A Theoretical Investigation of Cycloadditions of Hydrogen Isocyanide to CH_2=X and PH=X Dipolarophiles (X = CH_2, NH, O, SiH_2, PH, S)☆

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We performed a systematic investigation of [2 + 1] cycloadditions of HN≡C to dipolarophiles of the type CH_2=X and PH=X with X = CH_2, NH, O, SiH_2, PH, and S, as well as HN=NH and H_2Si=SiH_2. Ab initio MO calculations at the QCISD(T)/6-311G(d,p)//MP2/6-31G(d,p)+ZPE level were applied to construct the minimum-energy reaction pathways. Calculated results concerning the regiochemistry of the approaches and the stereochemistry of the product formation were analyzed in relation with established concepts such as frontier orbital, net charge distribution and stereoelectronic effect. For some systems, up to four distinct transition structures for cycloaddition were found. In general, there is a certain similarity between the behavior of both C and P series of dipolarophiles. The characteristics of the transition structures can be, in most cases, recovered by using qualitative concepts. The [2 + 1] cycloadditions are highly regioselective and stereospecific. Silicon-containing dipolarophiles are particularly attractive as they exhibit very small energy barriers to addition to isocyanides.

1. Introduction

The chemistry of isocyanides has been a widely developed field in organic and organometallic syntheses throughout the last 20 years. Owing to the fact that isocyanides possess a mono-coordinated carbon atom with a high-lying lone pair, they are well suited as 1,1-dipolar partners in diverse addition reactions. Isocyanides have been known to add to dipolarophiles containing double bonds such as disilenes (R_2Si=SiR_2)[1], diphosphenes (RP=PR)[2,3], silenes (R_2C=SiR_2)[4], phosphasilenes (R_2Si=PR)[5], and arsasilenes (R_2Si=AsR)[6]. In the opposite direction, thermal decomposition of cyclopropanimines (X, Y = CR_2), or their heteroatomic derivatives often occurs via cheletropic cycloreversion leading to an isocyanide and a dipolarophile such as ethene, imine, ketone or thioketone[7].

Recently, we reported on ab initio molecular orbital studies of the [2 + 1] and [2 + 2] additions of hydrogen isocyanide to thioformaldehyde (H_2C=S)[8], silene (H_2C=SiH_2)[9], phosphaethene (CH_2=PH)[10], and methanimine (H_2C=NH)[11]. Results obtained for these simplest model systems pointed out that there is a large difference in the reactivity of isocyanide toward the doubly bonded dipolarophiles. For example, the [2 + 1] addition of HN≡C to H_2C=SiH_2 can be rationalized by frontier orbitals or charge distribution but the primary adduct is not the most stable product. In the case of the [2 + 1] cycloaddition of HN≡C to CH_2=PH, the lower lying transition structure does not correspond to that suggested by frontier orbitals but the primary adduct is the most stable isomer. In the reaction HN≡C + H_2C=SiH_2, an initial C–Si attack is preferred whereas in the process HN≡C + H_2C=PH, a C–C attack is less energy-demanding. An initial C–C attack is also favored in the HN≡C + H_2C=NH addition. On the other hand, while a [2 + 2] addition seems to be in competition with the [2 + 1] one in the HN≡C + H_2C=SiH_2 reaction giving a quite stabilized four-membered cyclic carbene, such a reaction route is not realistic in both H_2C=NH and H_2C=PH cases. In the reactions considered, the stereochemistry of the cycloadduct determined by the position taken by the HNC moiety with respect to the heteroatom can be rationalized by a simple stereoelectronic effect directly related to the movement of electron pairs during the reaction. However, some exceptions cannot be ruled out.

In view of the diversity in the reactivity of this important class of reactions, a systematic survey of the possible [2 + 1] cycloadditions of the isocyanide molecule to the simplest dipolarophiles H_2C=X, with X = CH_2, NH, O, SiH_2, PH, and S should first be given. In connection with our current interest on phosphorus compounds[10,12], phosphorus-containing dipolarophiles HP=X were also considered. For the purpose of comparison, the present theoretical survey also includes the homoatomic dipolarophiles CH_2=CH_2, NH=NH, SiH_2=SiH_2, PH=PH. For each system, the heat of reaction and barrier height, the stereochemistry as well as the regiochemistry of the approach were examined.

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Particular attention was paid to the relationship between the quantitative results and the more qualitative concepts such as the frontier orbital (HOMO-LUMO) interaction, atomic charge distribution, stereoelectronic effect, and Evans-Polanyi relationship.

Calculations

Ab initio MO calculations were carried out by using a local version of the Gaussian 92 program[13]. Initial mapping of the potential energy surfaces was conducted at the HF/6-31G(d,p) level of accuracy to identify and characterize by harmonic vibrational analyses the relevant equilibrium and transition structures. Geometries of the latter were then refined at the second-order perturbation MP2/6-31G(d,p) level which partly includes correlation energy. Subsequently, using single-point electronic energy calculations at MP2 geometries, we brought the energies of all structures considered to a more sophisticated level, namely the quadratic configuration interaction [QCISD(T)] making use of the larger 6-311G(d,p) basis set. Throughout this paper, bond lengths are given in angströms, bond angles in degrees, total energies in hartrees, zero-point vibrational, and relative energies in kJmol^{-1}.

