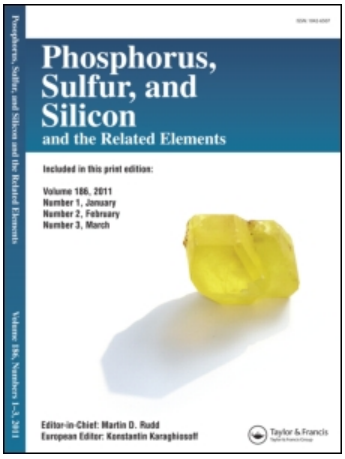

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PREPARATION OF 1,3-DIPHOSHAALLENE FROM 1,2-DIPHOSPHACYCLOPROPANES: A THEORETICAL INVESTIGATION

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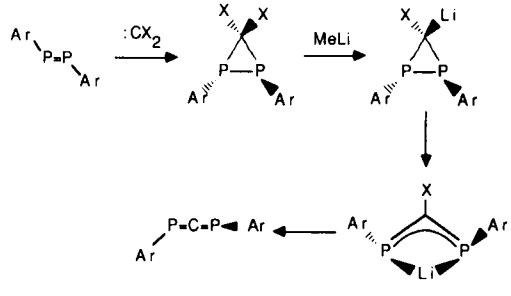
The ring opening of diphosphacyclopropane (**1a**), mono- (**1b**) and di-fluorodiphosphacyclopropane (**1c**) with methyllithium to give diphosphaallene is examined at the 3-21G(*) and 6-31G* Hartree–Fock level. In the first step, the diphosphacyclopropane opens to give the stable Li^+/diphosphaallyl anion pair. The next step, formation of the phosphaallene, is endothermic unless an ionic salt (LiF) is produced, which can be further stabilized by solvent. The overall reaction energetics are 148.7 kJ Mol^{-1} for **1a**, −169.7 kJ mol^{-1} for **1b**, and − 137.8 kJ mol^{-1} for **1c**. The calculated ring strain energy for **1a** is 61.8 kJ mol^{-1}.

Key words: 1,3-diphosphaallene; 1,2-diphosphacyclopropane; calculations; *ab initio*.

Phosphacumulenes present a new class of compounds containing interesting bonding properties. They combine a low valent phosphorus atom participating in a double bond to carbon within the cumulene framework. An interesting member of this class is 1,3-diphosphaallene. This system has been prepared with large, bulky groups attached to each phosphorus atom.[1] Recently, two groups independently developed a new route to this compound via the ring opening of a dihalodiphosphacyclopropane (Scheme 1).[2,3] Diphosphacyclopropanes can be readily prepared by reaction of a diphosphine with a carbene.[4] This new procedure appears to be quite convenient and general.



SCHEME 1

Gouygou, *et al.*[2] proposed the mechanism shown in Scheme 1. They discounted a carbene mechanism since conducting the reaction in the presence of olefin gave no spiranic products. Similarly, the production of allenes from dihalocyclopropanes also proceeds generally without carbene intermediates.[5] Koenig and coworkers[6] have subsequently reported NMR evidence for the existence of the

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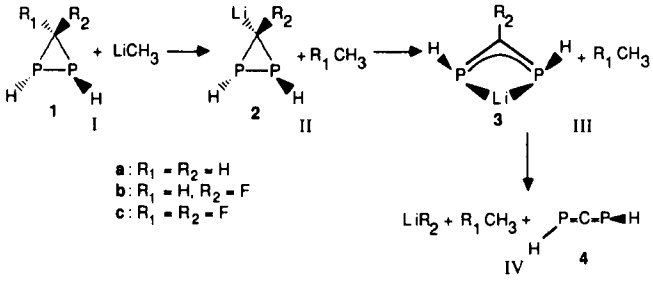
diphosphaallyl intermediate, but they find no signals indicative of the diphosphiranyl anion. We report here *ab initio* studies of this reaction. Examination of the energetics supports the proposed mechanism. The calculated structures of the intermediates have stereochemical consequences that will be detailed.

