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STRUCTURAL STUDY OF NEW CYCLO-1, 3-DIPHOSPHABUTANES

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ABSTRACT: A novel cyclic 1,3-diphospha-butane was obtained starting from 9-trimethylsilyl-fluorene and PCl_3 in a one-pot procedure and investigated through spectroscopic methods. Theoretical studies were also carried out, showing that the head-to-tail isomer of 1, 3-diphosphacyclo-butane is more likely to be formed during the reaction through the dimerization of a fluorenyl-substituted phopsphaalkene. This type of cyclic derivative can replace phosphaallenes as ligands in the synthesis of coordination compounds with potential biological activity.

Keywords: *phosphaalkenes, diphosphacyclo-butane, DFT calculations*

INTRODUCTION

Low-coordinated phosphorus centers involving multiple bonding, such as phosphaalkenes, have been recently used as ligands in the coordination chemistry of transition metals [1-3], with proof that they would have applications in catalysis [2, 3]. The synthesis of the first diphosphaallene Mes*P=C=PMes* [4] by stabilization with bulky organic groups was stimulated by the fact that the presence of two phosphorus atoms in the molecule gives rise to several intriguing possibilities as far as the coordination ability of such systems is concerned. Following our interest in the design of transition metal compounds coordinated by phosphapropenes [5] and in the study of heteroallenes [6-9] it became apparent that the cyclic compounds containing two or more phosphorus atoms could replace diphosphaallenes without raising the same problems related to their insaturation and instability. For instance, 1,3-diphosphacyclobutanes would be the equivalent of 1,3-diphosphaallenes as ligands in the synthesis of transition metal-complexes.

We report the synthesis of a novel 1,3-diphosphacyclobutane in a one-pot procedure, starting from the readily accessible trimethylsilylfluorenyllithium and PCl_3. The choice of the fluorenyl group as the substituent on the carbon

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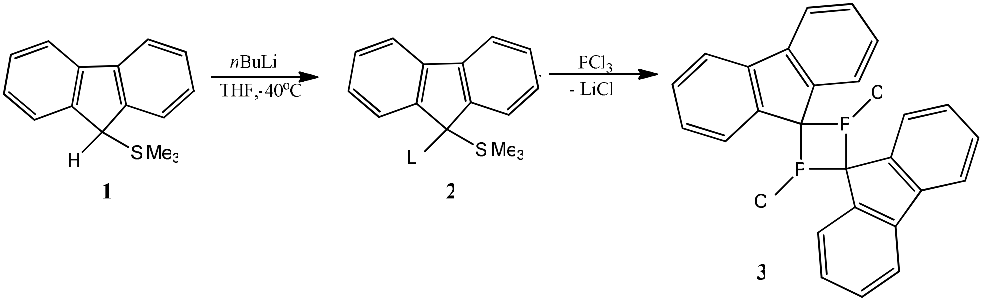
atoms represents a good compromise between the sterical hindrance needed and the availability of both sides of the four-member ring towards the transition metal. In addition, fluorenyl compounds are known to crystallize easily. Theoretical calculations also presented in this paper support the use of fluorenyl-derivatives in the synthesis of 1,3-diphosphacyclobutanes.

RESULTS AND DISCUSSIONS

A new derivative 1,3-diphosphacyclobutane **3** was obtained by reaction of the 9-trimethylsilylfluorenyllithium derivative **2** with PCl_3 at low temperature. This and the lack of evidence for the presence of the phosphaalkene lead us to believe that dimerization readily occurs with the formation of a diphosphacyclobutane (scheme 1).

