Heteroatom Chemistry
Volume 2, Number 2, 1991

Iminophosphanes as Pseudocarbenes: A Theoretical Study of Product Formation

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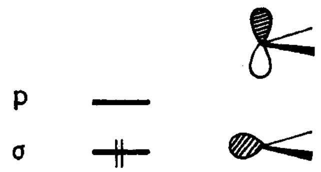
Received 29 June 1990.

ABSTRACT

P(III) double bond systems possess two closely spaced frontier orbitals, a π-orbital and a σ-orbital. In the parent iminophosphane the orbital sequence is σ (HOMO) and π (LUMO). Thus, it is isolobal to a singlet carbene and undergoes self-dimerization via a [2 + 1] cycloaddition. The resulting three membered ring system can be considered as a complex of two iminophosphanes. Contrary to the classical cyclopropanation reaction, in the pseudo-carbene iminophosphane the corresponding [2 + 1] reaction is only slightly exothermic, as established by ab initio calculations at the SCF/CEPA-1 and the MCSCF/ACPF level.*

INTRODUCTION

Carbenes are one of the best known and most investigated species in organic chemistry, as documented in numerous reviews [1–2] and books [3] on this subject. Within the concept of frontier orbital theory, a singlet carbene is characterized by a σ-orbital (HOMO) and a *p*-orbital (LUMO) [4–8] (Scheme 1). The former orbital possesses nucleophilic and the latter orbital electrophilic ability of a singlet species in a typical carbene reaction, e.g., such as the [2 + 1] cycloaddition towards olefines.



SCHEME 1

On the ground of the frontier orbital model of carbene reactivity, P(III) double bonded systems are potential "pseudocarbenes," since they possess two energetically closely spaced, doubly occupied frontier orbitals, a σ-orbital and a π-orbital. The former refers to the lone pair orbital at phosphorus (at methylenephosphane **1**) or a combination of lone pairs (at iminophosphane **2** and diphosphene **3**) [9]. A priori, two extreme situations can be recognized, schematically viewed in Scheme 2. (a) The HOMO is the π-orbital and the HOMO-1 the σ-orbital. The frontier orbital sequence is π and π* as it is known for olefines. The olefinic character of the P(III) double bond system will come to the fore and a common route of these systems is the [2 + 2] cycloaddition pathway; it is the case for methylenephosphanes. (b) Alternatively, the HOMO is the σ-orbital. Then the frontier orbital system is isolobal [10] to a singlet carbene, and it is amenable to [2 + 1] cycloaddition. A typical example for this route is alkyl substituted iminophos*phanes.* The qualitative theory has been worked out in detail by experiment [11, 12]. In iminophosphane **2** the sequence of frontier orbitals is σ (HOMO) and π*

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*To whom correspondence should be addressed.
This paper is dedicated to Professor Dr. Rolf Appel on the occasion of his 70th birthday.

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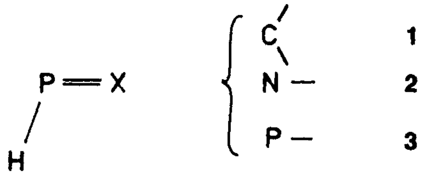
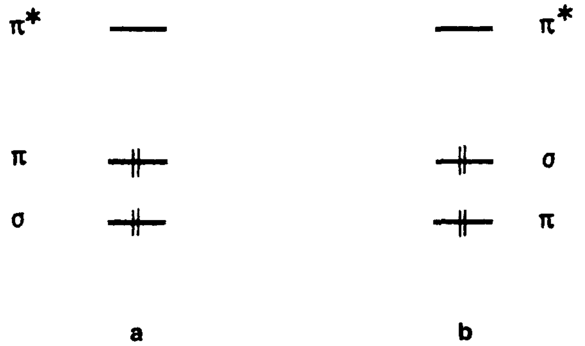




SCHEME 2

(LUMO) [9], as indicated in *b*, in accord with experimental evidence [11] as well as photoelectron spectroscopic investigations [12]. The quantum chemical investigations (see vide infra) evidence a sizable energy difference between σ and π (for the trans geometry) [9].

