Effect of methyl and vinyl substitution on the geometries, relative stabilities and Diels–Alder reactivities of phospholes: a DFT study

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epoc ABSTRACT: Equilibrium geometries and the relative stabilities of 1H-, 2H- and 3H-phospholes and their methyl- and vinyl-substituted analogs were computed at the B3LYP/6–31G* level. The transition states and products were located for the Diels–Alder reactions of all the dienes with ethylene. The effect of substitution on the geometries, relative stabilities and Diels–Alder reactivities of 1H-, 2H- and 3H-phospholes were analyzed. The relative stabilities predict that the substitution on phospholes prefers phosphorus over carbon. Computations show that the activation energies are not altered much by substitution of either methyl or vinyl groups on phospholes, but most of the substituted phospholes require slightly higher activation energies than the corresponding parent phospholes. 2H-phospholes require lower activation energies than 1H- and 3H-phospholes. The reactivity ordering based on FMO energy gaps and the activation energies are similar and follows the sequence 2H- > 3H- > 1H-phospholes. The quantaum of charge-transfer values from diene to dienophile at the transition states and distortion energies were calculated. Copyright © 2003 John Wiley & Sons, Ltd.
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KEYWORDS: relative stabilities; Diels–Alder reactivities; concerted mechanism; asynchronous pathway; transition states; activation energies; electron demand; charge transfer

INTRODUCTION

The syntheses of phospholes and substituted phospholes have generated considerable interest in order to study their stability, aromaticity, [1,5] sigmatropic shifts and Diels–Alder and other reactivities.[1–15] The synthesis of a highly substituted phosphole was reported in 1959,[15] and the parent 1H-phosphole (**1**) was synthesized and characterized in 1983 by Mathey and co-workers.[8] Phospholes have found several applications in organic synthesis and catalysis, e.g. some phosphole complexes with metal or metal halides have been used to catalyze hydrogenation, carbonylation and hydroformylation reactions.[6,16,17] Diels–Alder reactions of phospholes have constituted a dependable strategy to construct novel phosphorus-containing polycyclic compounds.[6–14] The lower aromaticity of 1H-phosphole (**1**) is expected to be more reactive and more exothermic than pyrrole, furan and thiophene in Diels–Alder reactions.[18,19] The [1,5]

sigmatropic shifts for substituted phospholes have generated considerable interest from both theoreticians and experimentalists.[3–6,12–14] Previous computational studies of sigmatropic shifts in parent phospholes and the relative stabilities of the methyl- and vinyl-substituted phospholes indicate that 2H-phospholes are more stable than 1H- and 3H-phospholes.[4,5] Mathey and co-workers proposed a mechanism which accounts for the [1,5] sigmatropic shifts prior to Diels–Alder additions and successfully explained the product distribution in Diels–Alder reactions of a variety of phospholes.[8–11] Previous experimental studies indicated that 2H-phospholes act as dienes and dienophiles, and also that 1-phosphanorbornadiene was obtained by the Diels–Alder reaction of 2H-phosphole (**2**) with acetylene.[11–13]

Computational chemistry has played an important role in modeling Diels–Alder reactions.[18–29] Earlier studies indicate that HF methods overestimate and MP2 methods underestimate barrier heights.[18,23–29] Previous studies indicated that the relative stabilities of phospholes obtained with the HF method were inconsistent with MP2 results.[5] This indicates that a dynamic electron correlation is necessary to obtain numbers of high accuracy. Recent computational studies adjudged that the B3LYP method, even with a 6–31G* basis set, is more reliable than the traditional HF and MP2

approaches.[18,23] We therefore adopted the B3LYP/6–31G* method to study the geometries, relative stabilities and Diels–Alder reactivities of phospholes and their substituted analogs. To our knowledge, the present study has given the first reliable energetics on Diels–Alder reactions of substituted phospholes with ethylene.