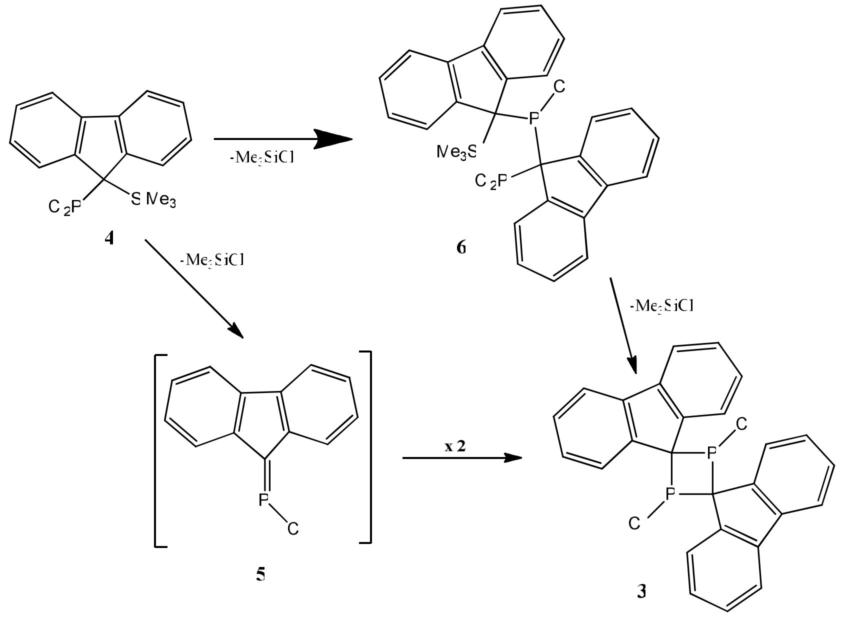


Scheme 1

The obtained derivative **3** was characterized in solution through multinuclear NMR spectroscopy. Only one signal in ^{31}P NMR at a chemical shift of 179.47 ppm is observed, so only one of the two isomers, *cis* and *trans* (indicating the position of the chlorine atoms with respect to the four-atom ring) is obtained.

Most likely, the formation of **3** is the result of the intramolecular elimination of Me_3SiCl from the sterically-hindered **4**, followed by the dimerization of the phosphaalkene **5**. The formation of **5** is the result of the more sterically favored head-to-tail dimerization. Other possible reaction routes are presented in scheme 2.

The presence of a triplet (121.47 ppm) in the ^{13}C NMR spectrum of the reaction product, indicating coupling with the phosphorus nucleus, supports our assumption for the formation of a 4 atom-cyclic derivative, in which the two carbon atoms would be equivalent. If the elimination of Me_3SiCl would occur with the formation of derivative **6**, two different signals should be observed for the carbon atoms bonded to phosphorus. Instead, only one such signal, a triplet, is observed, which could be attributed for either the *cis* or the *trans* isomer of the cyclic dimer. Lack of further experimental data stopped us from attributing the signal to one of them, so a theoretical study was undertaken in order to evaluate which one of the isomers is present. We excluded from the start the possibility of obtaining the head-to-head dimer for two reasons: first, that the head-to-tail dimerization should be thermodynamically favored, leading to the formation of two C-P bonds instead of one P-P and one C-C bond, and second because even though the fluorenyl groups are planar, their position should exert some strain on the head-to-head orientation of the monomers.



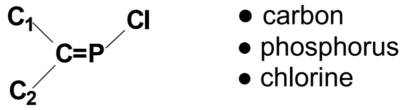
Scheme 2

However, with the available experimental proof, it was not possible to irrefutably state the presence of either one of the possible reaction products resulted from dimerization, so we turned to theoretical investigations in order to establish the outcome of the reaction.

In this study, we had to consider that elimination of Me_3SiCl during the reaction can occur via either intra- or intermolecular route, and considering the high reactivity of the monomer (due to the presence of the double bond, the chlorine substitution at a P(III) atom and the relatively low sterrical hindrance) in both cases cyclic diphosphabutanes would be obtained.

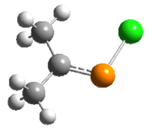
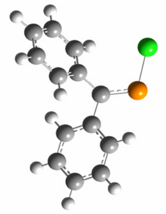
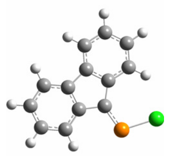
Supposing that the monomer is indeed the reaction product which readily undergoes dimerization, two different routes must be considered: “head to head” and “head to tail” dimerization.