2. Results and Discussion

In order to facilitate the analysis, we classified the additions considered into three categories: while the first describes the HNC addition to the ethylene derivatives CH_2=X, with X = C(H_2), N(H), O, Si(H_2), P(H), and S yielding the three-membered cyclic products **CX1**, the second consists of the phosphorus dipolarophiles PH=X whose cycloadducts are represented by the symbol **PX1** and the third category includes the homoatomic double bonds X=X denoted by **X1**. The fragments HN≡C + CH_2=X, HN≡C + PH=X and HN≡C + X=X are denoted by **CX2**, **PX2**, and **X2**, respectively. The resulting transition structures (TS) are symbolized by **CX2/CX1**, **PX2/PX1**, and **X2/X1**. In the cases where several TSs were located, they will be distinguishable by additional lower-case letters, namely **s** stands for a *syn* conformation and **a** for an *anti* conformation. There are three overlappings concerning H_2C=CH_2, CH_2=PH, and PH=PH, but for the sake of comparison, their results will be repeated. In total, thirteen distinct systems were considered.

2.1. Preliminary Frontier Orbital and Atomic Charge Analysis

Analysis of the frontier orbitals of the reactants indicates that their [2 + 1] cycloaddition is mainly characterized by an approach of the HOMO of the carbon lone pair of the isocyanide to the π* LUMO of the dipolarophile CH_2=X or PH=X. The isocyanide molecule behaves thus as a nucleophilic carbene, i.e. its filled n orbital overlaps with the π* orbital of its partner. As the latter is not homonuclear, two distinct TSs can thus be found. The predominance of one TS over the other determines the regioselectivity of the addition. In general, the TS in which the isocyanide carbon lone pair attacks the dipolarophile atom bearing the larger LUMO coefficient is expected to be favored over the other. In other words, the lone pair is expected to overlap with the most electrophilic site of the dipolarophile which could also be identified by the atomic charges.

Table 1 lists the orbital energies and coefficients along with the Mulliken atomic net charges of the dipolarophiles examined. A rapid inspection of Table 1 reveals that except for the H_2C=S case, predictions of the most favored approaches using frontier orbitals coincide well with that made by use of charge distribution. In most cases, the C atom in H_2C=X and the P atom in HP=X are predicted to be the most favored site for attack. The Si dipolarophile forms an exception in which the Si atom is consistently the preferred site for a nucleophilic attack. The Si dipolarophiles also contain the smallest HOMO-LUMO energy gaps in such a way that, for example in H_2Si=SiH_2, the HOMO(dipolarophile)−LUMO(HN≡C) interaction turned out to be more favorable than the HOMO(HN≡C)−LUMO(dipolarophile) interaction. This suggests that a [2 + 2] cycloaddition could compete with the [2 + 1] path. The validity of these predictions will be discussed in a following section after determination of the different TSs by calculations using the supermolecule approach.

Table 1. HOMO and LUMO energies, (ε in eV), LUMO coefficients (C_i) and Mulliken atomic net charge (q) of the X=Y dipolarophiles using HF/6-311G(d,p) wave functions

Dipolarophile X=Y	ε(HOMO)	ε(LUMO)	$C_i(X)$[b]	$C_i(Y)$[b]	q(X)	q(Y)
H_2C=CH_2 (X = C)	-10.2	4.4	0.83	0.83	-0.22	-0.22
H_2C=NH	-11.6	4.3	0.82	0.74	0.01	-0.51
H_2C=O	-12.0	3.4	0.79	0.61	0.20	-0.36
H_2C=SiH_2	-8.5	2.1	0.67	0.81	-0.65	0.66
H_2C=PH	-9.5	1.7	0.71	0.74	-0.44	0.22
H_2C=S	-9.6	1.2	0.71	0.63	-0.26	-0.05
HP=CH_2 (X = P)	-9.6	1.7	0.74	0.71	0.22	-0.44
HP=NH	-10.5	1.1	0.73	0.52	0.47	-0.59
HP=O	-10.8	0.3	0.74	0.49	0.75	-0.62
HP=SiH_2	-8.7	0.6	0.68	0.82	-0.18	0.50
HP=PH	-9.6	0.1	0.73	0.73	0.05	0.05
HP=S	-9.6	0.6	0.76	0.62	0.34	-0.29
HN=NH	-10.9	3.8	0.72	0.72	-0.19	-0.19
H_2Si=SiH_2	-7.9	3.3	0.96	0.96	0.27	0.27

[a] The orbital energies of HNC are: ε(HOMO) = −13.2 and ε(LUMO) = 5.3 eV. − [b] The signs are omitted for simplicity.

