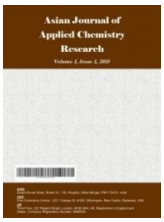

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Theoretical Study of the Reaction of Formation of Some Free Phosphines by Stereoselective Hydrophosphination through DFT Method

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Authors' contributions

This work was carried out in collaboration between all authors. Authors KVB and AB designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors MGRK, KB and NZ managed the analyses of the study. Author NYSD managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

In this work the formation of vinylphosphines was studied through the hydrophosphination reaction. The study aims to rationalize the stereoselectivity of these compounds using quantum DFT methods. This theoretical study of chemical reactivity was conducted at B3LYP/6-311 + G (d, p) level. Global chemical reactivity descriptors, stationary point energies and activation barriers were examined to foretell the relative stability of the stereoisomers formed. The various results obtained have revealed that the addition of arylphosphine to dihalogenoacetylene is stereospecific. The *Trans* form of vinylphosphines is more stable than the *Cis* form, when the substituent on

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phosphorus generates less or no π-conjugations. On the other hand, the *Cis* isomer is predominant when the aryl radical favors more π-conjugations. The theoretical results obtained are in agreement with the experimental results.

Keywords: Hydrophosphination; free phosphine; global descriptors; transition state; stationary point energies.

1. INTRODUCTION

Phosphorus compounds play a very important role in nature: transport of information in the body (ATP, ADP ...), anti-cancer activity, growth and treatment of plants, in strengthening the bone system. In organic synthesis, they act as ligands for the synthesis of complex molecules such as organic polymers. Organophosphorus compounds have enormous potential in various fields such as: agriculture [1], medicine [2], pharmacy, synthesis of organic polymers [3], asymmetric catalysis [4]. Also, mastering their syntheses will provide access to new organic compounds with interesting properties in various fields. With the development of computer techniques and computational chemistry, quantum chemistry gives insight into the electronic structures of molecules and strongly propels the development of traditionally experimental chemistry [5]. Currently, the method of density functional theory (DFT) has been accepted as a popular approach for calculating the structural characteristics and energies of molecules by the scientific community [6-9]. Its efficiency and accuracy in the evaluation of a number of molecular properties [10] has been recognized by all. In addition, Parr and Yang followed the idea that well-known chemical properties such as electronegativity, chemical potentials, and affinities could be accurately described and calculated by manipulating the electron density as the fundamental quantity [11-14].

This work is part of the design and synthesis of new series of organic phosphorus semiconductors from arylphosphines and vinylphosphines. The objective of this work is to determine, by means of theoretical chemistry, the global reactivity indices, the transition states and the reaction mechanism of some free phosphines synthesized by Bénié et al. [15]. They found that the addition of phenylphosphine or thiophenylphosphine on dichloroacetylene is stereoselective (Scheme 1). The *Trans* compound was obtained predominantly. When these phosphines were complexed with tungsten, the *Cis* compound was predominant.