Three model compounds were considered: Me_2C=PCl, Ph_2C=PCl and the presumed reaction intermediate, Fl_2C=PCl (Fl_2C= fluorenyl). The Me and Ph groups were chosen in order to evaluate any changes when going from an alkyl to an aryl substituent on the carbon atom. Sterical hindrance is relatively low in the case of the fluorenyl group, because of the planar conformation, so the steric factor was not evaluated. Presumably, a bulkier organic group on the carbon would prevent dimerization by both protecting the double bond and increasing the strain of the four-atom ring in the dimer; these considerations, are the basis of a separate on-going theoretical investigation and will not be discussed herein. The calculated energies, optimized structures and some relevant geometrical data are given in tables 1 and 2. The numbering of the atoms and color codes are given in scheme 3.



Scheme 3

Table 1. Calculated B3LYP/6-311G(d,p) energies for R_2C=PCl derivatives

Molecule			
E(HF)	-919.4957612	-1302.97658	-1301.784577

As expected, the P=C distances are around 1.70 Å and do not vary too much with the nature of the group, however, the same cannot be said about the bond order. The Wiberg bond order (WBO) is 1.73 for the methyl-substituted derivative, and lower for the aryl-derivatives (Table 2).

Table 2. Calculated selected geometrical data for the monomeric species

Molecule	**P-C (Å)**	**WBO**	**P-Cl (Å)**	**WBO**	**C-P-Cl (º)**	**C_1-C-P (º)**	**C_2-C-P (º)**
Me_2C=PCl	1.68	1.73	2.12	0.89	105.3	129.6	114.5
Ph_2C=PCl	1.70	1.61	2.11	0.90	106.7	130.0	112.3
R_2C=PCl	1.70	1.56	2.10	0.92	107.2	136.9	117.5

The NBO analysis shows that charge transfer from a lone pair on the chlorine atom to the antibonding orbital of π symmetry of the P=C bond is present for all the monomers, and the values of the second order perturbation energy are 7.72 kcal for $Me_2C{=}PCl$, 8.14 kcal for $Ph_2C{=}PCl$, and 8.04 for the fluorenyl derivative. Figure 2 presents the shape of the two NB orbitals involved in the charge-transfer for $Me_2C{=}PCl$. In addition to this, in the case of the aryl-substituted species, other interactions occur which lead to a greater population of the antibonding orbital, with contributions from orbitals of π symmetry localized on the double C=C bonds of the aliphatic rings. These lead to a decrease of the bond order of the P=C bond.

The HOMO orbitals have bonding character, but only in the case of $Me_2P{=}CCl$ they are situated on the P=C bond. The LUMOs present an antibonding character and π symmetry, and they are situated for all monomers on the double bond.

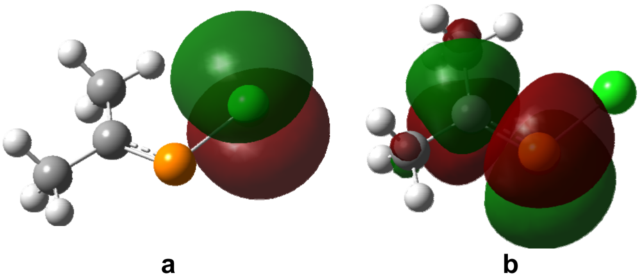


Figure 2. Shape of the NB orbitals involved in charge transfer for Me_2CPCl: (a) lone pair on the chlorine atom; (b) anti-bonding orbital of π symmetry localized on the P-C bond

In the case of dimeric species, two possible ways of dimerization for the monomers considered above, both involving the P=C double bond, and leading to either the *head-to-head* or the *head-to-tail* dimers. For each case, the chlorine atoms on the phosphorus can adopt either a *cis* or a *trans* orientation with respect to the plane of the four-atom ring. Thus, four different dimers were investigated through theoretical calculations (B3LYP/6-311G(d,p)) for each different monomer.