2.2. The Three-Membered Cyclic Products

It is also of interest to examine some properties of the cycloadducts, in particular their thermodynamic stabilities. As seen in Table 2, except for the aziridinimine **CN1**, oxiranimine **CO1** and cyclopropanimine **CC1** cycloadducts resulting from the addition of HN≡C to H_2C=NH, H_2C=O and H_2C=CH_2, respectively, every ring structure turns out to be an exothermic product. The exothermicity ranges from −3 kJmol^{-1} in HN=NH to −68 kJmol^{-1} in HP=S. As each cycloadduct contains a three-membered ring coupled with an exocyclic imine function, its stability is inherently related to the ring strain. It is clear that the ring strain decreases markedly by the presence of a third-row

atom (Si, P, S) within the ring. Owing to their hybridization, third-row atoms are known to accommodate the small structure more easily than their second-row homologues. The exothermicity also increases in the presence of a more electrophilic site such as Si. Nevertheless, the effect is not at all additive. The presence of two third-row atoms within the ring does not lead to a further stabilization. A case in point is the Si ring where the C–Si–P ring has a smaller exothermicity than in the C–Si–C ring (Table 2). This indicates that other effects are also important, such as the coupling between the ring and imine moiety or the lone pair repulsion. A parameter which measures quantitatively the ring-double bond coupling is the stretching wave number of the C=N bond. Its bond length and CN stretching frequencies are compiled in Table 3. As seen in Figure 1a, there is no linear relationship between these two parameters. The correlation using frequency shifts and distance variations is not much improved (Figure 1). In both cases, $\Delta\nu$ is roughly proportional to the shortening or elongation Δr of the C=N bond.

Table 2. Total and relative energies at the QCISD(T)/6-311G(d,p) level of the points on the [2 + 1] cycloaddition pathways[a]

System	Reactants	Transition structure	Cycloadduct
$H_2C{=}X$	CX2	CX2/CX1	CX1
C	-171.58026	-171.52300	-171.58770
	0	0	0
N	-187.60564	-187.54764	-187.60854
	0	164	14
O	-207.45608	-207.40597	-207.46167
	0	141	5
Si	-422.56449	-422.55352	-422.59403
	0	34	-60
P	-473.82856	-473.78624	-473.85068
	0	121	-37
S	-530.04817	-530.01708	-530.08062
	0	92	-67
H P=X	PX2	PX2/PX1	PX1
N	-489.85022	-489.81598	-489.87108
	0	101	-37
O	-509.70602	-509.68241	-509.72573
	0	74	-32
Si	-724.83973	-724.84010	-724.86200
	0	7	-43
P	-776.08875	-776.06053	-776.11288
	0	81	-47
S	-832.30982	-832.30174	-832.34222
	0	32	-68
X=X	X3	X3/X1	X1
N	-203.60302	-203.54943	-203.61177
	0	154	-3
Si	-673.57225	-673.56637	-673.60185
	0	22	-62

[a] Relative energies, presented directly under the total energies, are corrected for ZPE; only the lowest-lying transition structures and corresponding adducts are given; MP2/6-31G(d,p) optimized geometries are employed.

2.3. Mechanism of the [2 + 1] Cycloadditions

2.3.1. Stereospecificity of the HN≡C Moiety: Let us first consider the HN≡C addition to the four homodiatomic dipolarophiles, namely $H_2C{=}CH_2$, HN=NH, $H_2Si{=}SiH_2$ and HP=PH. Due to the presence of two identical atoms in each dipolarophile, the problem of regioselectivity does not exist, but instead this allows us to identify the stereochemistry of the HN≡C group. In principle, two distinct TSs could be located in each of these cases, which differ from each other by the relative disposition of the H atom bound to N. The free HN≡C molecule is linear. It approaches one dipolarophile atom by a rather large open intermolecular angle. When approaching its partner, HN≡C begins to bend at a certain point on the reaction path. Due to the dipolarophile symmetry in the $H_2C{=}CH_2$ and $H_2Si{=}SiH_2$ cases, the supersystem adopts a C_s symmetry in which HN≡C bends in the π plane of the dipolarophile, but in two opposite directions: while the one leads to a TS having a syn conformation between the H(N) atom and the dipolarophile with respect to the C=N group, the other bending leads to an anti conformation. For both $H_2C{=}CH_2$ and $H_2Si{=}SiH_2$ cases, two distinct TSs, *syn* **s** and *anti* **a**, were in fact located (Figure 2). The energy difference between both TSs is not large. The *anti*-TS is more favored (by 11 and 22 kJmol^{-1}, respectively) than the *syn* form. When hydrogen repulsion between the H_2C and H_2Si

Figure 1. Correlation between frequency shifts $\Delta\nu$ and distance variations Δr of the exocyclic C=N bond at the QCISD(T)/6-311G(d,p) level