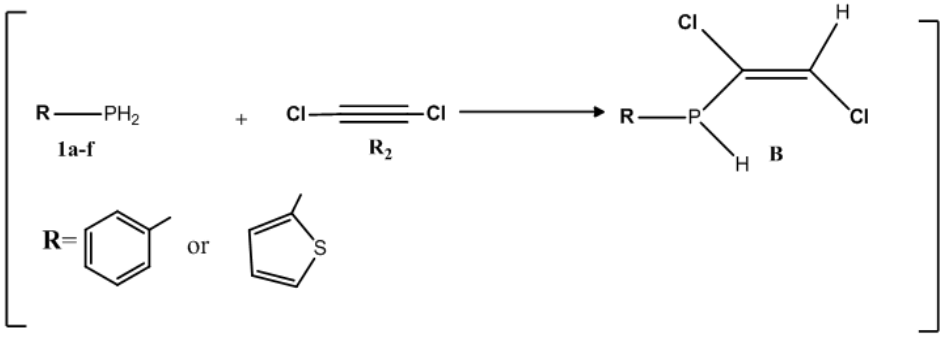
2. MATERIALS AND METHODS

The theoretical study of chemical reactivity was conducted based on two theoretical approaches. The first concerns the analysis of frontier molecular orbitals. The second approach is relative to the analysis of the energies of the different stationary points that are: **Er**: Energy of the reactants, **Ets**: Energy of the state of transition, **Ep**: Energy of the product and energies of activation. The optimization of the reactants and the products, as well as the calculations of the frequencies of vibrations, were performed with Gaussian-09 series of program package [16]. DFT calculations were carried out at the B3LYP / 6-311 + G (d, p) level of theory. All stationary points were characterized by frequency calculations in order to verify that the TS have one and only one imaginary frequency. The intrinsic reaction coordinate (IRC) path was traced in order TS to check the energy profiles connecting each TS to the two associated minima of the proposed mechanism. Calculations were performed in a vacuum using the DFT method with the functional B3LYP [17,18] in the 6-311 + G (d, p) basis set. This hybrid functional gives better energies and it is in agreement with the ab initio methods of high level [19,20]. As for the split-valence and triple-dzeta (6-311 + G (d, p)) basis set, it is sufficiently extended and the taking into account of the polarization functions and diffuse functions is important for the precision of the values of the global reactivity indices obtained from the conceptual DFT model [21].

2.1 Thermodynamic Parameters of Reaction

The Knowledge of the variations of energy contributions to the internal energy at 0K and at 298K between the products and the reactants contributes to the energetic characterization of a chemical reaction. For a given energy parameter X, its variation is determined according to the relation (1) [22,23]:

$$\Delta X = \sum X(products) - \sum X(\text{reactants}) \qquad (1)$$



Scheme 1. Addition reaction of free phosphine on dichloroacetylene

The thermodynamic quantities determined in this study are the Gibbs free energies ($\Delta_r\mathbf{G}$).

These quantities are calculated from the relationships (2):

$$\mathbf{\Delta rG} = \Delta_f\mathbf{G}\,(Products) - \Delta_f\mathbf{G}\ (\text{reactants}) \qquad (2)$$

2.2 Global Descriptors of the Conceptual DFT

To predict the chemical reactivity, some theoretical descriptors related to the conceptual DFT were determined. In particular, the energy of the lowest unoccupied molecular orbital ($\mathbf{E_{LUMO}}$), the energy of the highest occupied molecular orbital ($\mathbf{E_{HOMO}}$), the electronegativity ($\boldsymbol{\chi}$), the global softness (S) and the global electropilicity index ($\boldsymbol{\omega}$). These descriptors are all determined from the optimized molecules. It should be noted that the descriptors related to frontier molecular orbitals have been calculated in a very simple way in the framework of the Koopmans approximation [24].

LUMO energy characterizes the sensitivity of the molecule to a nucleophilic attack whereas the HOMO energy characterizes the susceptibility of a molecule to an electrophilic attack. Electronegativity (χ) is the parameter that reflects the ability of a molecule not to let its electrons escape. Global softness (S) expresses the resistance of a system to the change in its number of electrons. The overall electrophilicity index characterizes the electrophilic power of the molecule. These different parameters are calculated from equations (3):

$$I = -E_{HOMO}$$

$$A = -E_{LUMO}$$

$$\chi = -\mu = -1/2\,(E_{LUMO} + E_{HOMO}) \qquad (3)$$

The first partial derivative of μ with respect to N (the total number of electrons) is defined as the global hardness η of the system [25,26]. It is related to the quantity S which is the global softness of the system.

$$2\eta = \left(\frac{\partial\mu}{\partial N}\right)_{v(r)} = \left(\frac{\partial^2 E}{\partial N^2}\right) = \frac{1}{S} \qquad (4)$$