COMPUTATIONAL METHODS

The experimental studies[2,3,6] have all incorporated large substituents on the phosphorus. These molecules are too large for computational approaches and we have thus restricted this study to the hydrogen-substituted species. The experimental procedure has involved the dichloro- or dibromo-1,2-diphosphacyclopropane which are also too large for computational techniques. Instead, we have examined the reaction of three different 1,2-diphosphacyclopropanes: the parent compound **1a**, 3-fluoro-1,2-diphosphacyclopropane **1b**, and 3,3-difluoro-1,2-diphosphacyclopropane, **1c**. The reactions and intermediates examined are shown in Scheme 2. Note that the intermediate **3** for reaction **b** and **c** are identical, and will be referred to as **3b**.



SCHEME 2

All calculations were performed using Gaussian-86[6] at the Hartree–Fock self-consistent field level. Compounds **1a–3a** were completely optimized using the 6-31G* basis set, but, due to size considerations, the fluorinated compounds were optimized using the 3-21G(*) basis set.[7] Both basis sets have been shown to reasonably reproduce the geometries of organophosphorus compounds.[8,9] All structures were confirmed to be local minima via vibrational frequency analysis at the HF/3-21G level. While it is possible that the nature of the optimized structures may differ with basis set size, our previous work with organophosphorus compounds has never indicated this.[8,9] Even though we have not characterized the geometries obtained with the larger basis sets due to size constraints, we are confident that all the reported structures are local minima. Zero-point energies were calculated at the HF/3-21G level and have been scaled by 0.89.[10] Due to size and time constraints, our calculations have not included electron correlation. Neglecting correlation may cause some of the estimates of the reaction energies to be in error. However, the geometries of organophosphorus compounds are relatively unaffected by correlation.[8,9] Further, the trends indicated here should be unchanged by correlation due to cancellation of errors.

RESULTS AND DISCUSSION

Total energies and zero-point energies of all compounds examined are listed in Table I. Drawings of the structures with pertinent distances are shown in Figure 1. While a number of diphosphacyclopropanes have been synthesized, only one crystal structure has been reported: the triphenyl-phosphino, *t*-butyldipyridino-phosphino derivative.[11] The P–P and P–C distances in this molecule are 2.210 Å and 1.84 Å, respectively. The P–C–P angle is 73.2°. The only previous calculation of this molecule was done at the semi-empirical level.[12] We have determined the structure of the all-hydrogen parent **1a,** for which the P–P and P–C distances are 2.189 Å and 1.852 Å, respectively, and the P–C–P angle is 72.4°. The calculated structure is in remarkably good agreement with the crystal structure, particularly when one considers the differences in substituents and phases. We[13] have previously reported the structure of **4** at this computational level and found it to also be in excellent agreement with the experimental structure.

We have also calculated the *cis* structure of **1a,** shown in Figure 1. The P–P distance is 0.014 Å longer in *cis*-**1a** than in the *trans* form, so as to minimize the interaction of the phosphorus lone pairs. Due to this lone pair repulsion, the *cis* form is 8.20 kJ mol^{-1} higher in energy than the *trans* form. Since the ring opening reaction has been performed only with trans isomers, which are more stable, we will not consider any other *cis*-diphospha-cyclopropanes.

The ring structure of **2a** is little changed from that in **1a**. The C–Li distance of 1.96 Å is typical. The fact that formation of **2a** is exothermic (−61.71 kJ mol^{-1}) and that **3a** is much lower in energy (78.58 kJ mol^{-1}) then **2a** is consistent with the experimental inability to detect the diphosphiranyl anion.[6] Since accurate calculations of lithio-halide carbenoids (such as **2b**) are difficult at the SCF level[14] and the fact that **3b** is expected to be much lower in energy than **2b** (based on the comparision of **2a** and **3a**), we have not calculated the geometry or energy of **2b.** While an intermediate like **2** (which is a local minimum) may lie on the reaction

TABLE I

Total energies (hartrees) and zero-point energies (kJ mol^{-1})

Compound	E(3-21G(*))	E(6-31G*)	ZPE(3-21G)
1a		−721.608 288	113.0
2a		−728.452 486	84.5
3a		−728.482 415	85.4
1b	−816.439 317		93.7
3b	−823.282 991		65.3
1c	−914.757 039		73.6
4	−716.922 848	−720.381 916	52.7
CH_4	−39.976 877	−40.195 172	112.1
CH_3Li	−46.752 481	−47.015 544	83.7
CH_3F	−138.281 893		98.7
LiH		−7.980 868	7.5
LiF	−106.354 185		5.8

