is 3386 Hz. Also the larger doublet separation for P_A (P_A exhibits a doublet of doublets) matches that of P_D, which further supports their assignment as being trans to each other. For P_B, the larger doublet separation matches that of P_C, indicating that these two nuclei are trans to each other. The additional satellite peaks observed for P_B and P_C substantiate their position trans to the Pt–Pt bond, where strong $^2J_{Pt-P}$ coupling is present.

Complex **1** is the first example of a stable compound in which all three types of coordination geometries possible for a bidentate phosphine ligand are observed. The structural characterization of this particular Pt(I) dimer is important for several reasons. First of all, it supports the characterization made by low-temperature ^{31}P NMR spectroscopy of the $[Pt_2(dppm)_2PPh_3Cl]^+$ intermediate proposed by Blau and Espenson in which one of the dppm ligands is bridging and the other is chelating.[12a] Second, the formation of **1** can only result from the dissociation of one end of the bridging dppm ligand, a mechanistic step that has been previously proposed to occur in both mononuclear and dinuclear complexes during ligand substitution reactions.[12b,22] We suggest that the geometrical arrangement of the phosphine ligands in **1** results from the preference of the dppe ligand to chelate[23] and the ability of the dppm ligand to choose both a bridging and a monodentate position. Thus, the structure of **1** also emphasizes the coordination flexibility that makes the dppm ligand somewhat unique among phosphines.[24]

Conclusions

Our results show not only the general application of the homonuclear ^{31}P COSY experiment for the structural analysis of platinum phosphine complexes but also the following advantages of this technique: (1) the pulse sequence for the COSY experiment is available on all high-field instruments and is easy to use; (2) the positions of the observed cross-correlations provide the magnitude and sign of the $^2J_{Pt-P}$ coupling constants for the dinuclear complexes even when the one-dimensional satellite resonances are poorly resolved allowing the unambiguous assignment of the positions of the nonphosphine ligands; (3) the cross-peaks present between the satellite peaks facilitate the definitive assignment of the main phosphorus resonances, even when the main resonances are overlapping; (4) weaker couplings that cannot be determined in the one-dimensional spectra may be observed in the COSY spectra, i.e. $^3J_{Pt-P}$ found for **1**, **13**, and **15**; (5) the structures of compounds with relatively complex spin systems, such as **1**, can be assigned with confidence.

Acknowledgment. This project was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. CHE-8416730). J.V.Z.K. gratefully acknowledges this support and the valuable advice of Dr. Jerry Dallas, Medical Systems Group, GE Instruments, Fremont, CA. The Department of Chemistry and Biochemistry at San Francisco State University acknowledges support received from the National Science Foundation (Grant No. DMB-8516065) and the National Institutes of Health (Grant No. RR-02684) for the purchase of the General Electric QE-300 and GN-300 300-MHz NMR spectrometers.

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Supplementary Material Available: Figures showing one- and two-dimensional ^{31}P NMR spectra of complexes **5**–**8** and **14** (8 pages). Ordering information is given on any current masthead page.

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[22] (a) Azam, K. A.; Brown, M. P.; Hill, R. H.; Puddephatt, R. J.; Yavari, A. *Organometallics* **1984**, *3*, 697. (b) Brown, M. P.; Yavari, A.; Hill, R. H.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2421.

[23] (a) Sanger, A. R. *J. Chem. Soc., Chem. Commun.* **1975**, 893. (b) Knobler, C. B.; Kaesz, H. D.; Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F. *Inorg. Chem.* **1983**, *22*, 2324.

[24] Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99.

Contribution from URA 454, Université Paul Sabatier, 31062 Toulouse Cedex, France, and Laboratoire de Physico-Chimie Moléculaire, URA 474, Université de Pau et des Pays de l'Adour, Avenue de l'Université, 64000 Pau, France

Diphosphiranes: Formation and Ionic Ring Opening, a Theoretical Approach

C. Tachon,[‡] M. Gouygou,[‡] M. Koenig,[‡] M. J. Hervé,[§] D. Gonbeau,[§] and G. Pfister-Guillouzo[*,§]

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The process of addition of methylene to diphosphene was studied theoretically using ab initio theory (SCF + CI level). Two possible mechanisms (addition to the π system and addition to the lone pair of phosphorus) were analyzed. The preferential process corresponds to a π addition leading to the diphosphirane ring. The cationic and anionic ring opening processes of the diphosphirane have been investigated at the same level of theory (ab initio SCF + CI). The results were analyzed by comparison with those of cyclopropane and in terms of the Woodward–Hoffmann rules. For the cations, the cleavage of the P–P bond (disrotatory motion) leads directly to an exo–endo open-chain structure. In the case of the anions, in contrast, a cyclic intermediate was located, which leads to an exo–exo open-chain species in a conrotatory ring opening.

Introduction

The chemistry of phosphorus analogues of cyclopropane has only been developed recently.[1] Since 1986, some of us have reported that the reactivity of various carbenoids on the diphosphene series leads to stable functionalized diphosphiranes.[2,3]

Further work indicated the ability of these strained molecules to undergo ring opening under thermal,[4] photochemical,[5] anionic,[6] and cationic[7] reaction conditions. The resulting products were fully characterized.

In this paper, using ab initio theory (SCF + CI level), we have studied the possible mechanisms of attack of methylene. Although carbene addition to alkenes has been extensively studied, little work has been done on the reactivity of carbenes toward heteroatomic π bonds; in particular, the problem of the preferential site of addition (π system or lone pair)[8] has not been fully elucidated.

[‡] Université Paul Sabatier.

[§] Université de Pau et des Pays de l'Adour.

[1] Mathey, F. *Chem. Rev.* **1990**, *90*, 997.

[2] Bellan, J.; Etemad-Moghadam, G.; Payard, M.; Koenig, M. *Tetrahedron Lett.* **1986**, *27*, 1145.

[3] Etemad-Moghadam, G.; Bellan, J.; Tachon, C.; Koenig, M. *Tetrahedron*, **1987**, *43*, 1793.

[4] Gouygou, M.; Bellan, J.; Escudie, J.; Couret, C.; Dubourg, A.; Declercq, J. P.; Koenig, M. *J. Chem. Soc., Chem. Commun.* **1989**, 593.

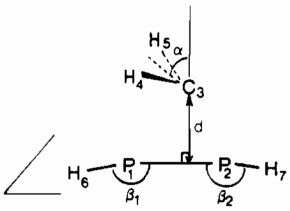
[5] Gouygou, M.; Tachon, C.; Koenig, M.; Dubourg, A.; Declercq, J. P.; Jaud, J.; Etemad-Moghadam, G. *J. Org. Chem.* **1990**, *55*, 5750.

[6] (a) Gouygou, M.; Tachon, C.; Koenig, M.; Etemad-Moghadam, G.; *New J. Chem.* **1989**, *13*, 315; (b) Karsch, H. H.; Reisacher, H.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 454.

[7] Gouygou, M.; Tachon, C.; Etemad-Moghadam, G.; Koenig, M.; *Tetrahedron Lett.* **1989**, *30*, 7411.

0020-1669/92/1331-2414$03.00/0 © 1992 American Chemical Society

Table I. Variations in Geometry and Energy as Functions of the Distance *d* for the π Addition of Singlet CH_2 to Diphosphene



	d, Å							
	1.5[a]	2	2.2	2.5	3	3.5	4	5
$l_{P_1-P_2}$, Å	2.190	2.135	2.084	2.039	2.003	2.001	1.993	1.993
$l_{C_3-P_1}$, Å	1.855	2.276	2.659	3.190	3.593	4.020	4.460	5.376
P_2	1.855	2.259	2.277	2.500	3.000	3.500	4.000	5.000
α, deg	0	11	45	54	60	20	18	15
β_1, deg	94.66	94.11	93.98	94.10	94.67	95.10	95.30	95.22
β_2, deg	94.66	94.22	96.11	96.09	95.13	95.77	95.52	95.27
HPPH, deg	171.06	176.97	177.72	178.77	179.20	179.23	179.68	180
E_{SCF} (hartrees)	−720.81249	−720.73898	−720.69462	−720.65600	−720.64168	−720.63853	−720.63503	−720.63402
E_{SCF+CI} (hartrees)	−721.13871							−720.95377

[a] Experimental values for the cycle $(PAr)_2CCl_2$.[10] $l_{P_1-P_2}$ = 2.245 Å; $l_{C_3-P_1}$ = 1.863 Å; $\beta_1 = \beta_2$ = 101.8°; CPPC = 176.37°. Exothermicity (SCF) = 468.6 kJ·mol^{-1}. Exothermicity (SCF + CI) = 485.1 kJ·mol^{-1}.