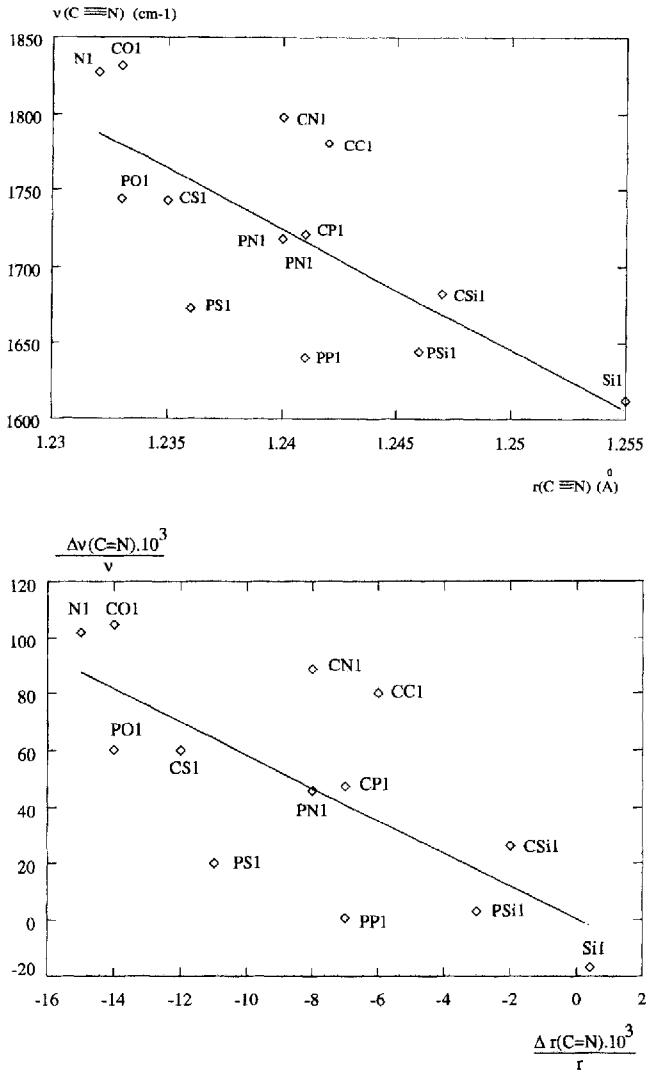
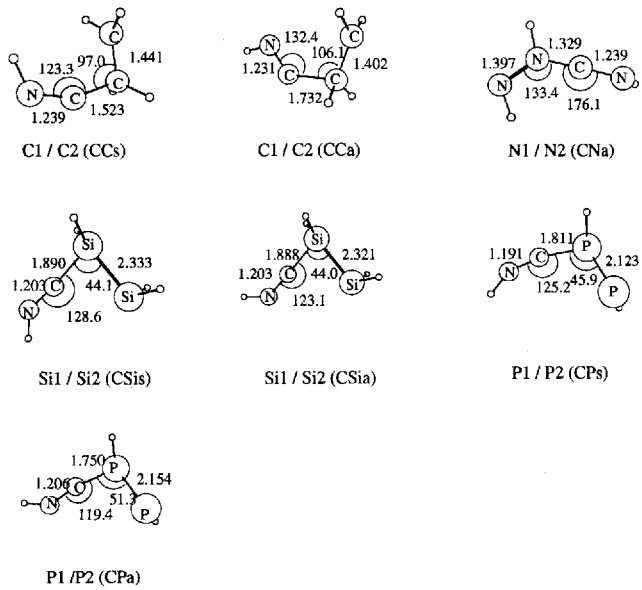


Table 3. CN distances [Å] and CN stretching frequency ($\tilde{\nu}$ [cm^{-1}]) of the lowest lying transition structures and the corresponding cycloadducts (HF/6-31G(d,p); imaginary wave numbers are given in parentheses

Dipolarophile	r(C=N)		ν_i(C=N stretching)[a]	
X=Y	TS	Product	TS	Product
CH_2=CH_2	1.227	1.242	1631(-771)	1781
CH_2=NH	1.185	1.240	1834(-762)	1798
CH_2=O	1.165	1.223	1972(-574)	1831
CH_2=SiH_2	1.191	1.247	1793(-422)	1683
CH_2=PH	1.148	1.241	2025(-771)	1721
CH_2=S	1.142	1.235	2072(-598)	1743
PH=CH_2	1.148	1.241	2025(-711)	1721
PH=NH	1.187	1.240	1827(-593)	1718
PH=O	1.205	1.233	1861(-641)	1744
PH=SiH_2	1.189	1.246	1798(-354)	1644
PH=PH	1.206	1.241	1916(-280)	1640
PH=S	1.191	1.236	1905(-363)	1673
NH=NH	1.226	1.232	1831(-379)	1827
H_2Si=SiH_2	1.186	1.255	1805(-512)	1612

[a] Scaled by a factor of 0.863, see ref.[8]; the imaginary wave numbers are not scaled; the data for HN≡C and H_2C=NH are: r(HN≡C): 1.155 Å, r(H_2C=NH): 1.250 Å; ν(HN≡C stretching) = 1990 cm^{-1} and ν(H_2C=NH stretching) = 1639 cm^{-1}.

