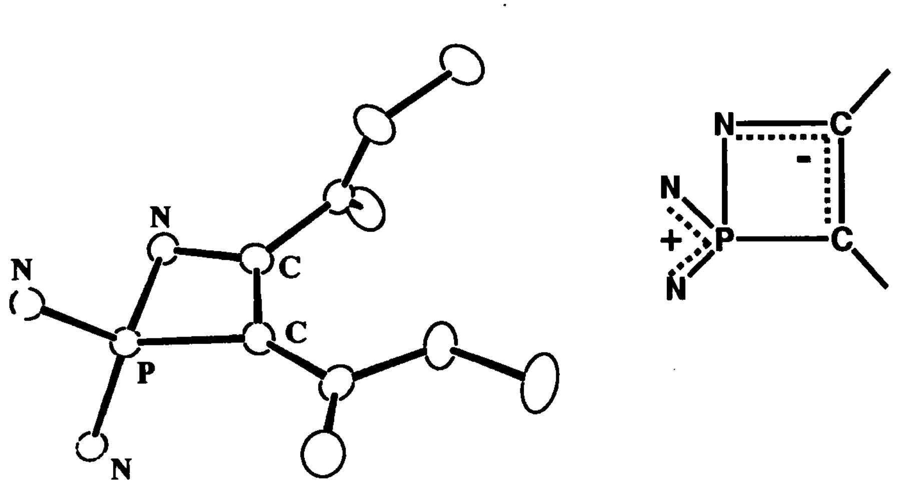


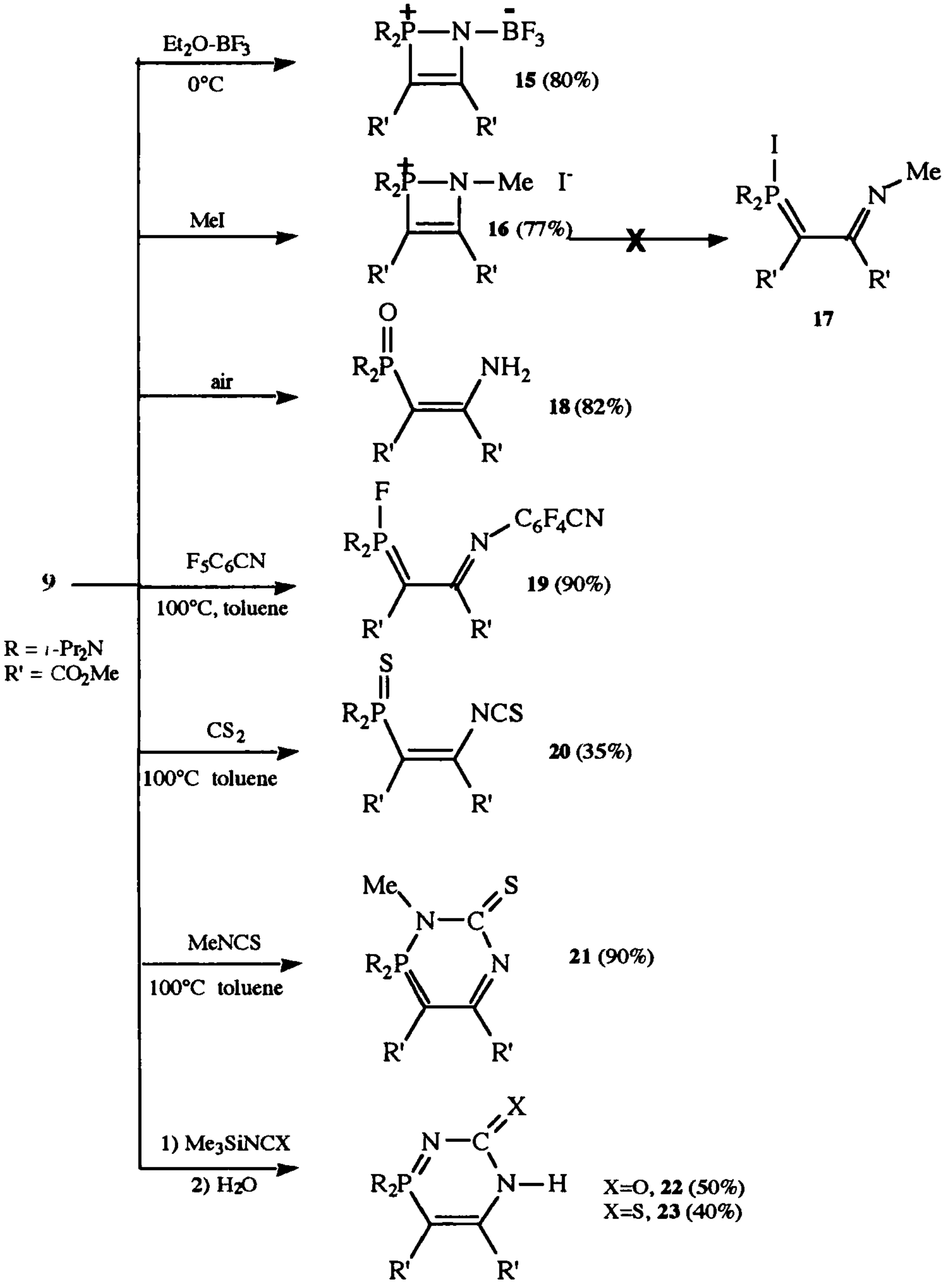
Figure 2. ORTEP view and bonding description of 9