The different acyclic isomers of diphosphirane are also considered herein.

The presence of heteroatoms in the molecule makes more difficult the application of the Woodward–Hoffmann rules[9] to the ring opening process of diphosphiranes. Therefore, a systematic quantum chemical study of ionic (cationic and anionic) ring opening of diphosphirane was undertaken.

Computational Details

The calculations were all performed using the Monstergauss program.[10] We used a modified 4-31G basis set in which one set of d polarization functions was added to the phosphorus atom (ζ_P^d = 0.57).[11] In order to obtain an appropriate description, s and p diffuse functions for phosphorus and carbon atoms were used for the anionic species (exponents: 0.0348 for P; 0.0438 for C).[12]

The molecular geometries were optimized at the SCF level with respect to all bond lengths and bond angles by a gradient method.[13] The detection of transition states was carried out using the Powell algorithm.[14] Each stationary point was characterized by force constant matrix analysis.

The effects of electronic correlation on these optimized geometries were estimated by configuration interaction using a variational perturbation method (CIPSI algorithm).[15] In this formalism, a variational zeroth-order wave function is built from iterative selection of the most important determinants according to a threshold on the coefficients. The perturbative step is a multireference second-order Moller–Plesset treatment and includes all single and double excitations from the main determinants.

Whereas the experimental work has been performed using very bulky substituents on the phosphorus atoms, these substituents were replaced by hydrogen atoms for our computational approach.

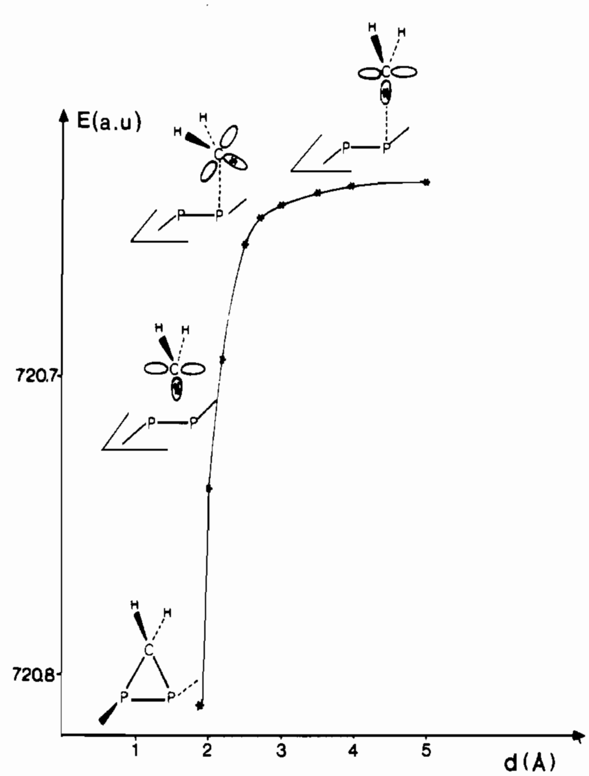


Figure 1. π addition of $^1CH_2$ to HP=PH. Energy change along reaction coordinate.

Addition Reaction of Singlet Methylene to Diphosphene

A priori, an addition mechanism similar to that observed for ethylene was likely for the diphosphene system; only the diffuse character of the P=P π bond and the energetic positions of $\pi_{P=P}$ and $\pi^*_{P=P}$ orbitals could lead to differences in the interactions governing the approach of the carbene. However this heteroatomic system is characterized in its ground state by a quasidegeneracy of $\pi_{P=P}$ orbital and n_P combination of the phosphorus lone pairs. Therefore, it is also necessary to consider the approach of the carbene in the σ plane of the molecule.

Addition to the π System. In order to describe this approach, we chose as the reaction coordinate the distance *d* between the carbon atom and the P–P bond. In preliminary calculations, we noticed at long distances *d* an analogy with the addition process to ethylene;[16] the methylene is situated preferentially above a

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(8) (a) Snyder, J. P.; Boyd, R. J.; Whitehead, M. A. *Tetrahedron Lett.* **1972**, *42*, 4347; (b) Carlsen, L.; Snyder, J. P. *J. Org. Chem.* **1978**, *43*, 2216.

(9) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(10) Peterson, M.; Poirier, R. Monstergauss (April, 1986), Chemistry Department University of Toronto, Ontario, Canada. Monstergauss is a modification of the Gaussian series of programs developed by J. A. Pople and co-workers.

(11) (a) Ditchfield, R.; Hehre, W. H.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724; (b) Kutzelnigg, W.; Wallmeier, H. *Theor. Chim. Acta* **1979**, *51*, 261.

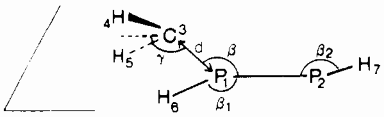
(12) Lohr, L. L.; Ponas, S. H. *J. Phys. Chem.* **1984**, *88*, 2992.

(13) Fletcher, R. *Comput. J.* **1970**, *13*, 317.

(14) Powell, M. J. D. In *Numerical methods for nonlinear algebraic equations*; Gordon and Breach: New York, 1981; p 87.

(15) (a) Huron, B.; Malrieu, J. P.; Rancurel, P. *J. Chem. Phys.* **1973**, *58*, 5745; (b) Pellissier, M. Thèse, Université P. Sabatier, Toulouse, France, 1980.

Table II. Variations in Geometry and Energy as Functions of the Distance *d* for the Addition (to the Lone Pair of Phosphorus) of Singlet CH_2 to Diphosphene[a]



	d, Å							
	1.628	1.65	1.9	2.2	2.5	3	4	5
$l_{P_1-P_2}$, Å	2.045	1.981	1.984	1.987	1.987	1.988	1.990	1.992
$l_{P_1-H_6}$, Å	1.409	1.414	1.414	1.414	1.414	1.414	1.413	1.413
$l_{P_2-H_7}$, Å	1.387	1.406	1.411	1.414	1.414	1.414	1.413	1.413
γ, deg	180.30	160	130	105.19	85.63	109.39	113.61	114.52
β, deg	138.55	136.30	131.82	120.79	121.17	134.81	130.68	131.92
β_1, deg	113.84	98.01	98.8	99.14	92.38	89.31	89.30	89.30
β_2, deg	91.83	93.35	93.81	94.17	94.74	96.38	96.37	96.41
HCH, deg	117.18	116.50	109	107.82	101.21	104.72	107.70	107.60
$H_4C_3P_1P_2$	0	80	100	125	128	129	130	130
E_{SCF} (hartrees)	−720.74622	−720.69090	−720.67226	−720.65801	−720.64605	−720.63810	−720.63433	−720.63396
E_{SCF+CI} (hartrees)	−721.08507							−720.95332

[a] Exothermicity (SCF) = 294.3 kJ·mol^{-1}. Exothermicity (SCF + CI) = 344.4 kJ·mol.

phosphorus atom, the hydrogen atoms being oriented toward the interior of the system.