From the chemical hardness is determined another reactivity parameter to define the energy stability due to charge transfer. The electrophilicity index (ω) is related to the chemical potential by the following relation [27]:

$$\omega = \frac{\mu^2}{2\eta} \qquad (5)$$

It is noted that the nucleophilicity index cannot be defined by a variational procedure, because there is no molecular electronic stabilization along the subtraction of the electron density of a molecule. In the absence of a nucleophile descriptor, Domingo et al. [28-30] proposed that the hypothesis that a weakly electrophilic molecule is systematically high ly nucleophilic is only true for single molecules. The empirical (N) nucleophilicity index (relative) is defined as follows [31,32]:

$$N = \left(E_{HOMO(Nu)} - E_{HOMO(TCE)}\right) \qquad (6)$$

$E_{HOMO(Nu)}$: Energy of the highest occupied orbital of the nucleophilic molecule.

$E_{HOMO(TCE)}$: Highest occupied orbital energy of the tetracyanoethylene molecule.

This index has been successfully validated by available experimental data for amines, diimines,

anilines, alcohols, ethers, alkenes, and Π-nucleophiles.

3. RESULTS AND DISCUSSION

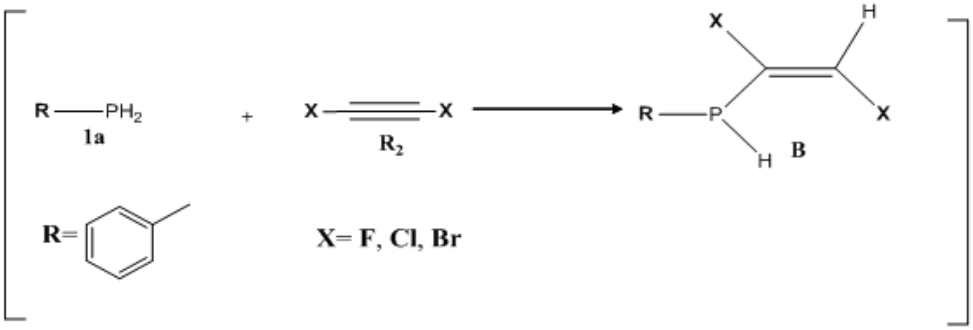
3.1 Effect of Halogen

The global reactivity of some dihalo-arylphosphines will be rationalized in the hydrophosphination reaction using the global nucleophile index N. The global indices of reactivity: the electronic chemical potential (μ), the electronegativity (χ), the hardness (η) of the system, the global softness (S) of the system, the electrophilicity index (ω) and the nucleophile index (N) which were computed at B3LYP/6-311 + G (d, p) are highlighted in Table 1 below of the global descriptors (Scheme 2). The change of dichloroacetylene with difluoroacetylene or dibromoacetylene gives the results below of the global descriptors (Scheme 2).

From Table 1, it can be seen that calculated global nucleophilicity values for each halogen series reveals that the Trans stereoisomers have higher nucleophilic potency than their *Cis* counterparts. Therefore, *Trans* compounds exhibit high chemical reactivity and low kinetic stability for the halogens used in the reaction of phenylphosphine with a dihalogenoacetylene. Moreover, this reactivity is further confirmed by the low values of the chemical hardness (η) around the *Trans* stereoisomers. Also, we note that the global softness values (S) of the *Trans* stereoisomers are greater than those of the *Cis* stereoisomers. This indicates that *Trans* compounds are more reactive than *Cis* stereoisomers.

The discussion then focuses on the transition state and regioselectivity of dihalogeno-vinylphosphines. The energies of the different stationary points (**Er**: Energy of the reactants, **Ets**: Energy of the state of transition, **Ep**: Energy of the product and energies of activation (**Ea** (kcal/mol)) are given in Table 2. The Fig. 1 (a) - (c) represent the energy profile.