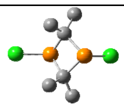
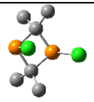
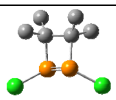
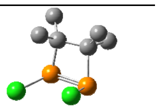
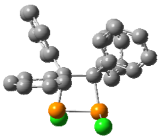
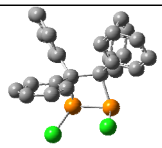
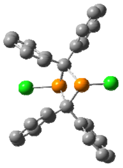
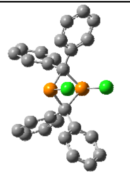
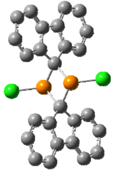
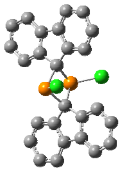
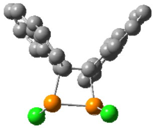
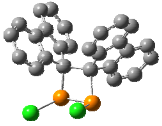
Table 3 contains the calculated B3LYP/6-311G(d,p) energies and relative energies (reported to the lowest-energy structure) for the dimeric species, six *head-to-head*, and six *head-to-tail* dimers. The optimized geometry is also presented. The hydrogen atoms have been omitted for clarity, and the rings are oriented so that the numbering of the atoms corresponds to that given in scheme 4.

- ● carbon
- ● phosphorus
- ● chlorine

Scheme 4

It can be noted that the presence of two phenyl groups on the carbon atom imposes greater strain on the four atom ring compared to the fluorenyl-substituted analogue. In the absence of any such constrain, that is, for the methyl-derivative, the energies of the four dimers are within less than 5 kcal/mol of each other. However, a slightly bigger group, like fluorenyl, significantly changes the situation, first by stabilizing the *trans head-to-head* dimer and then by increasing the energy difference to about 10 kcal/mol between the lowest-energy isomer and the *cis* head-to-tail one. This trend is not kept for the phenyl disubstituted dimers, where the *trans* head-to-tail isomer is the highest in energy. In all cases though, the difference between the *cis* and *trans* conformations of the same isomer are not significant.

Table 3. Calculated B3LYP/6-311G(d,p) energies (HF) and relative energies (kcal/mol) for the dimeric species

Dimer	*trans, head-to-tail*	*cis, head-to-tail*	*trans, head-to-head*	*cis, head-to-head*
R	**Me**	**Me**	**Me**	**Me**
				
E(	-1839.017129	-1839.012333	-1839.019696	-1839.013043
ΔE	1.61	4.62	0.00	4.17
R	**Ph**	**Ph**	**Ph**	**Ph**
				
E(HF)	-2605.951626	-2605.94615	-2605.929117	-2605.928376
ΔE	0.00	3.44	14.12	11.15
R	**Fluorenyl**	**Fluorenyl**	**Fluorenyl**	**Fluorenyl**
				
E	-2603.579908	-2603.579908	-2603.579908	-2603.579908
ΔE	0.00	3.21	8.24	9.83

Some relevant geometrical data for the dimers are given in table 4. The optimized geometrical parameters are similar to those found in the literature [12-15].

The relatively low values for the energy barrier between the four possible dimers do not allow to state the existence of only one of them during the reaction, although the experimental evidence points to the formation of only the *trans head-to-tail* dimer for R= fluorenyl. Although thermodynamically favored, the head-to-head isomers can be kinetically less stable, due to the presence of the P-P bond in the ring. Also, a solvent-induced rearrangement to the head-to-tail dimers can not be excluded.

However, by comparing the calculated energies of the dimers to the double of the monomer's value, we can establish if the dimerization is favored. The dimerization energy can be estimated as:

$$E_{dimerization} = 2 \times E_{monomer} - E_{dimer}$$

The dimerization energies calculated with the above formula for the formation of the *trans* head-to-tail dimer are: 17.68 kcal/mol for R=Me, -15.09 kcal/mol for R=Ph and 6.75 kcal for R=Fl_2C.