The methylene displacement toward the middle of the bond occurs only at the end of the reaction pathway for $d < 2.2$ Å and is associated with the strongest energetic stabilization (Figure 1). The reaction occurs without any energy barrier with an exothermicity of 468.6 kJ·mol^{-1} at the SCF level, and of 485.1 kJ·mol^{-1} after inclusion of CI.

The analysis of changes in geometric parameters (Table I) shows that the beginning of the reaction (d = 5–3.5 Å) corresponds to a "σ-type" approach. As a matter of fact, the angle α varies between 15° and 20°, which indicates a predominance of the interaction $\pi^*_{P=P} \leftrightarrow n_{CH_2}$ with respect to the $\pi_{P=P} \leftrightarrow p^*_{CH_2}$ interaction. Subsequently we observe, between 3.0 and 2.2 Å, a pivotal motion of the methylene group associated with a more important contribution of the $\pi_{P=P} \leftrightarrow p^*_{CH_2}$ interaction ($45° \leq \alpha \leq 60°$). We notice, simultaneously to the displacement of the methylene group toward the middle of the P–P bond, a further pivotal motion of this group leading to ring formation. The change in phosphorus lone-pair hybridization only takes place at the end of the reaction at $d < 2.2$ Å.

Distinguishing between the electrophilic and nucleophilic phases is more difficult than in the case of addition to ethylene. The lower position of the $\pi^*_{P=P}$ orbital with respect to the $\pi^*_{C=C}$ orbital leads to a more important $\pi^*_{P=P} \leftrightarrow n_{CH_2}$ interaction throughout the reaction pathway.

The reaction is stereospecific, giving a trans product. We have determined that the preferential isomer of diphosphirane has a trans configuration ($\Delta E^{total}_{trans-cis} = -102.7$ kJ·mol^{-1}).

Addition to the Phosphorus Lone Pair. In order to study the addition mechanism in the σ plane of the diphosphene, we have chosen the C–P distance as the reaction coordinate. The adopted arrangement corresponds to the addition mechanism rather than the insertion into a P–H bond. At the beginning of the reaction pathway, the methylene group approaches from a direction which makes an angle β of about 130° with the hydrogen atoms situated on each side of the σ plane of diphosphene (Figure 2, Table II).

The main interaction takes place between the unoccupied $p^*_{CH_2}$ orbital and the HOMO of the diphosphene associated with the symmetrical combination of phosphorus lone pairs. A further interaction, though of lesser importance, must be taken into account between the n_{CH_2} orbital and σ^*_{P-P} of diphosphene.

The major orbital interaction is reflected in the geometric changes taking place along the reaction pathway. The angle γ decreases from 114.5° at 5 Å to 85.6° at about 2.5 Å. From this point, with the formation of the P–C bond, we notice a methylene group displacement which can be described as a shift of the HCH fragment corresponding to an increase of the angle γ from 85.6° to around 160°. At the same time, we notice a carbon rehybridization (opening the HCH angle from 101.2° to 116.5°) and P–C bond formation (Figure 2).

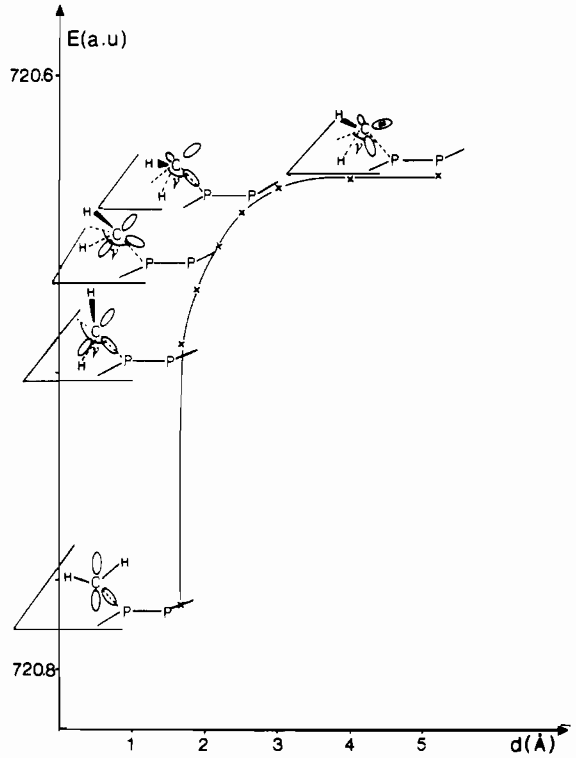


Figure 2. Addition (to the lone pair of phosphorus) of $^1CH_2$ to HP=PH. Energy change along reaction coordinate.

At the end of the reaction pathway, for a P–C length of 1.65 Å we observe a 90° rotation of the CH_2 group about the P–C bond, leading to the final addition product: the cis isomer of the methylenediphosphene with a perfectly planar structure.

In view of the nature of the main orbital interaction, methylene behaves as the electrophile up to the point of rotation about the P–C bond. The two electrons in the carbon σ orbital are then combined with the diphosphene π system to give the methylenediphosphene, a four-electron three-center system.

The energy decreases continuously during the geometric changes (Table II). The addition reaction of singlet methylene to the phosphorus lone pair corresponds to an exothermicity of 294.3

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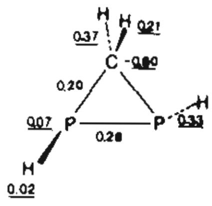
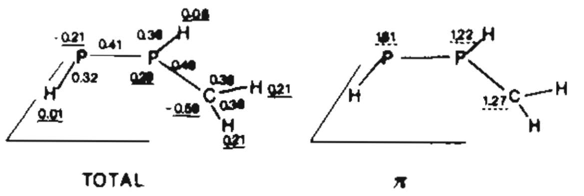
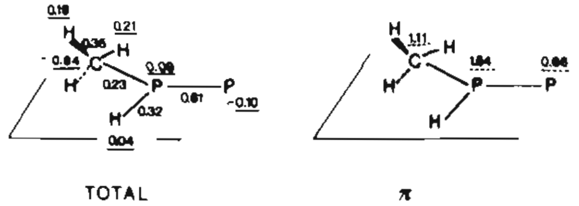
(16) (a) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475; (b) Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9096; (c) Zurawski, B.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1978**, *100*, 2654.



Diphosphirane



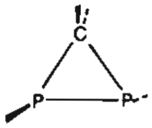
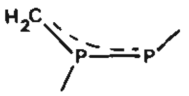
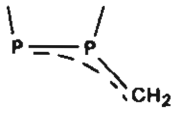
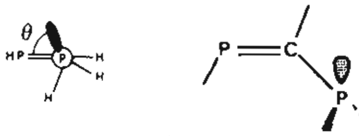
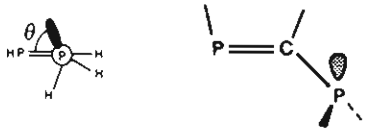
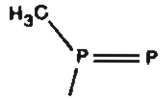
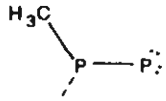
Methylene diphosphene (cis)



Methylphosphino phosphinidene

Figure 3. Mulliken populations: net total charges (full lines) and overlap populations π charges (dotted lines).

Table III. Energies (SCF + CI) of Diphosphirene and Acyclic Isomers Studied

	E_{SCF} (au)	E_{SCF}^{+CI} (au)
diphosphirane 	−720.81249	−721.13871
methylenediphosphene (cis) 	−720.74610	−721.08507
methylenediphosphene (trans) 	−720.73885	
diphosphapropene (cis θ = 102°) 	−720.78804	−721.11678
diphosphapropene (trans θ = 114°) 	−720.78760	−721.11643
methylphosphinophosphinidene (singlet) 	−720.77395	−721.10777
methylphosphinophosphinidene (triplet) 	−720.79934	−721.11589

kJ·mol^{-1} at the SCF level and 344.4 kJ·mol^{-1} after inclusion of CI.

Thus we can consider two processes for the addition of singlet methylene to diphosphene, associated with an enthalpy decrease. The preferential mechanism would correspond to the π addition due to the much higher exothermicity.