In the analysis of activation energies, it is found that the formation of the *Cis* isomer requires a weak activation barrier (**Ea** (Cis) < **Ea** (Trans)) compared to the *Trans* isomer for each halogen series used. The formation of the *Cis* isomer is favored in the transition state. Moreover, the energy profile (Fig. 1) indicates that the *Trans* isomer is much more stable than the *Cis* isomer at the end of the reaction(ΔrG^0_{298} (Trans) < ΔrG^0_{298} (Cis)). This stability of the *Trans* product is in



Scheme 2. Addition reaction of phenylphosphine on dihaloacetylene

Table 1. Global descriptors of the chemical reactivity of products B at B3LYP / 6-311 + G (d, p) level

Halogen	Isomer	E_{HOMO} (eV)	E_{LUMO} (eV)	μ (eV)	χ (eV)	η (eV)	S (eV^{-1})	ω (eV)	N
F	Trans	-7.070	**-1.223**	-4.147	4.147	**5.847**	**0.086**	1.471	**2.417**
	Cis	-7.132	-1.228	-4.180	4.180	5.904	0.085	1.480	2.357
Cl	Trans	-6.910	-1.451	-4.180	4.180	**5.459**	**0.092**	1.600	**2.579**
	Cis	-6.969	-1.337	-4.153	4.153	5.632	0.088	1.531	2.520
Br	Trans	**-6.831**	-1.537	-4.184	4.184	**5.293**	**0.094**	1.654	**2.658**
	Cis	-6.916	-1.393	4.155	4.154	5.494	0.091	1.570	2.573

agreement with the experimental results obtained by Bénié et al. [15]. They found that the reactions are stereo controlled and give *Trans*-addition with free phosphines and *Cis*-addition with phosphine complexes. The possible explanation for the stability of the "calc-Trans" isomers is justified by a conformational change after the transition state.

Table 2. Energies of the different stationary points (Er, Ets and Ep) and the activation barriers (Ea) (kcal /mol) for a variation of the halogen

R_2	Isomer	Er	Ets	Ep	Ea	ΔrG^0_{298}
F	Trans	-849.900	-849.750	-849.940	94.125	**-25.100**
	Cis	-849.900	-849.780	-849.890	**75.300**	6.275
Cl	Trans	-1570.570	-1570.425	-1570.640	90.988	**-43.926**
	Cis	-1570.570	-1570.520	-1570.567	**27.610**	1.883
Br	Trans	-5793.610	-5793.508	-5793.665	64.005	**-34.513**
	Cis	-5793.610	-5793.515	-5793.535	**59.613**	47.063

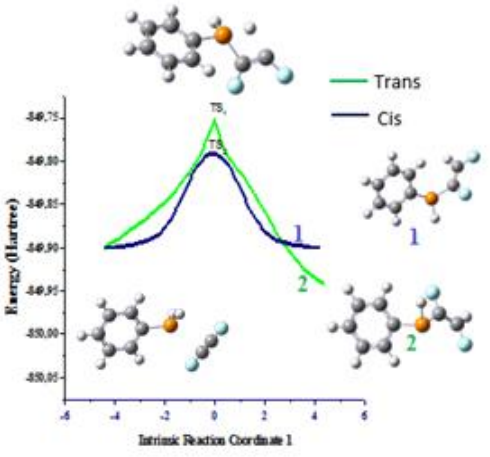


Fig. 1a) Reaction path with Fluorine (F) as Halogen (a)

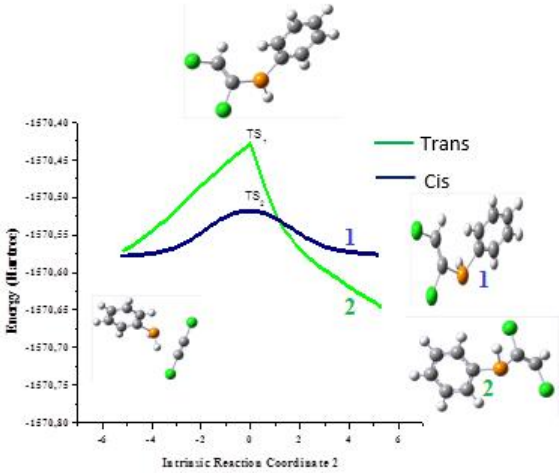


Fig. 1b) Reaction path with the Chlorine (Cl) as Halogen (b)