One principal question within this context remains to be solved. What is the difference in reactive behavior between a "classical" carbene, e.g. such as CF_2 or CCl_2, and the "pseudo-carbene" iminophosphane. In the present report we have a bearing on this problem and report quantum chemical calculations on the nature of bonding in the [2 + 1] self-dimerization product.

THEORETICAL PROCEDURE

The quantum chemical calculations that will be reported are based on the results of ab initio calculations at a double-ζ level. The following basis sets were constructed from Huzinaga bases [13]: N (9s, 5p) in the contraction [5, 4 × 1/3, 2 × 1] + 1d(0.95); P (11s, 7p) in the contraction [5, 6 × 1/4, 3 × 1] + 1d(0.5); and H (4s) in the contraction [3, 1] + 1p(0.65). All structures were determined at a single determinant SCF level, utilizing the Karlsruhe version of the COLUMBUS set of programs [14]. The energy optimizations of structures were directed with the Murtagh-Sargent algorithm [15]. The energy minima were obtained to an accuracy of 10^{-7} au. Thus, we obtained bond lengths (bond angles) to an accuracy of 0.001 Å (0.05 degrees). Additional CI calculations were carried out at various levels of sophistication: (a) At the CEPA-1 level with the self-consistent electron pair (SCEP) method [16a]; (b) At the ACPF (averaged coupled pair functional) level [16b] with a 2X2 MCSCF wave function [16c] as reference. All correlation calculations were carried out with the program system MOLPRO-89 [16].

RESULTS AND DISCUSSION

From the viewpoint of reactivity, the following self dimerization reactions of parent iminophosphane seen in Scheme 3 are feasible. Two molecules **2** dimerize in a [2 + 1] reaction to give **4a**. In such a reaction, one molecule of **2** acts formally as a carbene adding to a second one, which serves as an olefine unit. Alternatively, two molecules of **2** undergo a [2 + 2] reaction, to give either **4b** or **4c**. For iminophosphanes [2 + 1] as well as [2 + 2], reaction routes have been observed, depending on the electronic effects of the substituents [11, 12], while for methylenephosphanes the [2 + 2] reaction is the favored route [17].

First, we report the results of energy minimization on the various structures **2** and **4**. The geometrical parameters obtained are collected in Figure 1, and the corresponding energies are listed in Table 1. At all levels of sophistication, the relative energies indicate that the dimers **4** are more stable than the two monomers **2**. **4b** is the most stable species on the electronic hypersurface, while **4a** and **4c** are comparable in stability. The inclusion of electron correlation in the wave function favors slightly **4a** over **4c**. Of the monomeric iminophosphanes, **2**, the trans isomer is only slightly more stable than its cis isomer. This observation is in accord with previous findings [18].

The CI expansion coefficients of the 2X2 MCSCF wave function ($\Psi_I = |\ldots(\text{HOMO})^2(\text{LUMO})^0|$; $\Psi_{II} = |\ldots(\text{HOMO})^0(\text{LUMO})^2|$) for **4a**, **4b**, and **4c** reveal a dominant closed shell character of these species: c_I = 0.993, 0.998, 0.994; c_{II} = 0.118, 0.065, 0.111.

Of considerable interest is the geometry of **4a** (Figure 1). Of the two endocyclic PN bonds, the

TABLE 1 Relative Energies (in kcal per mole) of Iminophosphane **2** and Its Dimers **4**

Structure	SCF	CEPA-1[a]	ACPF[b]
2 (trans)	0.0	0.0	0.0
2 (cis)	0.74	0.92	0.98
4a	−15.80[c]	−11.19[c]	−9.86[c]
4b	−52.13[c]	−40.73[c]	−38.57[c]
4c	−16.88[c]	−9.54[c]	−7.38[c]

[a] At SCF optimized geometry.

[b] At SCF optimized geometry with a 2X2 MCSCF reference function.