The present study focused on how the relative stabilities and Diels–Alder reactivities of 1H-, 2H- and 3H-phospholes vary upon substitution by methyl and vinyl groups. All the dienes considered in this study are depicted in Scheme 1 and the designations for dienes end with **M** for methyl-substituted and **V** for vinyl-substituted phospholes. In this study, the Diels–Alder reactivities of parent and methyl- and vinyl-substituted phospholes were investigated only with ethylene as dienophile. Three parent and 11 methyl- and 11 vinyl-substituted phospholes (total 25 dienes) were studied. The geometries of all the substituted dienes are discussed and compared with the parent phospholes. FMO analysis and the quantum of charge transfer values from diene to dienophile at the transition state (q_{CT}) were used to study the Diels–Alder reactivities of all the dienes. The activation and reaction energies, thermochemical data

for all the reactions considered and the distortion energies of the reactants at the transition states were calculated and analyzed.

COMPUTATIONAL METHODS

The structures of all the parent and methyl- and vinyl-substituted phospholes were optimized at the B3LYP level using the 6–31G* basis set. Frequency calculations were carried out to ascertain the nature of the stationary points and eventually the minimum energy structures were obtained for all the reactants. Similarly, transition states and products of each of the dienes with ethylene were optimized and characterized by frequency calculations. Only the concerted pathway was pursued in the present study. However, an alternative stepwise pathway exists despite lying slightly over the concerted pathway.[21–23] Except the reactions of dienes, **1**, **4M** and **4V**, all other dienes considered in this study are asynchronous by symmetry. All the calculations were performed using the Gaussian 98 suite of programs.[30] The normal mode of the imaginary frequency of each of the transition states was verified using the MOPLOT program package.[31] In all cases, the reaction vector corresponds to the concerted transition state. The lowest energy conformations of vinyl and methyl substituents were taken in all the structures considered. The frontier orbital energies and the quantum of charge-transfer values from diene to dienophile at the transition states were also computed at the B3LYP/6–31G* level.

RESULTS AND DISCUSSION

In this section, the equilibrium geometries and relative stabilities of phospholes and their substituted analogs are discussed first. The geometries of the transition states and products for all the reactions considered in this study are then discussed. This is followed by the frontier orbital analysis and the activation and reaction energies. The distortion energies of the reactants are discussed at the end of this section.

Equilibrium geometries and relative energies of reactant dienes

Figure 1 depicts the optimized bond lengths of parent and methyl-substituted phospholes. Similarly, the vinyl-substituted phospholes are shown in Fig. 2. Figures 1 and 2 indicate that the bond lengths of the parent phosphole ring are not altered significantly by substitution. As the double bond of vinyl group attached to sp^2 carbons in vinylphospholes are in conjugation with the ring double bonds, C(ring)—C(vinyl) bond lengths range from 1.456 to 1.472 Å. In the case of methyl-substituted
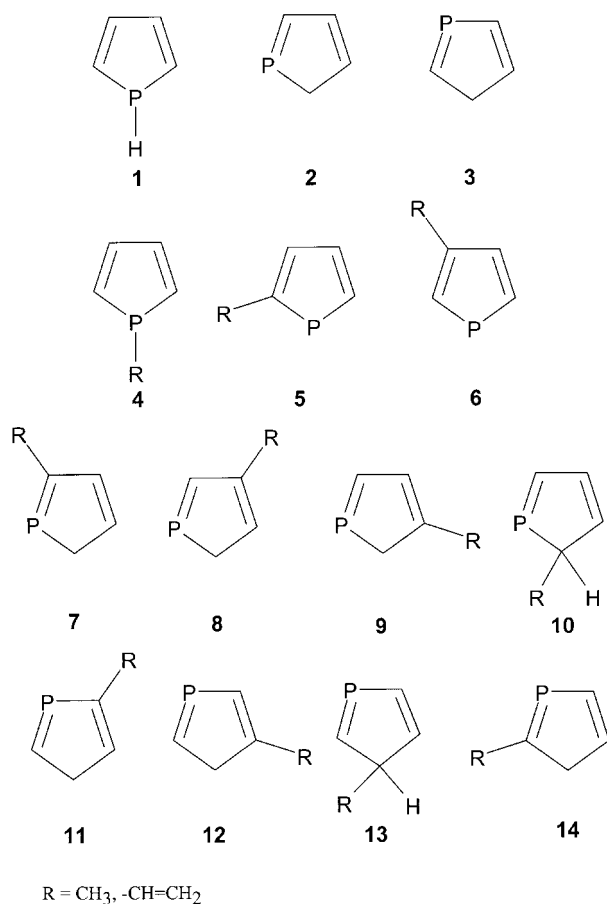
Scheme 1. 1H-, 2H- and 3H-phospholes and methyl and vinyl substitution at various positions
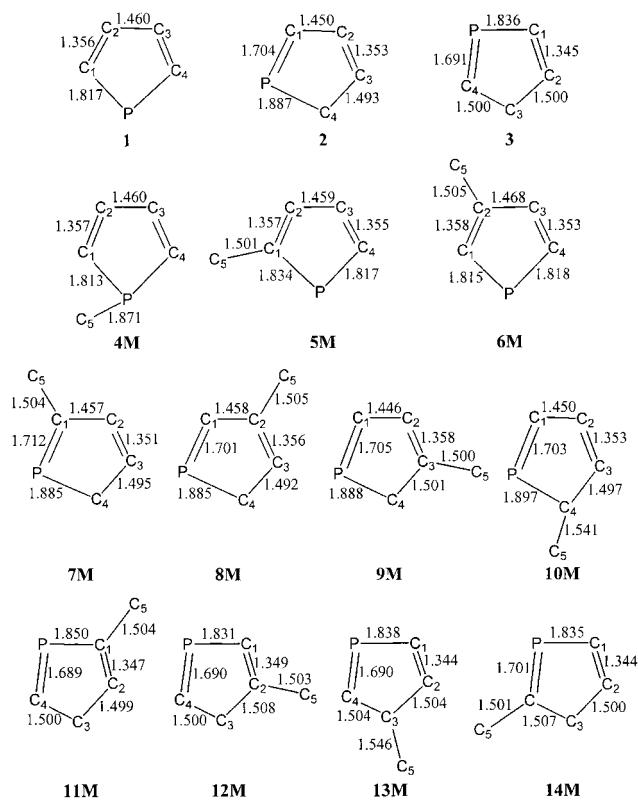
R = CH$_3$, -CH=CH$_2$