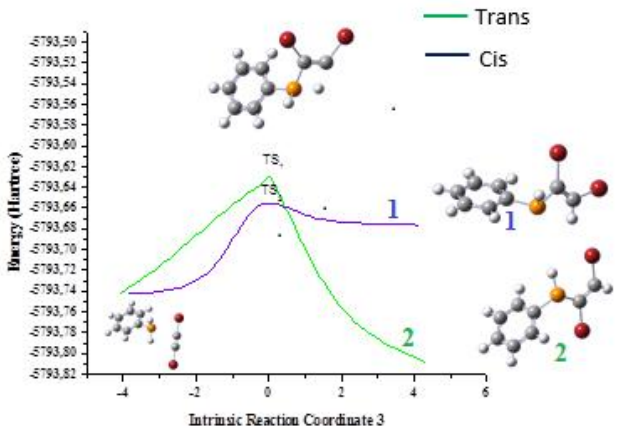


Fig. 1c). Reaction path (Equation 2) with Bromine (Br) as Halogen (c)

Fig. 1. Curve of the reaction paths giving "*Trans*" or "*Cis*" (1,2-dichlorovinyl)(phenyl)phosphine respectively with fluorine (a), chlorine (b) and bromine (c) as halogen

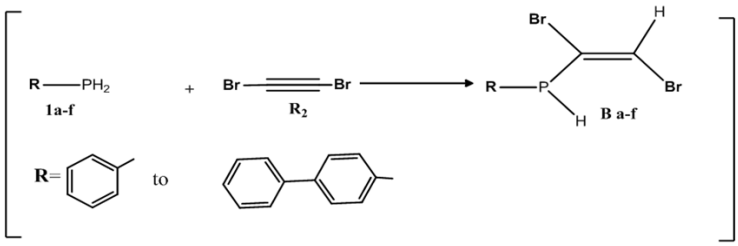
3.2 Substituent Effect on Phosphorus

3.2.1 Global reactivity

The effect of the substituent on phosphorus is examined during the addition of a primary phosphine to dibromoacetylene (Scheme 3).

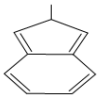
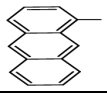
The global reactivity of some dibromo-arylphosphines will be rationalized in the hydrophosphination reaction using the global nucleophile index N. The global indices of reactivity: the electronic chemical potential (μ), the electronegativity (χ), the hardness (η) of the system, the global softness (S) of the system, the electrophilicity index (ω) and the nucleophilicity index (N) calculated at B3LYP/6-311 + G (d, p) level are shown in Table 3.

The values of the global nucleophilicities calculated for this series of phosphines show that the *Trans* stereoisomers have a higher nucleophilic power than their *Cis* counterparts. As a result, *Trans* compounds exhibit high chemical reactivity and low kinetic stability as the size of the radicals on phosphorus increases. The ionization potential **I** is a parameter that reflects the susceptibility of a chemical system to yield or capture an electron. The ionization potential **I** values of the *Trans* stereoisomers are all lower than those of the *Cis* stereoisomers. This indicates that *Trans* compounds are likely to give up electrons. The energies of the different stationary points (**Er:** Energy of the reactants, **Ets**: Energy of the state of transition, **Ep**: Energy of the product and energies of activation **Ea**) are shown in Table 4. Fig. 2a-g favor the observation of the energy profile of these reactions.