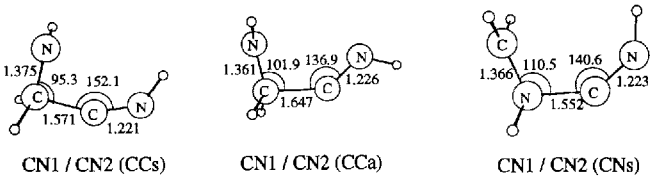
Figure 2. Transition structures in the HN≡C cycloaddition to H_2C=CH_2, H_2Si=SiH_2, HN=NH, and HP=PH. **s** stands for the *syn* conformation, **a** for *anti* conformation



groups and the H(N) atom occurs, the energy is in favour of the *anti*-TS. For HN=NH, only one TS was found (Figure 2). Owing to the omnipresence of three nitrogen lone pairs the supersystem adopts a linear configuration which minimizes the lone pair repulsion. Of the two TSs located for HP=PH, the *syn* conformer displayed in Figure 2 is more favored than the *anti* conformer by 13 kJmol^{-1}. In previous papers[10,11], we rationalized that a *syn*-TS is preferred over an *anti*-TS by a simple stereoelectronic effect. Accordingly, during the addition process, the electron pairs of two partners participating in the formation of two new σ bonds display a natural tendency to migrate in the same direction in order to harmonize the electron flow, thus ensuring an optimal overlap and avoiding disfavorable electron repulsion. In this reaction, such an electronic reorganization is possible in the *syn*-TS. Therefore, the *syn*-TS is stereoelectronically favored. In contrast, the electron pairs in the *anti*-TS move in the opposite direction thus disfavoring the corresponding pathway. It is clear that the stereoelectronic effect is only operative in the HN≡C + HP=PH additions. In the remaining cases, either hydrogen repulsions (H_2C=CH_2 and H_2Si=SiH_2) or lone pair repulsions (HN=NH) emerge as more important factors than the disposition of the migrating electrons.

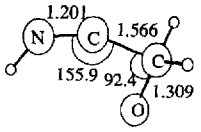
2.3.2. Regioselectivity of the Cycloaddition: In heteroatomic dipolarophiles, two distinct attacks of the carbon lone pair could occur at both dipolarophilic centers giving rise to a regioselectivity of the addition. As mentioned above, this selectivity could be interpreted by frontier orbitals and/or net charge distribution. We will briefly examine the approaches in each of the reactions. In the following, the transition structures will be displayed within the text at the end of each section. Regarding the notations mentioned above, the letters given in parentheses indicate the most advanced formation of the new bond and the stereochemistry of the HNC group (*syn* or *anti*). The barrier heights of the most favored additions, if not mentioned, can be found in Table 2.

HN≡C + H_2C=NH: The potential energy surface relative to this addition was reported in a recent paper[11]. We only mention here the main results. The C-addition with an energy barrier of 164 kJmol^{-1} is largely favored over the N-addition in accord with frontier orbital and charge analysis. In the N-addition, only the *syn*-TS is located. The difference between both TSs for C- and N-additions amounts to 65 kJmol^{-1}. Within the C-addition, the *syn*-TS was calculated to be favored by 3 kJmol^{-1} over the *anti* form in line with the stereoelectronic effect.

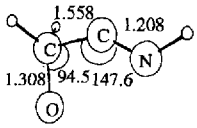


HN≡C + H_2C=O: A similar situation emerges. The C-addition is favored as revealed by frontier orbital and charge analysis and confirmed by supermolecule calculations. The TS for the O-addition lies very high in energy. The barrier height for C-addition amounts to 141 kJmol^{-1} which is somewhat smaller than that in the H_2C=NH case. The *syn* form of the TS for the C-addition is preferred by 14 kJmol^{-1} over the *anti* form, in qualitative agreement with the stereoelectronic effect.

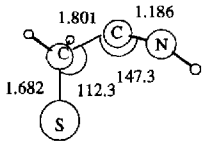
HN≡C + H_2C=SiH_2: This reaction was analyzed in detail in a previous paper[9]. The Si atom is by and large the most favored electrophilic center. While the Si-addition is



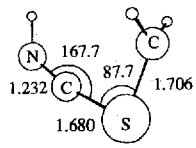
CO1 / CO2 (CCs)



CO1 / CO2 (CCa)

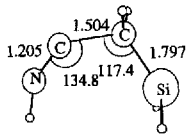


CS1 / CS2 (CCs)

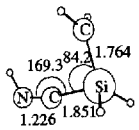


CS1 / CS2 (CSs)

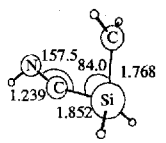
required to overcome a small energy barrier of 34 kJmol^{-1}, the C-addition is associated with an energy barrier of 84 kJmol^{-1}. Note that the latter is even much smaller than those obtained for the C-addition in previous cases. On the other hand, the *syn*-TS is more favored than the *anti*-TS by 7 kJmol^{-1} in accordance with the stereoelectronic effect. Thus, this addition is highly regioselective and stereospecific and its mechanism can be rationalized by qualitative arguments.



CSi1 / CSi2 (CCs)

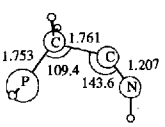


CSi1 / CSi2 (CSis)

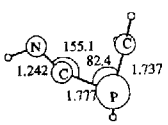


CSi1 / CSi2 (CSia)

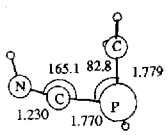
HN≡C + H$_2$C=PH: This reaction was also investigated in detail[10]. Here another picture emerges for the C-addition which was now calculated to be favored over the P-addition by 15 kJmol^{-1}, in disagreement with predictions based on both frontier orbital and charge distribution (Table 1). Note, however, that the LUMO coefficients of C and P are not very different. The higher regioselectivity at carbon likely arises from the repulsion between the lone pairs of the incoming carbon atom and the receiving phosphorus atom. The C-addition was however found to be stereospecific in agreement with the stereoelectronic effect. The *syn*-TS is 3 kJmol^{-1} more favorable than the *anti*-TS.