[c] Computed in reference to twice the energy of **3a** (trans).

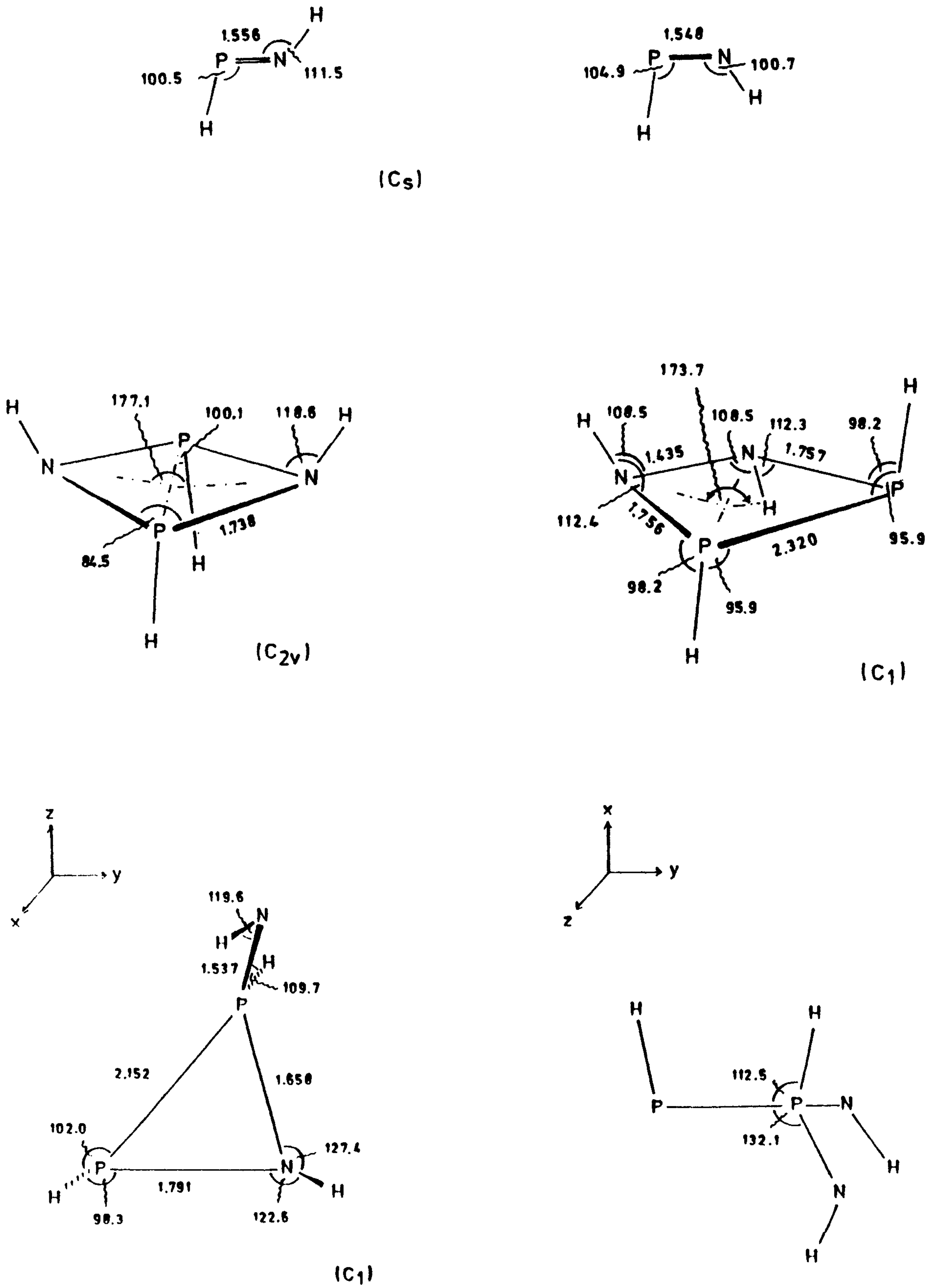
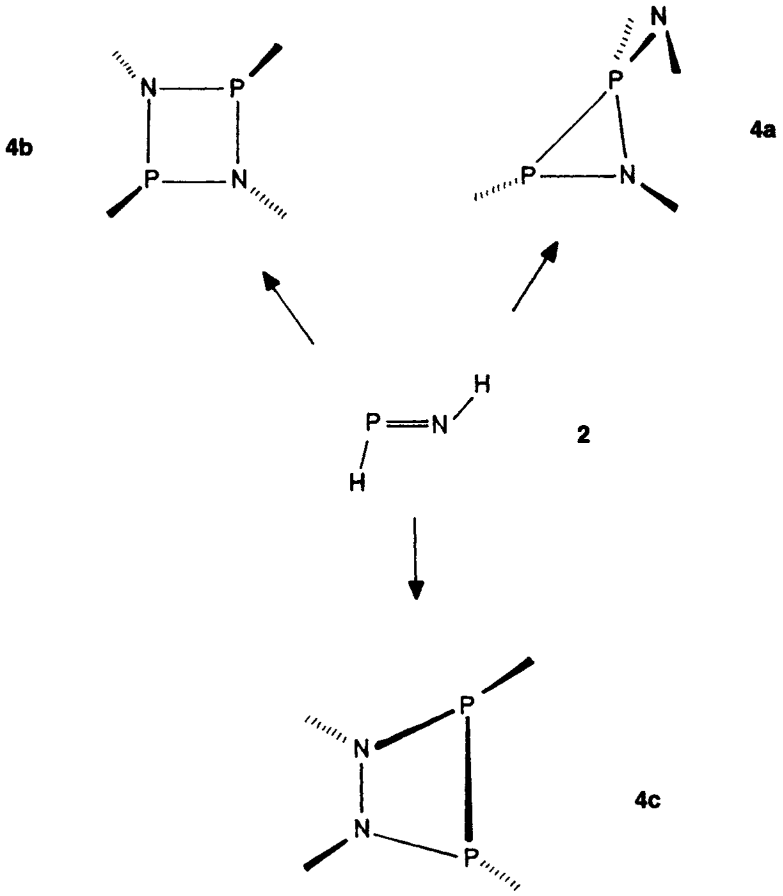
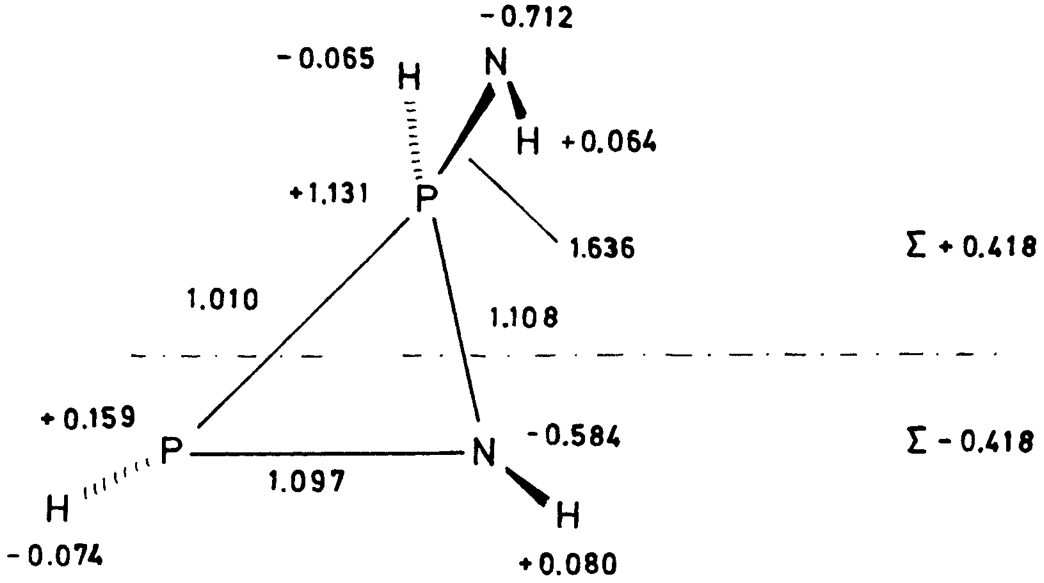


FIGURE 1 Geometrical parameters of the various monomers and self dimers of iminophosphane; bond lengths are in Angstrom units, bond angles in degrees.