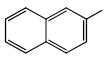
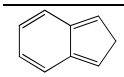
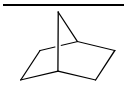
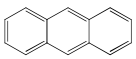
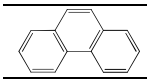
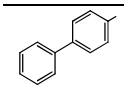
Scheme 3. Addition reaction of free phosphine on dibromooacetylene

Table 3. Global descriptors of the chemical reactivity of products B a-f at B3LYP/6-311 + G (d, p) level

R	Isomer	I (eV)	A (eV)	μ (eV)	χ (eV)	η (eV)	S (eV^{-1})	ω (eV)	N
	Trans	**6.673**	1.638	-4.155	4.155	5.035	**6.673**	1.638	**2.816**
	Cis	6.760	1.269	-4.015	4.015	5.491	6.760	1.269	2.729
	Trans	**6.190**	1.673	-3.935	3.935	4.517	**6.190**	1.673	**3.299**
	Cis	6.286	1.825	-4.055	4.055	4.461	6.286	1.825	3.203
	Trans	**5.666**	2.435	-4.051	4.051	3.231	**5.666**	2.435	**3.823**
	Cis	5.696	2.473	-4.085	4.085	3.223	5.696	2.473	3.793
	Trans	**6.590**	1.424	-4.007	4.007	5.166	**6.590**	1.424	**2.899**
	Cis	6.692	1.160	-3.926	3.926	5.532	6.692	1.160	2.797
	Trans	**5.626**	2.350	-3.988	3.988	3.276	**5.626**	2.350	**3.863**
	Cis	5.754	2.296	-4.025	4.025	3.458	5.754	2.296	3.735
	Trans	**7.988**	1.485	-4.736	4.736	6.503	**7.988**	1.485	**1.501**
	Cis	8.016	1.469	-4.743	4.743	6.547	8.016	1.469	1.473
	Trans	**6.188**	1.676	-3.932	3.932	4.512	**6.188**	1.676	**3.301**
	Cis	6.517	1.616	-4.066	4.066	4.901	6.517	1.616	2.972

E_{HOMO} (TCE) =- 9,489 eV at B3LYP/6-311+ G (d, p) level

Table 4. Energies of the different stationary points (E_R, E_{TS} and E_P) and the activation barriers Ea (kcal /mol) for a radical variation R

R	Isomers	Er	Ets	Ep	Ea	ΔrG^0_{298}
	Trans	-5793.610	-5793.508	-5793.665	64.005	**-34.513**
	Cis	-5793.610	-5793.515	-5793.535	**59.613**	47.063
	Trans	-5947.365	-5947.16	-5947.375	128.637	-6.272
	Cis	-5947.365	-5947.351	-5947.445	**8.785**	**-50.177**
	Trans	-5909.210	-5909.158	-5909.211	32.630	-0.627
	Cis	-5909.210	-5909.191	-5909.290	**11.922**	**-50.177**
	Trans	-5835.360	-5835.090	-5835.380	7.347	-12.544
	Cis	-5835.360	-5835.24	-5835.360	**3.265**	**0.000**
	Trans	-6101.030	-6100.955	-6101.035	47.063	-3.136
	Cis	-6101.030	-6101.01	-6101.11	**12.550**	**-50.177**
	Trans	-6101.024	-6100.950	-6101.022	46.436	1.254
	Cis	-6101.024	-6101.004	-6101.104	**12.550**	**-50.177**
	Trans	-6024.805	-6024.707	-6024.804	61.495	0.627
	Cis	-6024.805	-6024.786	-6024.885	**11.922**	**-50.177**

The results in Table 4 show that the formation of the *Cis* isomer is favored because this formation requires a lower activation barrier, compared to that leading to the *Trans*-transition isomer.