CP1 / CP2 (CCs)



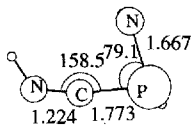
CP1 / CP2 (CPa)



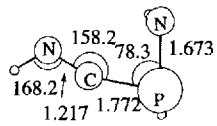
C P1 / CP2 (CPs)

HN≡C + H$_2$C=S: While the carbon atom in H$_2$C=S has the larger orbital coefficient in the LUMO, it represents a negatively charged center. Supermolecule calculations show that the C-addition is by far the preferred approach[8]. The barrier height amounts to 92 and 226 kJmol^{-1} for the C-addition and S-addition, respectively. The presence of the lone pairs at S is undoubtedly responsible for such a large energy difference. In this C-addition, only the *syn* conformer could be located; any geometry optimization starting with an *anti* conformation of the TS ends up with the *syn*-TS.

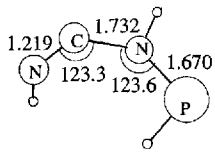
HN≡C + HP=NH: Although the phoshorus atom of the dipolarophile bears the larger LUMO coefficient, it turned out that both TSs for N-addition and P-addition have similar energies; the difference is only 2 kJmol^{-1} in favor the P-addition. With regard to the stereospecificity, the P-addition follows the path having a minimum electron overlap by favoring the *syn*-TS by 12 kJmol^{-1} over the *anti*-TS. In the N-addition, the *anti*-TS becomes favored due to the strongly hydrogen repulsion present in the *syn* conformation.



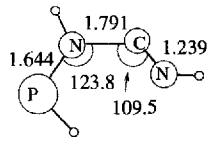
PN1 /PN2 (CPs)



PN1 / PN2 (CPa)

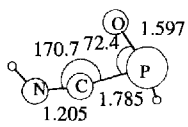


PN1 / PN2 (CNs)

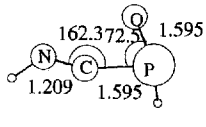


PN1 / PN (CNa)

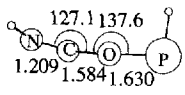
HN≡C + HP=O: Calculations emphasized the preference for the P-addition in agreement with the fact that the P-atom possesses the larger LUMO coefficient and the positive charge (Table 1). The O-addition is associated with an energy barrier of 159 kJmol^{-1}. In both approaches, the *syn* conformations of the HN≡C moiety in the TS are lower in energy than the corresponding *anti* forms.



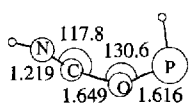
PO1 / PO2 (CPs)



PO1 / PO2 (CPa)

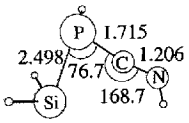


PO1 /PO2 (COs)

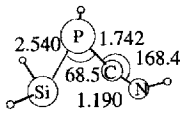


PO1 /PO2 (COa)

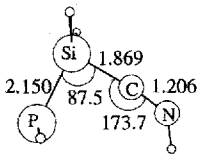
HN≡C + HP=SiH$_2$: The presence of Si results again in an extremely low-energy barrier when the addition at silicon takes place. The corresponding energy barrier is only 7 kJ mol^{-1}, a value too small to be realistic. The Si-addition in substituted derivatives is likely to become a barrier-free process. Considering the energy of the two *syn-anti* pairs of the four located TSs, their relative energy ordering is in agreement with that suggested by the stereoelectronic model. In this case, the *syn*-TS lies 20 kJmol^{-1} below the *anti* counterpart.



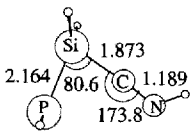
PSi1 / PSi2 (CPs)



PSi1 / PSi (CPa)

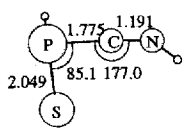


PSi1 / PSi2 (CSis)

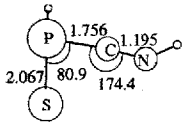


PSi1 / PSi (CSia)

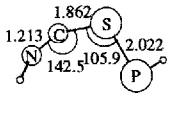
HN≡C + HP=S: The more advanced formation of the C–P bond in the TS, as predicted by qualitative analysis, was confirmed by supermolecule calculations. The additive process is again relatively easy with a calculated barrier of 32 kJmol^{-1} in the P-addition. The *syn* addition is also favored over the *anti* addition by an amount of 19 kJmol^{-1}. In the S-addition, only the *syn* addition TS could be located.



PS1 / PS2 (CPs)



PS1 / PS2 (CPa)



PS1 / PS2 (CSs)

In summary, supermolecule calculations confirmed that, except for a few cases, the regioselectivity of the [2 + 1] addition of HN≡C to dipolarophiles can be rationalized in terms of frontier orbitals. The exceptions emerge when the difference between LUMO coefficients is not unambiguously large. Regarding the stereospecificity, which determines the *syn* or *anti* conformations of the cycloadduct, the behavior of the most favored TS is in fact in accordance with the stereoelectronic model describing the electronic movement in the same sense. Exceptions are the cases where the nuclear repulsion between terminal groups becomes significantly strong. Table 4 summarizes the behavior of the different systems under consideration.