These results allow us to explain the experimental data; only diphosphiranes with trans configuration have been obtained from cycloaddition reaction of singlet carbenes to diphosphenes stabilized with bulky substituents.[2-5]

Nevertheless, in the carbene/alkene reaction, we must note that recent work of pulsed flash photolysis[17] has indicated, in the case of electrophilic carbenes, the importance of the entropic factor and the possibility of a free energy barrier as the consequence of an unfavorable activation entropy.

Diphosphirane and Acyclic Isomers. Diphosphiranes obtained experimentally show a genuine stability. We decided to compare the stability of diphosphirane with respect to acyclic isomers likely to be formed by ring opening (cleavage of P–P or P–C bonds).

Diphosphirane. The minimized values of the geometric parameters of the diphosphirane are close to those determined experimentally[1] and to those optimized recently.[18] We notice, in the case of the diphosphene optimized under the same conditions, a lengthening of 0.2 Å of the P–P distance, HPP angles very close, and a slightly modified (by approximately 9°) HPPH torsion angle. Similar results have been obtained based on experimental data.[5] Thus, methylene addition to the π system of the diphosphene induces only slight changes in the HPPH σ skeleton.

Analysis of the Mulliken populations (Figure 3) shows low and close values for overlap populations, which indicates the weakness of bonding in the ring and its propensity to opening by P–C and P–P cleavage. The phosphorus atoms are slightly positive and the carbon atom is strongly negative; the rather excessive nature of this charge on carbon is probably due to the absence of polarization functions on the hydrogens.

In agreement with previous work,[19,20] we assign the HOMO of the diphosphirane at 9.39 eV to the symmetrical combination of the phosphorus lone pairs, which one should note is strongly coupled in view of the symmetry with the σ_{P-P} orbital; the LUMO at 3.88 eV is essentially localized on the σ^*_{P-P} orbital.

Methylene Diphosphene. The methylenediphosphene adduct which is the product of addition of singlet methylene to the phosphorus lone pair could equally well be the product of P–C cleavage of the diphosphirane. The calculations have enabled the characterization of two minima with planar structures associated with the two isomers (cis and trans). The cis isomer, which corresponds to the addition product of singlet methylene to a lone pair of the diphosphene (Table III), is preferred energetically by 19.5 kJ·mol^{-1} with respect to the trans isomer. It is, however, clearly less stable than the disphosphirane (ΔE_{SCF-CI} = 140.7 kJ·mol^{-1}). This isomer has a P–P bond length of 2.045 Å, which is longer than the one determined for the diphosphene (1.99 Å); in contrast, the P–C bond length of 1.628 Å is much shorter than in the diphosphaethene. This indicates the allylic π character of the four-electron three-center system. This allylic character

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(17) (a) Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleclay, C., Jr.; Hacker, N. R.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Mussjal, R. C.; Perez, L. A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1587; (b) Houk, K. N.; Rondon, N. G.; Maredo, J. *Tetrahedron* **1985**, *41*, 1555.

(18) Liu, M.; Bachrach, S. M. *Phosphorus Sulfur Silicon Relat. Elem.* **1990**, *53*, 7.

(19) Gleiter, R.; Bohm, M. C.; Baudler, M. *Chem. Ber.* **1981**, *114*, 1004.

(20) Gleiter, R.; Schafer, W.; Baudler, M. *J. Am. Chem. Soc.* **1985**, *107*, 8043.

equally appears on examination of the molecular orbitals. The HOMO at 7.19 eV corresponds to the antibonding combination of the π atomic orbitals of the terminal phosphorus and the carbon. The fully bonding combination of the π atomic orbitals of the three heavy atoms mainly localized on the central phosphorus is at 11.41 eV. The orbital associated with the σ lone pair of the terminal phosphorus has an intermediate position at 10.76 eV. The LUMO at 2.38 eV is π antibonding between the two phosphorus atoms.

From the Mulliken analysis of total charges, the central phosphorus is found to be positively charged whereas the terminal phosphorus and the carbon atom are negative. The π system is polarized in a similar manner but to a greater extent (Figure 3).

Diphosphapropenes. The diphosphapropene corresponds to the product of P–P cleavage of the diphosphirane. For this system, the analysis of rotation about the P–C bond brings to light the existence of four stable conformers of similar energy, two with cis and two with trans configuration.[21]

Letting θ define the dihedral angle between the phosphorus lone pair and the σ_{P-C} bond, one finds that the two cis conformers are associated with values $\theta = 0°$ and $\theta = 102°$; the two trans conformers are associated with the values $\theta = 0°$ and $\theta = 114°$.

The two most stable conformers are the cis ($\theta = 102°$) and the trans ($\theta = 114°$). The preferred configuration corresponds to the cis conformer where there is strong conjugation between the phosphorus lone pair and the $\pi_{P=C}$ bond (Table III). The structural and electronic characteristics of these diphosphapropenes have been reported in detail elsewhere.[22]

The preferred isomer (cis; $\theta = 102°$) is less stable than the diphosphirane ($\Delta E_{SCF+CI} = 57.5$ kJ·mol^{-1}) but more stable than the cis methylenediphosphene ($\Delta E_{SCF+CI} = +83.2$ kJ·mol^{-1}).

(Methylphosphino)phosphinidene. Another possible isomer is the (methylphosphino)phosphinidene, which may also be considered as the product of P–C cleavage in the diphosphirane.

The calculation carried out on the closed-shell singlet state indicates a planar structure with a high degree of delocalization of the central phosphorus lone pair toward the vacant orbital of the phosphinidene creating a P═P double bond. The optimized P–P bond, 1.916 Å, is very close to that obtained using an equivalent basis set for phosphinophosphinidene (1.924 Å).[23]

Analysis of the Mulliken populations shows a slightly negative charge on the terminal phosphorus; in contrast, the central phosphorus carries a slightly positive charge. In addition, the overlap population of the P–P bond is particularly high (Figure 3).

The HOMO calculated at 7.66 eV corresponds to the p lone pair of the terminal phosphorus. At 9.28 eV we find the "$\pi_{P=P}$" orbital. The LUMO, at 1.99 eV, is essentially localized on the "$\pi^*_{P=P}$" orbital.

From an energetic point of view, the singlet (methylphosphino)phosphinidene is less stable than the cis isomer ($\theta = 102°$) of the diphosphapropene ($\Delta E_{SCF+CI} = 23.6$ kJ·mol^{-1}) but more stable than the cis methylenediphosphene ($\Delta E_{SCF+CI} = 59.5$ kJ·mol^{-1}).

In agreement with previous studies on the phosphinophosphinidene[23,24] we have determined for the (methylphosphino)phosphinidene a strongly pyramidal triplet state ($\sum P = 293.5°$) more stable than the closed-shell singlet state ($\Delta E_{SCF+CI} = 21.3$ kJ·mol^{-1}).

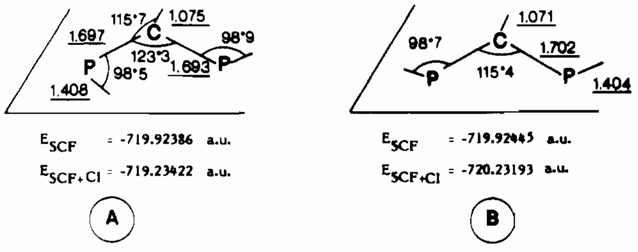


Figure 4. Cationic species. Optimized geometries (bond lengths in Å, angles in degrees); energy values.