So far, we have not been able to obtain crystals of 1,3,2λ^5-diazaphosphete 14 suitable for an X-ray diffraction study. It is noteworthy that the synthesis of a 1,3,2λ^5-diazaphosphete has been claimed,[29] but the product proved to be in fact a mixture of 1,3,5,2λ^5-triazaphosphinine and 1,3,5,2λ^5,4λ^5-triazadiphosphinine.[30] However, the 4-membered ring structure of 14 has been clearly established by multinuclear NMR and mass spectroscopy. Of particular interest, in the ^{13}C NMR spectrum the ring carbon gives a signal at low field (δ = 194.7 ppm) with a large phosphorus-carbon coupling constant ($^2J_{PC}$ = 48.4 Hz). The same phenomenum is observed for the 1,2λ^5-azaphosphete 9 (δ = 182.7, $^2J_{PC}$ = 28.0 Hz).

REACTIVITY

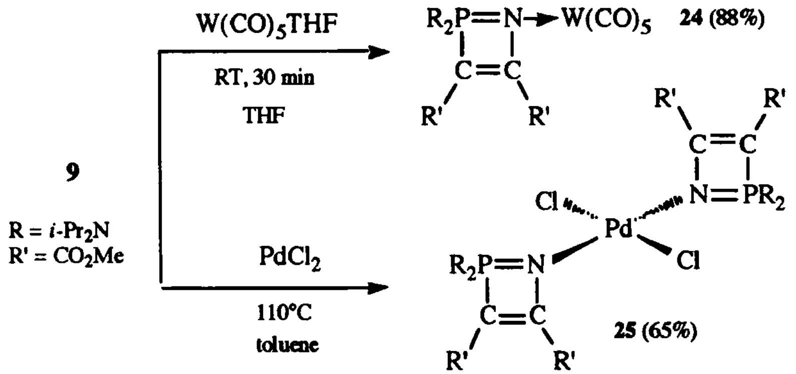
Up to now, the study of the reactivity of cyclodiphosphazene 3 and $1,3,2\lambda^5$-diazaphosphete 14 has been hindered by the lack of synthetic route allowing the preparation of substantial amounts of these products. In contrast, $1,2\lambda^5$-azaphosphete 9 is available in multiple gram quantities and although it is highly thermally stable (it only starts to decompose in solution at 170°C, giving rise to a complicated mixture of products), it is quite reactive. This cyclic 4-π-electron ylide 9 is almost inert toward nucleophiles, but readily reacts with inorganic and organic electrophiles. As expected, the most reactive site is the nitrogen atom. Addition of Lewis acids, such as boron trifluoride, gave rise to a new type of phosphorus heterocycle, the unsatured 4-membered phosphonium ring 15 (80% yield), already demonstrating the synthetic potential of 9. In the same way, addition of a stoichiometric amount of iodomethane to 9 afforded cyclic phosphonium salt 16 (77% yield), which surprisingly did not rearrange into the ylidic opened form 17. In contrast, compound 9 is readily converted into (Z)-1-(amino)-2-(phosphoranyl)alkene 18 (82% yield), when exposed to air. This can be rationalized by the formation of the strong covalent phosphorus-oxygen bond, converting the phosphonium center into a pentacoordinated phosphorus atom, which favors a ring opening reaction. A similar mechanism also explains the formation of 19 (90% yield), in the reaction of $1,2\lambda^5$-azaphosphete 9 with pentafluorobenzonitrile at 100°C. A classical aza-Wittig reaction was observed by adding carbon disulfide to 9, in refluxing toluene, giving (Z)-1-(isothiocyanato)-2-(thiophosphoranyl)alkene 20 (35% yield).[11b]