SCHEME 3



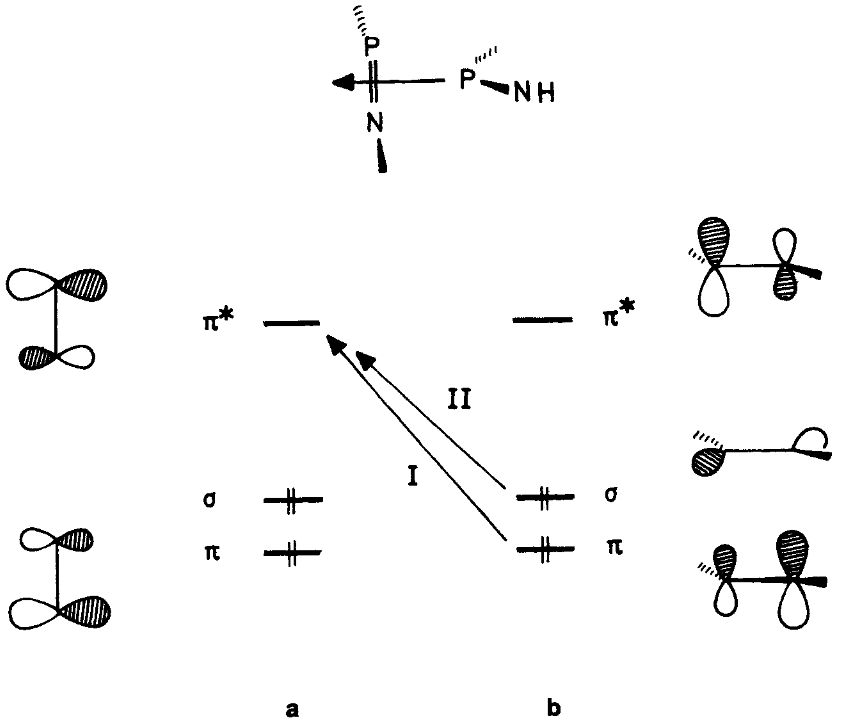
SCHEME 4

distal bond is essentially longer than the lateral bond. On the other hand, the exocyclic PN bond is shorter than the double bond in **2**. A deeper insight into the bonding situation of **4a** is provided by a population analysis (Scheme 4). The results were obtained by the Roby-Heinzmann-Ahlrichs procedure [19], which is known to provide more reliable populations for polar bonds. The electron shared numbers refer to the number of electron pairs between bonds. All the ring bonds reveal an electron shared number of about 1. This indicates essentially single bonds. The lateral PN ring bond is superimposed by a strong ionic contribution (Δq_{PN} = 1.72 e). On this basis, the lateral PN bond is shorter than the distal PN bond (Δq_{PN} = 0.74 e). As one expects, the largest charge separation is obtained for the exocyclic PN bond (Δq_{PN} = 1.84 e). Hence, on this basis, it is not surprising that this bond is even shorter than the PN bond in the parent iminophosphane, due to an enhanced dipolaric contribution.