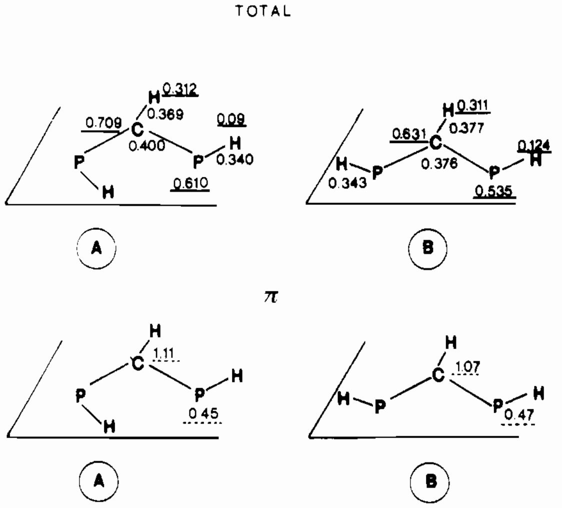
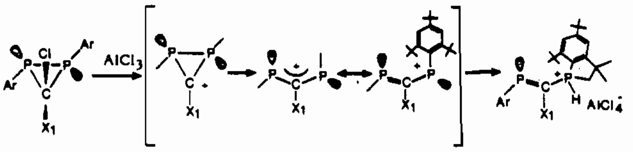


Figure 5. Cationic species. Net total charges (full lines) and overlap populations; π charges (dotted lines).

Ring Opening Reactions of Diphosphirane

We have undertaken a detailed study of the cationic and anionic ring opening of diphosphirane in order to further elucidate the reaction mechanisms and to compare them with the well-known case of cyclopropane.

Cationic Ring Opening Reactions. Experimentally, the action of a Lewis acid on the monohalogenated and dihalogenated diphosphiranes leads to the cleavage of an extracyclic C–X bond followed by the diphosphiranyl ring opening.[7]



From experimental results,[7] the diphosphiranyl cation appears to be unstable. The phosphonium phosphaalkene is the unique isolated product, resulting from the cleavage of a P–P bond followed by an oxidative addition to the lone pair of phosphorus. The ^{31}P NMR parameters of this product, in particular the coupling constant $^2J_{PP}$, indicate the presence of a trans isomer.

The calculations performed for a nonsubstituted system show that there is no stationary point corresponding to a cationic ring. Nevertheless, two minima were found which can be attributed to slightly unsymmetrical exo–endo structure A and to the exo–exo structure B. Due to the bulkiness of the compounds studied experimentally, the endo–endo structure will not be considered in the following calculations. The two systems A and B both have a planar conformation and similar molecular geometry as well as close energy values (Figure 4). However, structure A is the most stable after CI ($\Delta E \simeq 6$ kJ·mol^{-1}).

The preferred open-chain structure has been also observed in the case of $C_3H_5^+$, which is isoelectronic with our system. In this case, the allyl cation is the most stable.[25] However, unlike the

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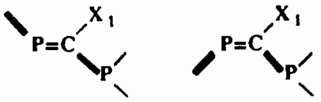
[21] Owing to the difference of the atomic numbers of X_1 substituents (C, Cl, Br) that changes *E* to *Z*, we have used cis and trans instead of the classical *Z* and *E*.



[22] Gougygou, M.; Koenig, M.; Herve, M. J.; Gonbeau, D.; Pfister-Guillouzo, G. *J. Org. Chem.* **1991**, *56*, 3438.

[23] Ha, T. K.; Nguyen, M. T.; Ruelle, P. *Chem. Phys.* **1984**, *87*, 23.

[24] Allen, T. L.; Scheiner, A. C.; Yamaguchi, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1986**, *108*, 7579.

[25] Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.

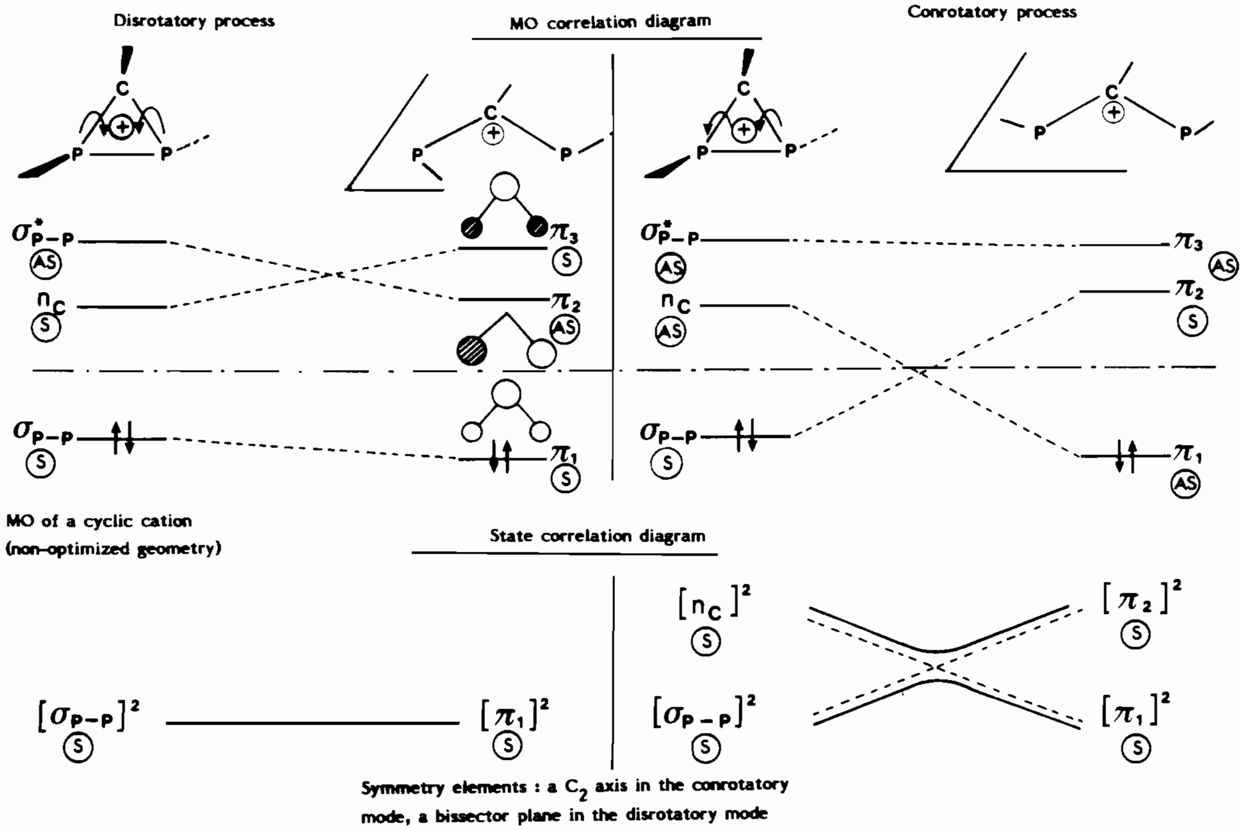


Figure 6. Cationic ring opening of diphosphirane; MO correlation diagram.

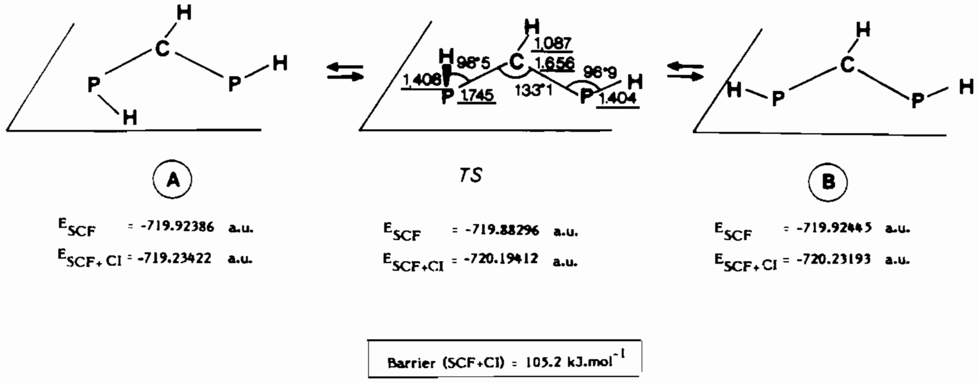


Figure 7. Isomerization of diphosphaallyl cation A into diphosphaallyl cation B.

diphosphiranyl cation, the cyclopropyl cation is also a stable moiety, i.e., a corresponding minimum can be found on the potential energy hypersurface.[25]

The P–C bond lengths in the two systems A and B (A, 1.693, 1.697 Å; B, 1.702 Å) are intermediate between single and double bonds. The very close values of HPC angle (A, 98.5°, 98.9°; B, 98.7°) correspond to the mean value obtained for the isomers of diphosphapropenes[4,5,26] (98.7°). The most important difference is found for the PCP angle, which is larger for A (123.3°) than for B (115.4°) (Figure 4).