Table 4. Characteristics of the [2 + 1] cycloadditions considered, in terms of a frontier orbital (F. O.), net charge, stereoelectronic effect (SE) as well as nuclear and electronic repulsions[a]

X	F. O.	Electrophilic site	SE	Repulsion
		CH_2=X		
CH_2			NO	YES
NH	YES	YES	YES	NO
O	YES	YES	YES	NO
SiH_2	YES	YES	YES	NO
PH	NO	NO	YES	YES
S	YES	NO		
		PH=X		
CH_2	NO	NO	YES	YES
NH	YES	YES	YES	NO
O	YES	YES	YES	NO
SiH_2	YES	YES	YES	NO
PH			YES	NO
S	YES	YES	YES	NO
		X=X		
NH			NO	YES
SiH_2			NO	YES

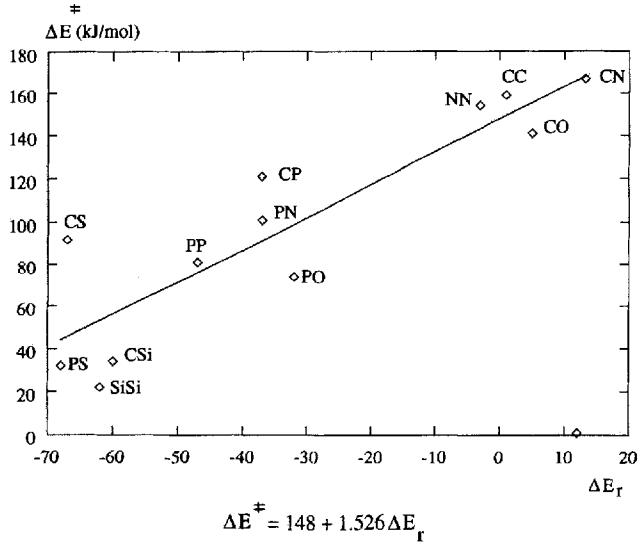
[a] YES implies that the effect mentioned is operative.

Comparisons: From the results mentioned above, a number of general trends governing the cycloadditions can be emphasized.

i) Roughly, a correlation exists between energy barriers and frontier orbital energy gaps. The smaller the HOMO-LUMO gap, the stronger the interaction and the lower the energy barrier.

ii) A correlation between energy barriers and exothermicities can also be established. Figure 3 shows a behavior which is associated qualitatively with the Hammond postulate and quantitatively with the Evans-Polanyi relationship. Hence, the larger the exothermicity, the lower the barrier height. HP=SiH$_2$ constitutes an exception in view of its extremely small barrier.

Figure 3. Correlation between the energy barriers to the [2 + 1] approach and the associated reaction energies at the QCISD(T)/6-311G(d,p) level



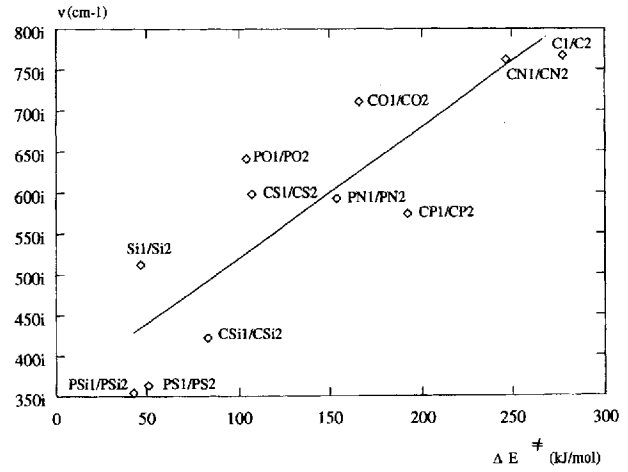
$\Delta E^{\ddagger} = 148 + 1.526\Delta E_r$

iii) The barrier height is also partly reflected in the intermolecular distance. Within a series of C-additions, we note

that a longer C–C distance implies an earlier TS and a lower barrier.

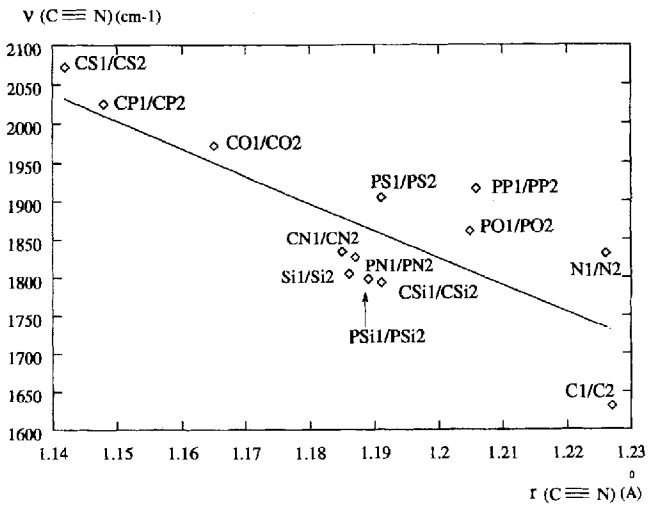
iv) The barrier height is also manifested in the imaginary vibrational wave numbers of the TS. As this vibrational mode corresponds in fact to the reaction coordinate, the imaginary wave number is a measure of the barrier shape. Figure 4 suggests a rough proportionality between the barrier heights and the imaginary wave numbers.