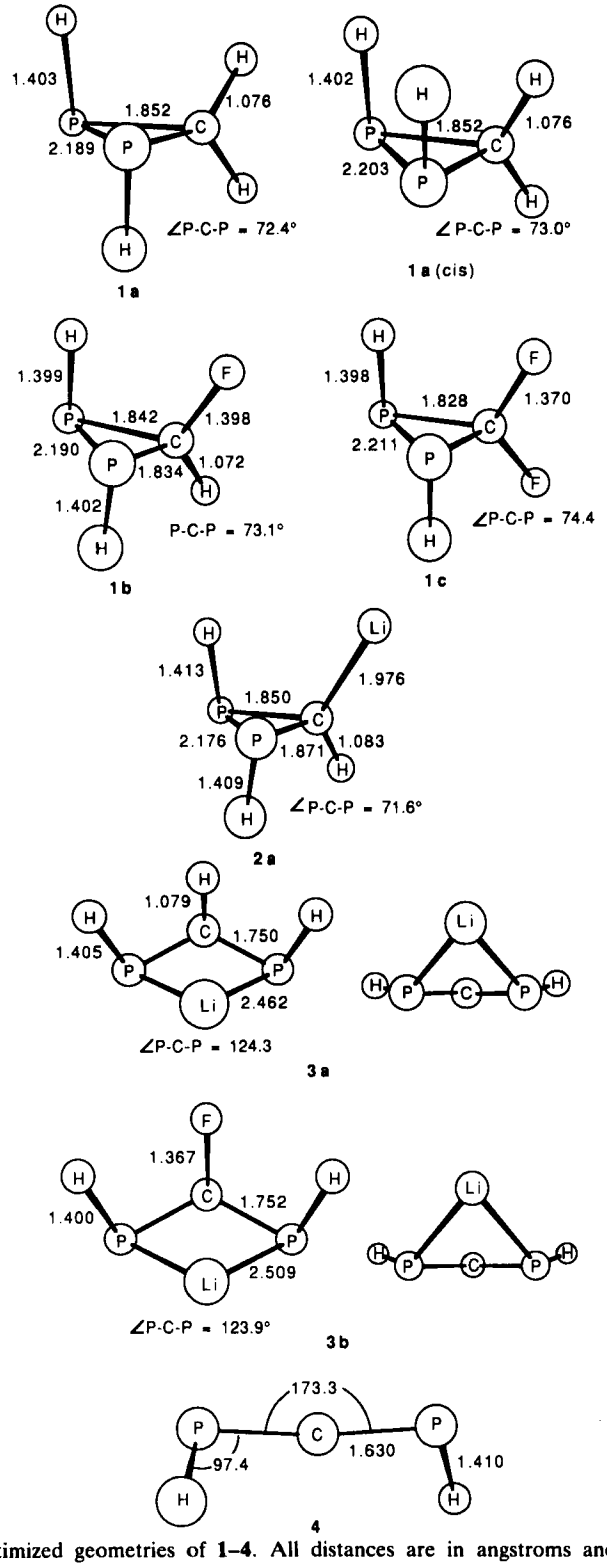


FIGURE 1 Optimized geometries of **1–4**. All distances are in angstroms and all angles are in degrees.

pathway, the bridging structure **3** is much lower in energy, and more likely to be identifiable.

The two calculated lithium-bridged structures show the expected allyl structure. Both structures are local minimum and can be intermediates along the reaction path. The C–P distance in **3a** and **3b** are 1.750 Å and 1.752 Å, respectively, significantly shorter than a typical C–P single bond (1.85 Å) but longer than a C–P double bond (1.65 Å). The lithium atom lies above the plane of the P–C–P allyl system, symmetrically bridging across the terminal P atoms. This structure has been well established for allyllithiums,[15] and can be understood in terms of a nearly complete ionic interaction between allyl anion and lithium cation. The hydrogen atoms attached to the phosphorus atoms in both **3a** and **3b** are bent upwards, out-of-plane towards the lithium cation (shown in the end-on view in Figure 1). This bending hybridizes the π orbitals so that they point towards the cation and affects a stronger electrostatic interaction. Niecke, Klein, and Nieger[16] have recently reported the crystal structure of a P–Si–P allyl anion system with the bridging lithium in the plane of the allyl system. Our system differs in that the P–P separation is about 0.35 Å shorter than in the Si system, which allows for a stronger P–Li interaction (reflected in the smaller P–Li distances: 2.462 (**3a**), 2.509 Å (**3b**) and 2.65 Å in the Si system). Also, the Si system has bulky substituents on the P, which may prohibit the out-of-plane bending that orients the anion towards the cation.