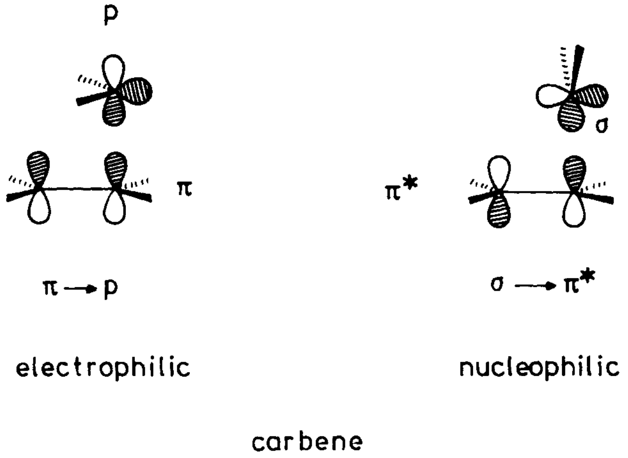
Formally, **4a** can be divided into two **2** (dashed line in **4**). It results in an excess of positive charge for the iminophosphane unit with the pentavalent phosphorus atom ($\Sigma = +0.418$ e). Why is this so?

The reason becomes apparent when one considers **4a** by compositive interaction of two fragments **2** (Scheme 5). This view resembles the picture for formation of three-membered ring systems [20a] and relates to the Dewar-Chatt-Duncanson model [20b,c] of bonding in metal-olefine complexes. Accordingly, the transfer of electron density by interaction of two molecules **2** is unidirectional. Electron density is transferred from π (at fragment b) to π^* (of fragment a) (as indicated in I) and to a lesser extent from the σ orbital into π^* (as indicated in II). The coefficient at the more electropositive phosphorus is larger, compared to the coefficient at the more electronegative nitrogen, enhancing bonding overlap towards phosphorus and diminishing antibonding overlap toward nitrogen. (In the case of an unpolar π-bond, e.g. ethene for fragment *a*, a corresponding transfer of electron density from σ into π^* would be nihil for symmetry reasons.) Overall, this indicates a predominant nucleophilic interaction of fragment *b* with fragment *a*. It causes a buildup of negative charge in *a* with depletion of electron density in *b*. On the basis of the electron density analysis, one expects that electron π-accepting substituents, such as silyl groups, at the nitrogen atoms will stabilize the three-membered ring systems. This view is in fact supported by experimental observations [11, 12].

We are now able to compare a "classical" carbene, such as CF_2, $C(OR)_2$ with the "pseudo-carbene" iminophosphane. The former has been classified as predominantly electrophilic, nucleophilic, or ambiphilic [1]. Such a distinction is based on the initial phase in the approach path (Scheme 6). The "classical" (electrophilic) carbenes (e.g. CF_2, CCl_2 etc.) possess low energy barriers for the 1,2-addition reaction [1], and the reaction energies in-



SCHEME 5



SCHEME 6

dicate strong exothermicity. Their approach path occurs in two separate steps. In the initial phase, the carbene attacks as an electrophilic (nucleophilic respectively) species. In the second step, the reaction is completed (under cyclopropane formation) in the nucleophilic (electrophilic) phase. For a detailed discussion of this subject the reader might be referred to a recent exhaustive discussion on the principal facets of carbene chemistry [1].

In the case at hand, that of the "pseudo-carbene" iminophosphane, the situation is different. The addition is only slightly exothermic, and the corresponding reaction product (analogous to the three-membered ring system in the conventional carbene 1,2-addition reaction) can easily separate thermally into two iminophosphanes via a retro reaction. A clearcut experimental verification of the electron demand of **2** in the [2 + 1] addition process requires competition experiments that have not been undertaken so far.

CONCLUSIONS

The dimer resulting from [2 + 1] self addition is more stable than two monomers, although the alternative route to the four-membered ring system, referring to a [2 + 2] head to tail self-addition process, is energetically more exothermic. The [2 + 1] dimer can be considered as a complex, and the pseudo-carbene iminophosphane plays the nucleophilic part in the addition process [11b, 21]. Of the various possible isomers we have investigated, only one has been considered in detail. However, further investigations of the various possible conformers of **4a** provide evidence for comparable stabilities and similar bonding features.

ACKNOWLEDGMENT

This work has been supported by the Fonds der Chemie and the Deutsche Forschungsgemeinschaft. The quantum chemical calculations were performed at the Comparex and Convex C240 at the University at Bielefeld and the Cray-YMP at the KFA Jülich.

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