A graphical representation is found in figures 3-5. It can be noticed that the calculated energies of the dimers are 17.68 kcal/mol (table 5) smaller that the double of the monomer's value which means that the dimerization is favored. Interesting is that the lowest in energy is the *trans* head-to-head dimer.

Regarding the phenyl-derivative the double of the monomer's energy is 15.09 kcal/mol (table 4) smaller that the energies of the dimers which means that the dimerization is not favored. This fact is due to the presence of the two phenyl groups which impose a greater strain on the four atom ring compared to the methyl-derivative. However the difference between the double of the monomer's energy and the *trans head-to-tail* dimer is very small (figure 4).

The head-to-tail dimers with fluorenyl have the calculated energies smaller with 6.75 kcal/mol (table 5) that the double of the monomer's energy. Instead the *head-to-head* dimers have values of the energies higher than the double of the monomer's calculated energy. This means that the dimerization is favored only for the two *head-to-tail* isomers. Although a bulkier organic group like phenyl on the carbon would prevent dimerization, the dimerization occurs in the case of the fluorenyl-derivative because of the planar conformation of the substituent and the *trans* orientation with respect to the four-atom ring.

Table 4. Calculated selected geometrical data and Wiberg bond orders for the dimeric head-to-head and head-to-tail species

Molecule	P1-C1 (Å)	WBO	P1-Cl1(Å)	P2-P1 (Å)	WBO	C1-C2(Å)	WBO	P-P-C(º)	P-C-C(º)	P1···C2(Å)	P-C-C-P(º)
R=Me, head-to-head, *trans*	1.92	0.87	2.09	2.30	0.93	1.59	0.96	75.2	101.4	2.60	22.2
R=Me, head-to-head, *cis*	1.94	0.86	2.11	2.24	0.96	1.58	0.96	76.1	94.0	2.59	33.1
R=Ph, head-to-head, *trans*	1.98	0.84	2.16	2.27	0.95	1.62	0.95	80.6	99.2	2.73	10.4
R=Ph, head-to-head, *cis*	1.97	0.83	2.08	2.28	0.92	1.65	0.94	81.6	100.8	2.63	21.4
R=Fl$_2$C, head-to-head, *trans*	1.95	0.83	2.12	2.30	0.94	1.61	0.94	79.7	100.1	2.74	5.2
R=Fl$_2$C, head-to-head, *cis*	1.93	0.84	2.09	2.32	0.91	1.62	0.92	81.6	102.6	2.60	20.8
Molecule	**P1-C1(Å)**	**WBO**	**P1-Cl1(Å)**	**P2-C2(Å)**	**WBO**	**P2-Cl2(Å)**	**P-C-P(º)**	**C-P-C(º)**	**P···P(Å)**	**C···C(Å)**	**P-C-P-C(º)**
R=Me, head-to-tail, *trans*	1.90	0.87	2.13	1.93	0.85	2.12	90.9	85.3	2.72	2.61	18.6
R=Me, head-to-tail, *cis*	1.92	0.86	2.11	1.92	0.86	2.11	95.0	84.8	2.83	2.59	4.4
R=Ph, head-to-tail, *trans*	1.92	0.84	2.11	1.94	0.82	2.10	89.1	88.1	2.71	2.66	20.5
R=Ph, head-to-tail, *cis*	1.93	0.84	2.10	1.93	0.84	2.10	94.2	84.2	2.83	2.59	13.8
R=Fl$_2$C, head-to-tail, *trans*	1.94	0.80	2.09	1.94	0.80	2.09	90.8	87.5	2.76	2.68	13.6
R=Fl$_2$C, head-to-tail, *cis*	1.93	0.80	2.10	1.93	0.80	2.10	90.9	89.1	2.75	2.71	0.0

CONCLUSIONS

A novel cyclic 1,3-diphospha-butane was obtained starting from 9-trimethylsilyl-fluorene and PCl_3 in a one-pot procedure. The derivative was characterized in solution through multinuclear NMR spectroscopy. The proposed mechanism of formation involves the presence of the phosphaalkene $Fl_2C{=}PCl$. Theoretical investigations were carried out at the B3LYP/6-311G(d,p) level in order to gain an insight on the dimerization of the phosphaalkene to the 1,3-diphospha- cyclobutane.