Figure 1. B3LYP/6–31G* optimized bond lengths (in Å) of 1H-, 2H- and 3H-phospholes and their methyl-substituted analogs

Figure 2. B3LYP/6–31G* optimized bond lengths (in Å) of the vinyl-substituted 1H-, 2H- and 3H-phospholes

phospholes, the C(ring)—C(methyl) bond lengths are shorter than the normal C—C bond lengths and these bond lengths range from 1.500 to 1.505 Å, which may be traced to the pseudo C—H π-orbital participation.

Table 1 gives the computed relative energies of parent phospholes and methyl- and vinyl-substituted phospholes. 2H-Phosphole (**2**) is more stable than 3H-Phosphole (**3**) and 1H-phosphole (**1**), which is in agreement with previous studies reported at the MP2/6–31G* level.[5] The isomers **9M** and **7V**, which are substituted 2H-phospholes, are the most stable isomers in methyl- and vinyl-substituted phospholes, respectively. In case of methyl-1H-phospholes **4M–6M**, the isomer **4M**, which has the methyl group attached to phosphorus, is calculated to be more stable than **5M** and **6M**. In contrast, in vinyl-1H-phosphole **4V** is 3.1 and 2.0 kcal mol^{-1} (1 kcal = 4.184 kJ) less stable than **6V** and **5V**, respectively. In the positional isomers of methyl-2H-phospholes, **7M–10M**, the least stable isomer is **10M**, where the methyl group is attached to the sp^3 carbon, and the isomers **7M–9M** are more stable compared to all other methyl-substituted phospholes. A similar situation is observed in the case of vinyl-2H-phospholes. The isomers **13M** and **13V** are the least stable isomers among the positional isomers of methyl-3H-phospholes and vinyl-3H-phospholes, respectively. The isomer **4M** is 0.9 and 4.3 kcal mol^{-1} more stable than **10M** and **13M**,

respectively. In case of vinyl-substituted phospholes, **4V** is energetically competitive with **10V** and is about 5.6 kcal mol^{-1} more stable than **13V**. This indicates that the substituent will prefer to attack on phosphorus rather than sp^3 carbon owing to less steric repulsion, since the C—P bond is longer than the C—C bond.