These two forms both possess a delocalization of positive charges over the two phosphorus atoms whereas the carbon atom is negatively charged (Figure 5). The electron deficiency of the phosphorus atoms is attributed to the π system, while the electron excess on the carbon atoms is closely related to the positive charge of neighboring hydrogen. We assume this value to be more likely overestimated. The Coulombian repulsions due to the positive charges on the phosphorus atoms promote an open structure rather than a ring structure.

For the cationic ring opening mechanism of diphosphirane, we find that the geometry optimization leads directly to the diphosphaallyl cation A, without any potential energy barrier. This corresponds to a disrotatory process for the ring opening, and hence the conrotatory case will not be considered.

Qualitatively, if we consider the behavior of the molecular orbitals, the ring HOMO of σ_{P-P} type[27] and the first two ring LUMOs (n_C with an important localization on carbon atom in a direction perpendicular to the plane of the ring and σ^*_{P-P}) correlate with the π system of the open molecule. For this two-electron three-center system, the results presented in Figure 6 clearly show a HOMO–LUMO crossing in a conrotatory process. Thus, according to the Woodward–Hoffmann rules, this is a "forbidden" process. On the contrary, such a crossing does not occur in the case of a disrotatory ring opening. Moreover, the correlation diagram shows a direct correlation between the ground states $(\sigma_{P-P})^2$ and $(\pi_1)^2$ in the disrotatory case, whereas the ground

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[26] (a) Appel, R.; Knoch, F.; Laubach, B.; Sievers, R. *Chem. Ber.* **1983**, *116*, 1873; (b) Appel, R.; Folling, P.; Josten, B.; Siray, M.; Winkhas, V.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *96*, 619; (c) Appel, R.; Kochta, J.; Knoch, F. *Chem. Ber.* **1987**, *120*, 131.

[27] The σ_{P-P} bond is strongly coupled with the symmetric combination of phosphorus lone pairs.

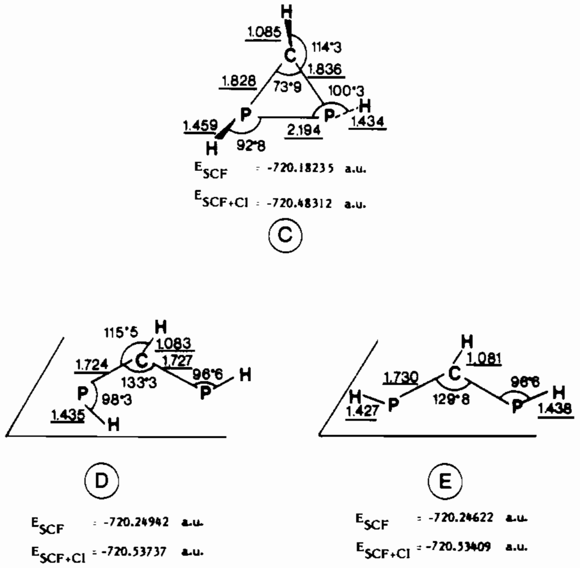


Figure 8. Anionic species. Optimized geometries (bond lengths in Å, angles in degrees); energy values.

state of the cycle correlates with a doubly excited state of the open cation in the conrotatory case.

In agreement with the calculated results showing preferential disrotatory ring opening, there is an avoided crossing and a barrier in the conrotatory process only.

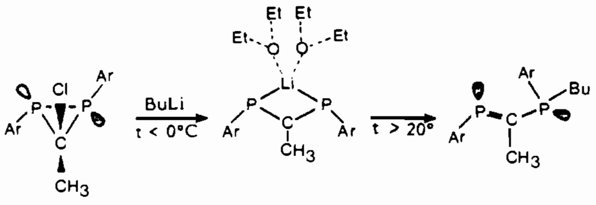
In order to consider diphosphaallyl cation B as a final product, we studied the isomerization process A $\rightleftarrows$ B through a rotation about the P–C bond. The transition state of this isomerization process corresponds to the conformation having the dihedral angle PCPH of 90° (Figure 7). Loss of conjugation during the rotation causes the two P–C bonds to be of different lengths (Figure 7).

The value of the potential energy barrier involved in the process is quite important, 105.2 kJ·mol^{-1} after CI. We note that for the bulky substituted derivatives studied experimentally, this barrier will necessarily be even higher.

The above discussion of the results leads to the following conclusion: the cationic ring opening of diphosphirane corresponds to the formation of a diphosphaallyl cation A through a disrotatory path; this cation A can lead to a cis or trans diphosphapropene. Experimentally, it was not possible to detect the cyclic cation, but the diphosphaallyl cation has been considered as an intermediate in the formation of phosphonium phosphaalkenes in agreement with our theoretical results.

Further confrontation of theoretical results with experimental ones for the ring-opening mechanism has not been possible because of the oxidative addition to the phosphorus lone pair.[28]

Anionic Ring Opening Reactions. By action of butyl lithium on monohalogenated diphosphiranes, an allylic type intermediate was characterized by ^{31}P NMR at low temperature. At room temperature this unstable intermediate leads to a diphosphapropene which has been isolated and shown to have a trans configuration.[6]



Before going into further details of the ring opening process, we first determined the possible stable anionic species. Three minima were found: one of them is the diphosphiranyl anion C which has a ring structure, the other two correspond to diphosphaallyl anions D and E, which are open-chain structures. The anionic open forms D and E are close in energy (ΔE_t = 8.6 kJ·mol^{-1}) (Figure 8) and much more stable than the corresponding cyclic form.

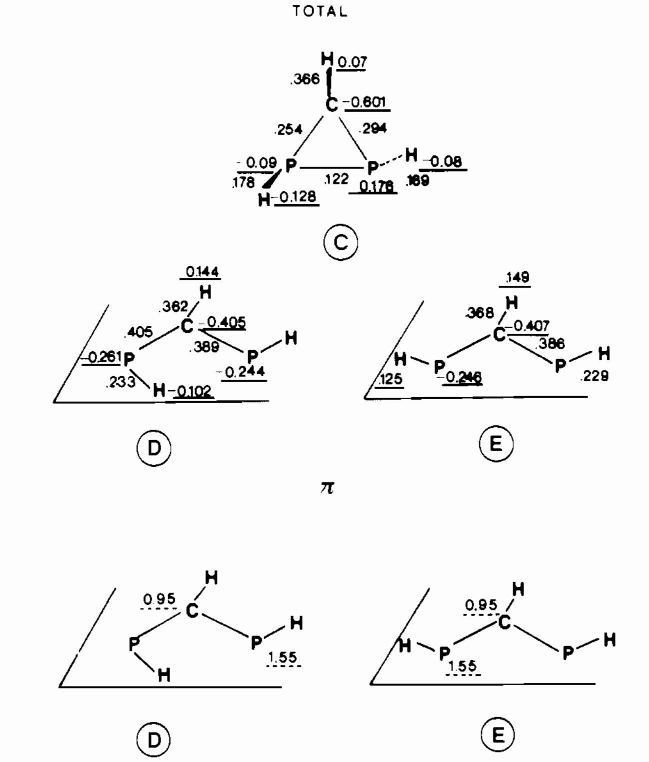


Figure 9. Anionic species; net total charges (full lines) and overlap populations; π charges (dotted lines).