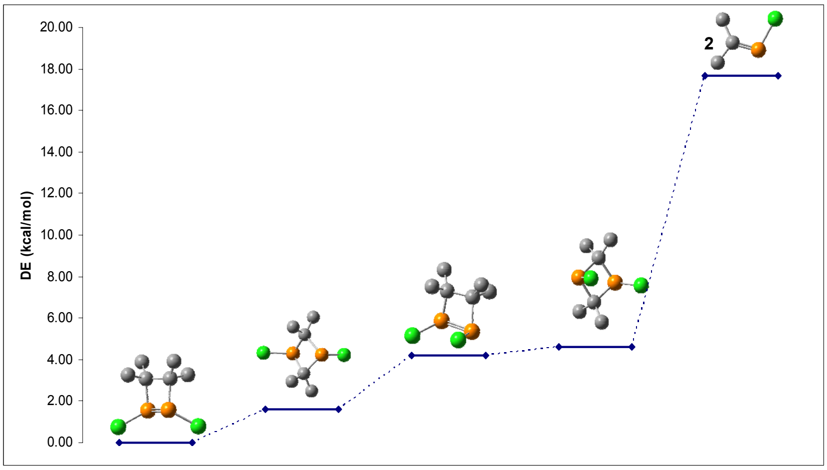


Figure 3. Energy barriers between possible dimers for $[Me_2CPCl]_2$

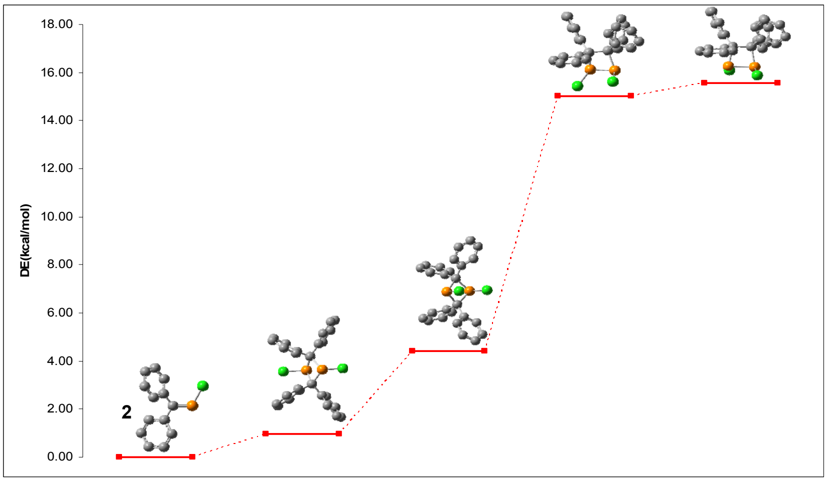


Figure 4. Energy barriers between possible dimers for $[Ph_2CPCl]_2$

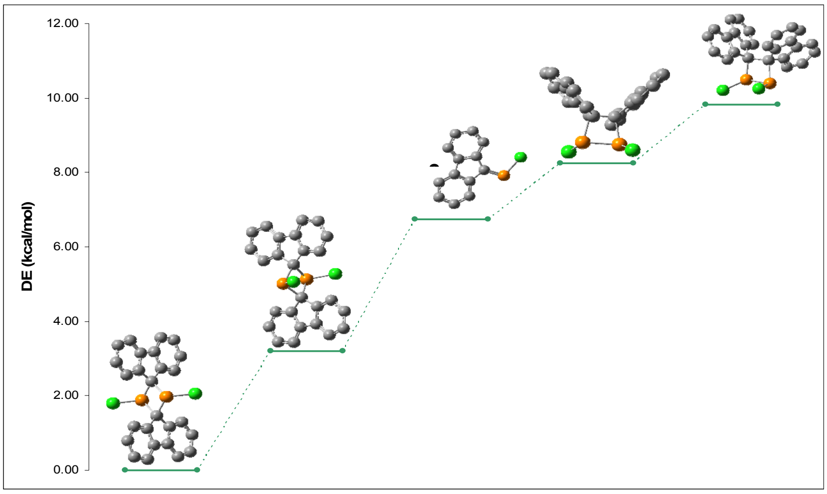


Figure 5. Energy barriers between possible dimers for $[Fl_2CPCl]_2$

Three model compounds were considered: $Me_2C{=}PCl$, $Ph_2C{=}PCl$ and the supposed reaction intermediate, $Fl_2C{=}PCl$ ($Fl_2C=$ fluorenyl). The energies of the possible dimers were calculated and the energy barriers between them were estimated in every case. The calculated dimerization energies showed that in the case of the less hindered methyl- and fluorenyl-substituted phpsphaalkenes, dimerization should readily occur, with the formation of mainly the head-to-tail dimer.

The 1,3-diphosphacyclobutane will be employed as the equivalent of phosphaallenes in organometallic chemistry, with focus on the synthesis of Pt and Pd-coordinated compounds which can be tested for biological activity.

EXPERIMENTAL SECTION

Theoretical calculations were carried out on model compounds of the monomeric (R_2CPCl) and dimeric ($[R_2CPCl]_2$) species, at the B3LYP[10]/6-311G(d,p) level, using Gaussian09 [11]. Starting geometries were built with GaussView4.1, and then optimized and a frequency analysis was performed in order to confirm that the optimized structure is indeed a true minimum. In the case of the dimers, the chlorine atoms on the phosphorus can be in either *cis* or *trans* orientation with respect to each other, relatively to the plane of the 4-atom ring, so four structures were optimized for each dimer.