Figure 4. Correlation between the imaginary vibrational wave numbers of the TS and the associated barrier heights



v) A certain correlation between the stretching frequency (wave numbers) and the length of the C=N bond in the TS also exists (Figure 5).

Figure 5. Correlation between the stretching frequencies ν and the distances r of the C≡N bond of the TS



vi) The energy barriers are consistently smaller for the HP=X dipolarophiles than the H_2C=X dipolarophiles. Smaller barriers are also found for dipolarophiles containing third row atoms. Replacement of X by an element belonging to a higher element group favors the [2 + 1] addition. Si dipolarophiles present the smallest energy barriers, due to the fact that Si is the most electropositive element of the entire series.

3. Concluding Remarks

With regard to the [2 + 1] cycloaddition of the hydrogen isocyanide to several dipolarophiles, the calculated results discussed in the present paper point to a certain similarity in the behavior of both C and P dipolarophile series. They undergo both regioselective and stereospecific addition. In the former series, the C-addition is favored in most cases while in the latter series, the P-addition is preferred. Although the barrier heights for P-additions are consistently smaller than those of C-additions, the C-addition turned out to be favored when there is a competition between both C and P centers of the same dipolarophile, presumably due to the presence of a P lone pair. Otherwise, the regioselectivity and stereospecificity of the cycloadditions in both series are mainly governed by frontier orbitals, net charge distribution of the reactants and stereoelectronic effect in the transition structure. The more electropositive Si atom is consistently the preferential site of attack, irrespective of its partner within the double bond.

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☆ We dedicate this paper to the memory of our friend and colleague, Prof. Dr. *Gerrit L'Abbé*, who untimely passed away on August 27, 1996.

[1] H. B. Yockelson, A. J. Millevolte, K. J. Haller, R. West, *J. Chem. Soc. Chem. Commun.* **1987**, p. 1605.

[2] M. Baudler, J. Simon, *Chem. Ber.* **1987**, *120*, 421.

[3] D. Lentz, R. Marshall, *Z. Anorg. Allg. Chem.* **1992**, *617*, 53.

[4] A. G. Brook, Y. K. Kong, A. K. Saxena, J. F. Sawyer, *Organometallics* **1988**, *7*, 2245; A. G. Brook, A. K. Saxena, J. F. Sawyer, *Organometallics* **1989**, *8*, 850.

[5] M. Driess, H. Pritzkow, *J. Chem. Soc. Chem. Commun.* **1993**, p. 1585.

[6] M. Driess, H. Pritzkow, M. Sander, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 283; *Angew. Chem.* **1993**, *105*, 273. M. Driess, *Adv. Organomet. Chem.* **1996**, *39*, 139; M. Driess, H. Pritzkow, S. Rell, U. Winkler, *Organometallics* **1996**, *15*, 1845.

[7] G. L'abbé, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 276; *Angew. Chem.* **1980**, *92*, 277; H. Quast, A. Fuss, A. Heublein, H. Jakobi, B. Seiferling, *Chem. Ber.* **1991**, *124*, 2545; H. Quast, S. Aldenkortt, E. Heller, P. Schäfer, E. Schmitt, *Chem. Ber.* **1994**, *127*, 1699.

[8] M. T. Nguyen, H. Vansweevelt, L. G. Vanquickenborne, *J. Org. Chem.* **1991**, *56*, 5651.

[9] M. T. Nguyen, H. Vansweevelt, A. De Neef, L. G. Vanquickenborne, *J. Org. Chem.* **1994**, *59*, 8015.

[10] M. T. Nguyen, A. Van Keer, K. Pierloot, L. G. Vanquickenborne, *J. Am. Chem. Soc.* **1995**, *117*, 7535.

[11] M. T. Nguyen, A. Van Keer, L. G. Vanquickenborne, *J. Chem. Soc., Perkin Trans. 2* **1996**, 299.

[12] M. T. Nguyen, A. Van Keer, T. K. Ha, L. G. Vanquickenborne, *J. Mol. Struct. Theochem.* **1994**, *130*, 125; M. T. Nguyen, E. Van Pract, L. G. Vanquickenborne, *Inorg. Chem.* **1994**, *33*, 1153; M. T. Nguyen, P. J. Groarke, S. Malone, A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2* **1994**, *33*, 1153; M. T. Nguyen, L. Landuyt, L. G. Vanquickenborne, *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1771.

[13] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. G. Replogle, R. Gompert, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. DeFrees, J. Baker, J. J. P. Stewart, J. A. Pople, *GAUSSIAN 92*, Gaussian Inc., Pittsburgh, PA, **1992**.

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