All these reactions show that 9 behaves as a classical aza-Wittig reagent. However, some unexpected reactions were also observed. For example, isocyanates and isothiocyanates have been widely employed in aza-Wittig reactions, affording unsymmetrical carbodiimides and the corresponding phosphine oxides and sulfides, respectively.[21a,31] In marked contrast, methylisothiocyanate reacted with 9 to give heterocycle 21 in 90% yield. These results are reminiscent of the Dimroth rearrangement[21a,31b] and demonstrate the applicability of 4-π-electron 4-membered rings in heterocyclic synthesis. Clean reactions also occured with trimethylsilyl isocyanate and isothiocyanate leading, after hydrolysis, to heterocycles 22 and 23, which were isolated in 50 and 40% yield, respectively.[11b]



The combination of the chemistry of aromatic and antiaromatic compounds with that of transition metal complexes has led to many crucial discoveries. The electrophilic character of coordinated arenes,[32] or the stabilization of the parent cyclobutadiene with $Fe(CO)_3$,[4] are representative examples. Thus it was of interest to study the coordination behaviour of **9** which must differ notably from that of its organic analogs.[4,27,33]

Compound **9** readily reacts with $W(CO)_5(THF)$ at room temperature affording (η^1-azaphosphete)$W(CO)_5$ complex **24** in 88% yield, while the reaction with palladium dichloride requires two hours in refluxing toluene to give the bis(η^1-azaphosphete)palladium(II) complex **25** in 65% yield.[11c]



The similarity between the geometric data for the free ligand **9** with those for the coordinated ring of **25** is very striking (Figure 3). In both cases, the 4-membered ring is almost planar [maximum deviation from planarity, **9**: 0.003(4); **25**: -0.013(3) Å)], and the diagonal P...C2 distance short [**9**: 2.109(4); **25**: 2.156(4) Å]. Thus, in contrast to its organic analogs, especially the azetes,[27] 1,2λ^5-azaphosphete **9** acts as an η^1-ligand giving stable complexes and retains its 4-π-electron ylide structures in the coordination sphere of the metal.

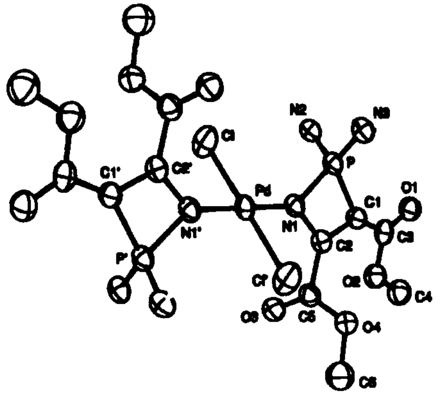


Figure 3. ORTEP view of **25**

CONCLUSION

These results demonstrate the high thermodynamic stability of the 4-π-electron 4-membered rings featuring one or two third row elements. These heterocyclobutadienes are not anti-aromatic and are best described by zwitterionic structures. As examplified by the 1,2-λ^5-azaphosphete **9**, although thermally stable, these heterocycles present a high reactivity toward organic, inorganic and organometallic electrophiles. New synthetic routes to a variety of "heterocyclobutadienes" are under active investigation since there is no doubt that this new class of compounds would find numerous applications.

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