The starting geometries were approximated by the software user, since the built-in GaussView minimizer led to improbable structures as starting point. As in the case of phosphaalkenes, the optimization was followed by a vibrational analysis which allowed us to establish that there are no imaginary frequencies for the diphosphacyclobutanes involved.

Due to the air and moisture sensitivity of most of phosphorus derivatives, all experiments were carried out in flame-dried glassware under an argon atmosphere using high-vacuum-line techniques.

All the employed solvents were purified using an automated solvent purifying system (MBRAUN AUTO SPS). NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 300 spectrometer

Synthesis and characterization of 1,3-diphosphacyclobutane 3

A solution of 6 ml *n*-BuLi 1,6 M (9.6 mmol) was added at – 40° C to a solution of $FlSiMe_3$ (2g, 8.4 mmol) in 30 ml of diethyl-ether. The reaction mixture was stirred for 20 minutes and at the same temperature, then 0.74 ml of PCl_3 (8.5 mmol) were slowly injected into the reaction mixture by a syringe. The solvent was then removed under vacuum and replaced with a mixture of 10 ml THF and 10 ml toluene. Lithium salts were removed by filtration and a white-yellow precipitate appeared.

^1H NMR ($CDCl_3$): 7.47-7.62 ppm, m, 4H, H_b,H_c; 7.90 ppm, d, 2H H_d ($^2J_{H\text{-}H}$ = 7.50Hz); 8.06 ppm d, 2H, H_a ($^2J_{H\text{-}H}$ =7.80 Hz);
^{13}C NMR ($CDCl_3$): 120.50- 122.45 ppm, t, 2C, ($^2J_{P\text{-}C}$ = 117.61 Hz);
^{31}P NMR ($CDCl_3$): 179.47 ppm, s.

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