We also note that the hydrogens attached to each phosphorus in **3a** and **3b** are *cis*. Geometry optimization beginning with a *trans* arrangement led to a minimum energy structure identical to the minimum located when Cs symmetry (i.e. *cis* hydrogens) was invoked. The stereochemistry of the reactant diphosphine (either *cis* or *trans*) is lost with the formation **3.** Therefore, any stereochemical outcome for the synthesis of phosphacumulenes must be determined in the last step, III → IV.

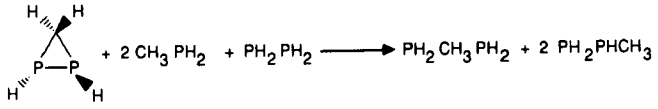
Reaction energetics are listed in Table II. These energies incorporate the zero-point energies. The ring opening of the parent compound is endothermic, while the mono- and diluorinated diphosphacyclopropanes will ring open with release of energy.

The formation of the bridged-lithium species **3a** from **1a** is quite exothermic, about 140.3 kJ mol^{-1}; however, this is an overestimation since there is a change in the coordination number for lithium. Dimerization of methyllithium is approximately 177.82 kJ mol^{-1} exothermic,[17] which reduces the exothermicity of this first step (I → III) to approximately 59.6 kJ mol^{-1}. Lithiation of the fluorine-substituted diphosphacyclopropanes are slightly more exothermic than for the parent species: in energies of reaction of **1b** and **1c** are 178.7 and 146.5 kJ mol^{-1}, respectively.

TABLE II

Reaction energetics in kJ mol^{-1}

Reaction	I → III	III → IV	overall
a	−140.29	288.99	148.70
b	−178.70	8.95	−169.74
c	−146.52	8.95	−137.57



SCHEME 3

The energy of conversion of **3a** to product **4** is +288.99 kJ mol^{-1}; there is no driving force for this step, reflecting the high energy of the phosphacumulene and the stability of the Li$^+$/diphosphaallyl anion pair. However, the conversion of **3b** to product is only 8.95 kJ mol^{-1} endothermic. The formation of LiF is much more favorable than LiH; the bond energies are 243 kJ mol^{-1} for LiH and 573 kJ mol^{-1} for LiF. Further, the solvation energy of LiF is quite large and would undoubtably aid in driving the reaction. Thus, halide substitution on the carbon facilitates both steps in the reaction, but particularly the final step, where the solvation of the salt overcomes the energy needed to form the "strained" phosphacumulene.

We have also estimated the ring strain energy in **1a** using the homodesmic reaction shown in Scheme 3. All structures were completely optimized using the 6-31G* basis set and zero-point energies were estimated at the 3-21G level. The reaction energy is −61.76 kJ mol^{-1}. **1a** is therefore less strained than phosphirane (where we[9] have previously estimated the ring strain energy (RSE) as 84.1 kJ mol^{-1}) and cyclopropane (RSE[18] of 116.3 kJ mol^{-1}). Replacing a carbon in a three-member ring with phosphorus reduces the strain for two major reasons: (1) the C–P distances are longer than C–C distances and thus afford greater separation of the bond pairs and (2) phosphorus utilizes a greater amount of p-character in its bonds than carbon and can better accommodate the small ring angles. Interestingly, these two effects outweigh the effect of having adjacent phsophorus lone pairs, which of course, are mediated in the *trans* form.

CONCLUSION

The ring opening of diphosphacyclopropanes is understood in terms of the energies of the two steps involved. In the first step, the diphosphacyclopropane opens to give the allyl anion, driven by two exothermic processes: (1) relief of the relative small ring strain (estimated as 61.8 kJ mol^{-1}) and (2) formation of the stable Li$^+$/diphosphaallyl anion pair. The next step, formation of the phosphaallene, is endothermic unless an ionic salt is produced, which can be further stablized by solvent.

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