Thus, these results are similar to those obtained in the previous work on $C_3H_5^-$.[29] In this particular case, the allyl anion is much more stable than the cyclopropyl anion. In diphosphiranyl anion as in cyclopropyl anion, we found a tetrahedral structure for the anionic carbon atom, in agreement with a strained cyclic model. In contrast, in the two diphosphaallyl anions, we obtained a planar structure for the central atom of the open forms.

The geometry of the diphosphiranyl anion C ($d_{P\text{-}C}$ = 1.828, 1.836 Å, PCP = 73.9°) is slightly different from the diphosphirane ($d_{P\text{-}C}$ = 1.855 Å, PCP = 72.6°).

The length of the P–C bond in the diphosphaallyl anions D and E is slightly longer than that in the cations examined above. The value (1.73 Å) is intermediate between single and double bonds.

The PCP angle in D (133.3°) is larger than the corresponding value in E (129.8°). These values are close to those of the allyl anion (between 131° and 133°).[29,30]

Examination of charges of the diphosphaallyl anions (Figure 9) reveals different polarities in the σ and π systems with the negative charges delocalized over the phosphorus atoms in π.

The calculations show that the two conrotatory ring-opening processes are the most likely mechanisms. For each case, the transition state was determined between the cyclic form and the open minimum (endo–endo or exo–exo). The P–P bond length together with the rotation angle of the PH group are the main parameters of this reaction pathway. One of the two conrotatory processes leads to a diphosphaallyl anion with an endo–endo conformation. This conformation is very unlikely in the highly substituted derivatives, and we will not consider it further. A low barrier of 15.5 kJ·mol^{-1} is associated with the other conrotatory ring-opening mode which leads to the diphosphaallyl anion E with an exo–exo conformation. At the transition state, the P–P bond is equal to 2.74 Å, and some rotation of the PH groups has

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(28) Recently, we have been able to stabilize the diphosphaallyl cation by anionic transition metal complexes. This complexation reaction should provide more detailed information on the cationic ring opening mechanism.

(29) Froelicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2853.

(30) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 4793.

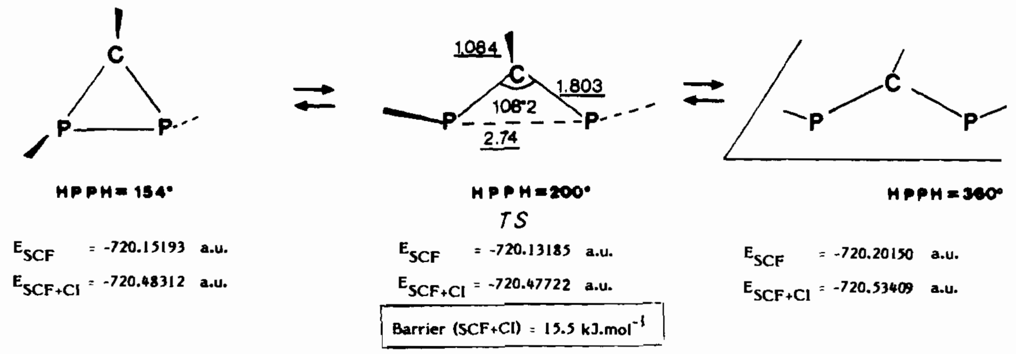
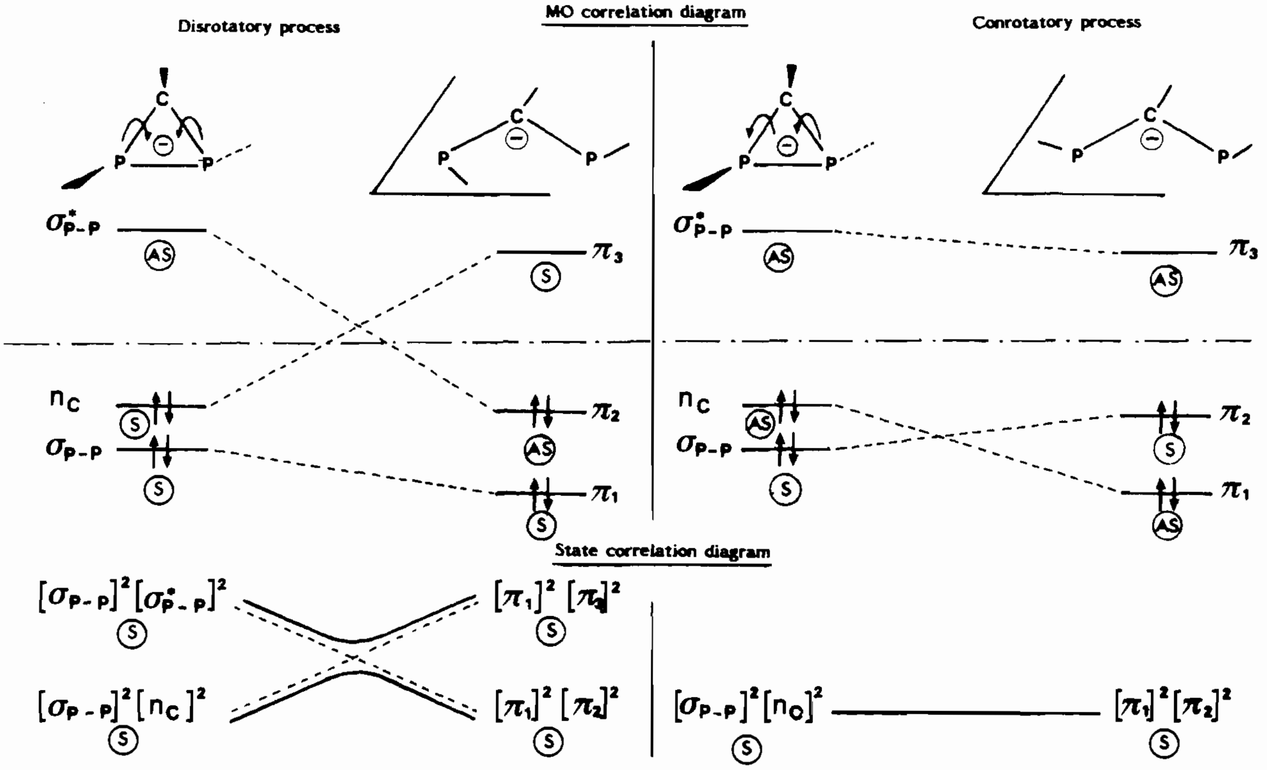


Figure 10. Ring opening of diphosphiranyl anion.



Symmetry elements : a C_2 axis in the conrotatory mode, a bissector plane in the disrotatory mode.

Figure 11. Anionic ring opening of diphosphirane; MO correlation diagram.

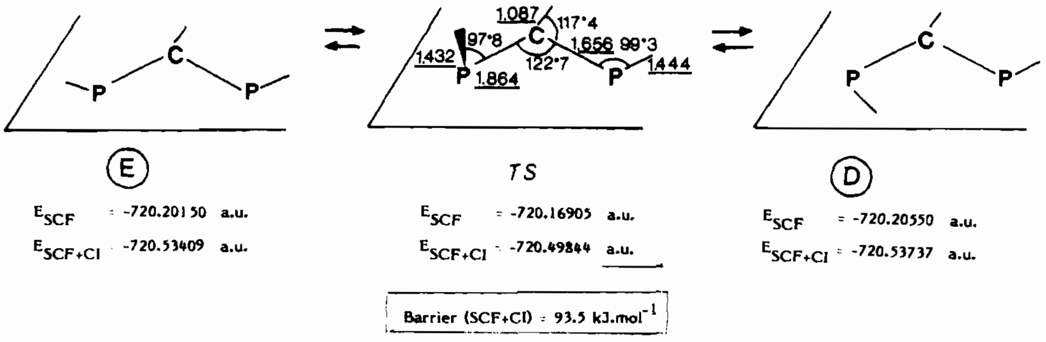


Figure 12. Isomerization of diphosphaallyl anion E to diphosphaallyl anion D.

occurred (hydrogen and carbon atoms on the same side of the P–P bond) (Figure 10).