The energy profile of these reactions reveals that the *Cis* isomer is favored in the transition state, because its formation requires a lesser activation barrier. The formation of this isomer is

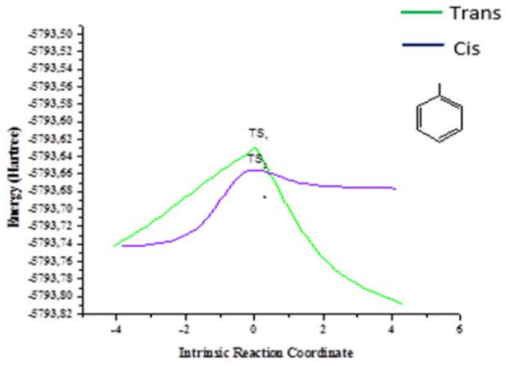


Figure 2a

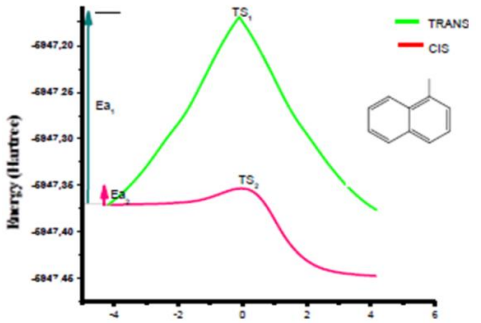


Figure 2b

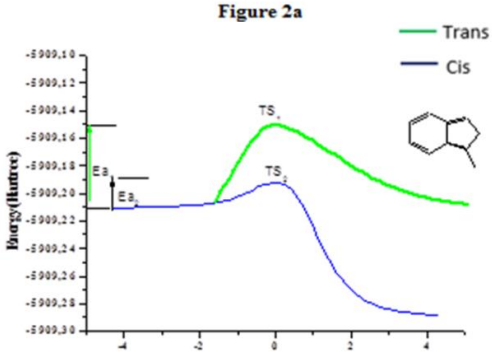


Figure 2c

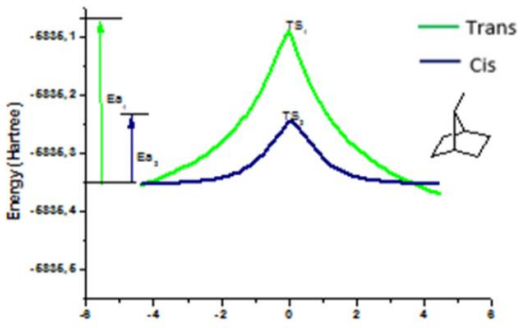


Figure 2d

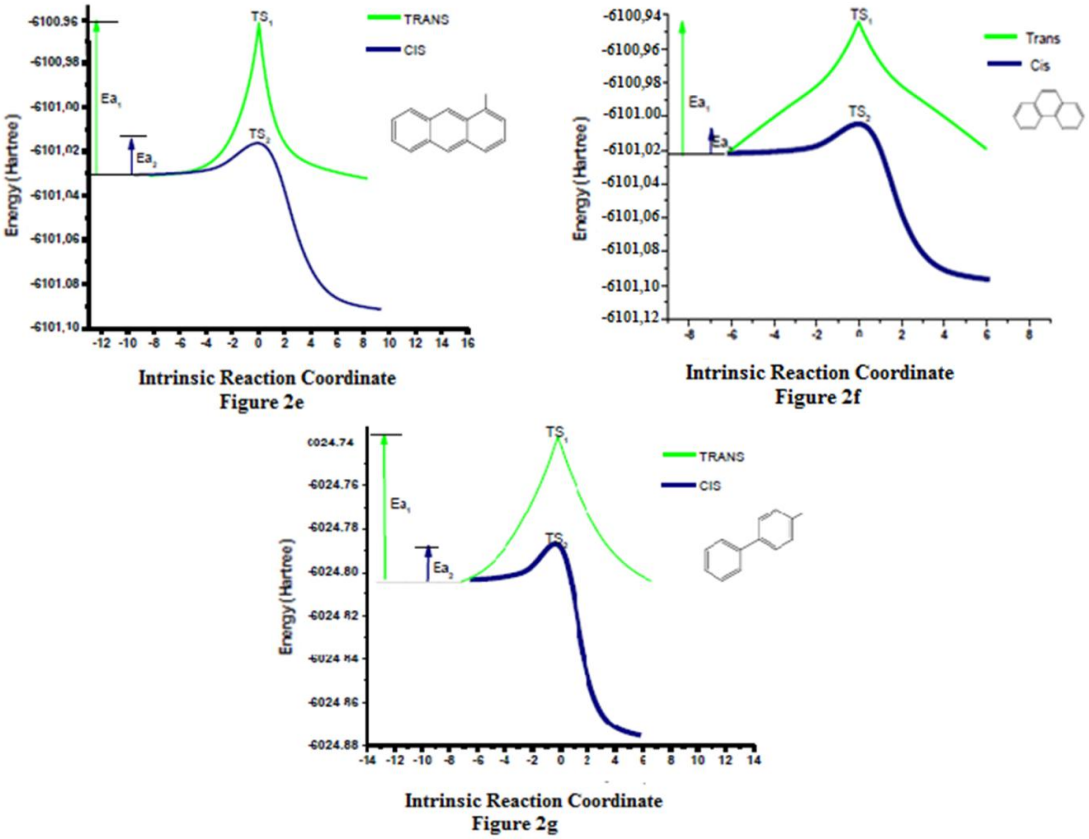
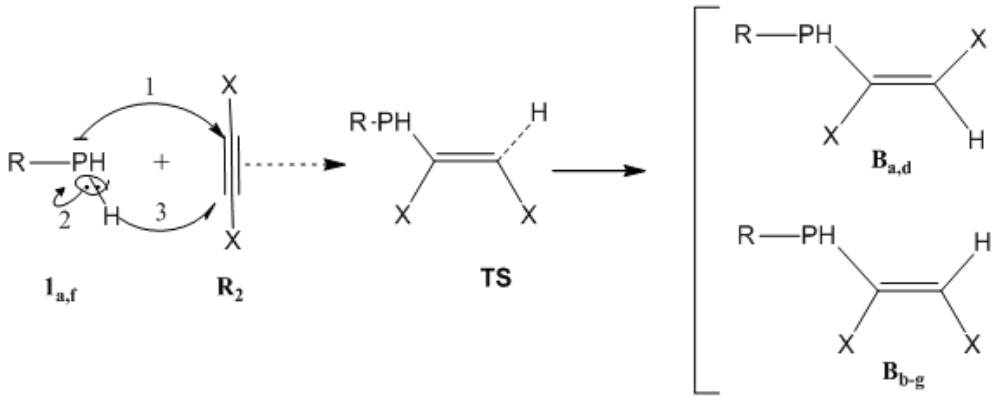


Fig. 2. IRC curve of reaction pathway 2a-g



Scheme 4. Proposed Mechanism for the Hydrophosphination of free phosphine with dihalogenoacetylene

[a, d] fewer or not π-conjugations, [b-g] more π-conjugations

predominant because its formation requires less energy than *Trans* counterpart ($\Delta rG^0_{298}(cis) < \Delta rG^0_{298}(trans)$). In addition, *Trans* vinylphenylphosphine and *Trans* vinylbicycloheptane have good kinetic stabilities compared to their *Cis* counterparts (Fig. 2). The small size of these substituents promotes the conformational change after the transition state. Reaction pathway therefore makes it possible to propose the following reaction mechanism (Scheme 4).

4. CONCLUSION

The use of the conceptual DFT method has made it possible to study the reactivity of free phosphines on the carbon-carbon triple bond ($-C\equiv C-$). Analysis of the thermodynamic quantities of the reaction and the potential energy surface allowed us to conclude that: the presence of halogens on acetylene promotes stereospecific addition. The *Trans* form of vinylphosphines is more stable than the *Cis* form, when the phosphorus substituent generates fewer π-conjugations. On the other hand, the *Cis* isomer is predominant when the aryl radical favors more π-conjugations. The nature of the halogen does not affect the stereoselectivity of the reaction. It is envisaged in perspective, to synthesize phosphines which are more stable and more reactive to various applications in medicine and catalysis.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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