For the disrotatory process, we were not able to obtain any convergent results at a SCF level, probably due to the important contribution of doubly excited configurations.

For this ring-opening process, the correlation diagrams of states and molecular orbitals (Figure 11) can be discussed.

The three molecular orbitals of the cyclic molecule correlate with the π system of the open-chain anion as found above for the cation; but for this four-electron system, two MOs are occupied. Consequently, a HOMO–LUMO crossing will happen for a disrotatory process. In this case, the ground state $(\sigma_{P-P})^2$ $(n_C)^2$ correlates with a doubly excited configuration of the open-chain anion. In contrast, for a conrotatory process a direct correlation is found between the two ground states $(\sigma_{P-P})^2$ $(n_C)^2$ and $(\pi_1)^2$ $(\pi_2)^2$.

The above analysis shows that the conrotatory ring-opening process is preferred.

As for the cation, the two open-chain species have equal stability. Thus we will also make an analysis of the isomerization process E $\rightleftarrows$ D through a rotation about the P–C bond. The transition state for this process corresponds to a structure with the PCPH dihedral angle of 90° in which the two P–C bonds have quite different lengths (Figure 12). The barrier is lower compared to the case of cations but still quite important (93.5 kJ·mol^{-1}). Since an increase of this barrier is expected in the case of substituted derivatives, experimental observation of the isomerization is very unlikely.

From the above discussion, a mechanism can be proposed for the anionic ring opening of diphosphirane: the cyclic anion undergoes a conrotatory process with a low barrier to a much more stable open form. Taking into account the molecular geometry constraints, we believe that the substituted derivatives allow only an exo–exo conformation.

These results are in good agreement with experimental observations. We found that the reaction of organolithium with symmetric monohalogenated diphosphiranes is stereoselective. Our calculation corroborate the exo–exo structure of the allyl intermediate, identified experimentally at low temperature.

Conclusion

Throughout this study we have specified the characteristics of the addition mechanism of singlet carbene to diphosphene. The preferential process corresponds to a π addition leading to the most stable structure, the diphosphirane.

In agreement with the experimentally observed isomerization, the most stable product of P–P bond rupture appears to be the 1,3-diphosphapropene.

The cationic and anionic ring-opening processes of diphosphirane were examined. In the case of cations there is no potential energy barrier toward P–P bond rupture which leads directly to exo–endo open-chain species through a disrotatory process. In the case of anions, the ring opening process goes through a cyclic anionic intermediate and then leads to exo–exo open-chain species through a conrotatory process.

Our results are in good agreement with the recently published study of Liu and Bachrach,[18] who examined the possible formation of 1,3-diphosphaallene from the lithio supersystem.

Acknowledgment. We thank the Direction Chimie du CNRS for the calculation time allocation on the VP 200 computer of the CIRCE and the GRECO Basses coordinences.

Registry No. CH_2, 2465-56-7; HP═PH, 41916-72-7; CH═P—PH·H$^+$, 140390-35-8; HP═CH—P$^+$H, 102146-41-8; HC$^-$—Ph—PH, 140390-36-9; HP═CH—P$^-$H, 140390-37-0; diphosphirane, 66272-09-1; methylenediphosphene, 140390-33-6; *cis*-diphosphapropene, 133349-80-1; *trans*-diphosphapropene, 133349-79-8; methylphosphinophosphinidene, 140390-34-7.

Contribution from the Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali dell'Università di Torino, Via P. Giuria 7, 10125 Turin, Italy, Dipartimento di Chimica dell'Università di Firenze, Via Maragliano 76/77, 50144 Florence, Italy, and Bracco SpA, Via E. Folli 50, Milan, Italy

Synthesis, Characterization, and $1/T_1$ NMRD Profiles of Gadolinium(III) Complexes of Monoamide Derivatives of DOTA-like Ligands. X-ray Structure of the 10-[2-[[2-Hydroxy-1-(hydroxymethyl)ethyl]amino]-1-[(phenylmethoxy)methyl]-2-oxoethyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic Acid–Gadolinium(III) Complex

Silvio Aime,*[,†] Pier Lucio Anelli,[‡] Mauro Botta,[†] Franco Fedeli,[‡] Maurizio Grandi,[‡] Paola Paoli,[§] and Fulvio Uggeri[‡]

Received September 16, 1991

The synthesis of two novel DOTA-like ligands (**5a,b**) containing a polyhydroxy(benzyloxy)propionamide substituent and their Gd(III) complexes (**6a,b**) is reported. Debenzylation by hydrogenolysis of the latter complexes in the presence of Pd/C leads to the corresponding derivatives (**7a,b**) with a primary alcoholic function. Water proton relaxation rates of aqueous solutions of **6a,b** and **7a,b** strongly suggest that these complexes contain only one water molecule in their inner coordination sphere, as was previously found for the parent DOTA complex. The high formation constants measured for complexes **6a,b** ($\log K_{ML}$ = 25.9 and 26.4, respectively) support the hypothesis of a direct involvement of the amide functionality in the coordination cage. This was shown by the determination of the solid-state structure of **6a**, which was accomplished in a single-crystal X-ray diffraction study. The structure consists of a $Gd(C_{27}H_{40}N_5O_{10})(H_2O)$ unit and three water molecules; space group $P2_1/c$ ($Z = 4$) with $a = 17.378$ (4) Å, $b = 8.283$ (7) Å, $c = 22.813$ (5) Å, $\beta = 100.33$ (2)°, $V = 3230$ (3) Å^3, $d = 1.590$ g/mL. The coordination polyhedron around the gadolinium ion is best described by a distorted-square antiprism capped by the coordinated water oxygen. All Gd–O distances (ranging from 2.34 to 2.43 Å) are very similar and this unambiguously proves the coordination of the carboxamide oxygen to the gadolinium ion. The $1/T_1$ NMRD profiles of aqueous solutions of **6a,b** and **7a,b** reveal that at the higher frequencies, the solvent proton relaxation rates are dominated by the molecular reorientational time τ_R; i.e., the observed relaxivities are linearly related to the molecular size. However, the main effect associated with the transformation of carboxylate to carboxamide is the drastic reduction of the electronic relaxation time τ_{SO}, which is responsible for a decrease in relaxivity at the low fields.

Introduction

In recent years, magnetic resonance imaging (MRI) has been recognized as a powerful diagnostic tool in clinical practice.[1] The images (mainly due to the NMR signal of water protons) are the result of the complex interplay between a number of parameters, such as proton density, flow, and T_1 and T_2 relaxation times. An improvement in the contrast may be achieved by the administration of exogenous chemicals that significantly alter the NMR properties of water resonance.[2,3] Paramagnetic gadolinium complexes, owing to their capability of decreasing the relaxation time of nearby nuclei via dipolar interaction, are under intense scrutiny,[2,3] and a few of them are already in clinical use as contrast agents for MRI.[4]

[†] Università di Torino.

[‡] Bracco SpA.

[§] Università di Firenze.

(1) For extensive references, cf.: Stark, D. D., Bradley, W. G., Jr., Eds. "Magnetic Resonance Imaging" The C.V. Mosby Company, St. Louis, Missouri (USA), 1988.

(2) Lauffer, R. B. *Chem. Rev.* **1987**, *87*, 901.

(3) Koenig, S. H. *Isr. J. Chem.* **1988**, *28*, 345.

(4) Gd-DTPA, diethylenetriaminepentaacetic acid gadolinium complex di-*N*-methylglucamine salt, MAGNEVIST, Schering; Gd-DOTA, 1,4,7,10-Tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid gadolinium complex *N*-methylglucamine salt, DOTAREM, Guerbet.

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