Table 1. Relative energies of parent, 1H-, 2H- and 3H-phospholes (**1–3**) and methyl-substituted (**4M–14M**) and vinyl-substitute (**4V–14V**) phospholes obtained at the B3LYP/6–31G* level (all values are in kcal mol^{-1})

Diene	ΔE	Diene	ΔE
1	4.8		
2	0.0		
3	4.5		
4M	4.5	**4V**	8.2
5M	6.0	**5V**	6.2
6M	5.2	**6V**	5.1
7M	0.9	**7V**	0.0
8M	0.6	**8V**	2.7
9M	0.0	**9V**	0.2
10M	5.4	**10V**	8.1
11M	5.6	**11V**	7.3
12M	4.8	**12V**	5.7
13M	8.8	**13V**	13.8
14M	5.5	**14V**	5.2

Geometries of transition states and products

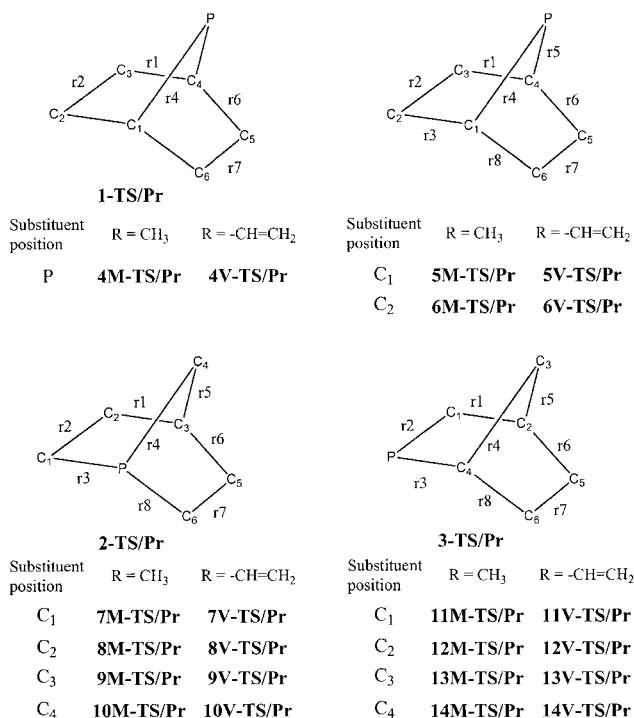The number of positional isomers possible for 1H-, 2H- and 3H-phospholes is 3, 4 and 4, respectively, resulting in 11 different reactant pairs each for methyl- and vinyl-substituted phospholes. Additionally, 1H-phosphole (**1**) and methyl- and vinyl-substituted phospholes of **4**, **5**, **6**, **10** and **13** give rise to *syn* and *anti* transition states and products. In the *syn* transition state/product, the substituent or hydrogen attached to phosphorus or the substituent attached to an sp^3 carbon is disposed towards the diene moiety, whereas in the *anti* form it is disposed away from the diene. A total of 36 transition states and products, 16 each for methyl- and vinyl-substituted compounds and 4 for the parent phospholes, were computed in the present study. The designation of the important bond lengths and the nomenclature used in this study for the transition states and products are shown in Scheme 2. The bond length values for all the transition states and products are given in the Supplementary Material.

The percentage stretching/shortening values of the important bonds in the transition states are provided in Table 2. This percentage is calculated as the ratio between the variation of bond length from reactant to transition state and the same from reactant to product for a given bond. The analysis shows that the transition states obtained for 1H-phosphole (**1**) and its substituted analogs

Table 2. Percentage stretching and shortening of the important bonds in the transition states for parent (**1–3**) and methyl-substituted (**4M–14M**) and vinyl-substituted (**4V–14V**) phospholes obtained at the B3LYP/6–31G* level (values in parentheses are for the *anti* form)

Diene	% Stretching at the TS			% Shortening at the TS:
	$r1$	$r3$	$r7$	$r2$
1	26.4 (32.1)	–	27.7 (26.9)	48.8 (52.5)
2	25.2	25.0	22.1	45.0
3	24.4	31.7	24.5	46.6
4M	25.5 (35.4)	–	27.6 (27.0)	47.5 (55.6)
5M	28.2 (33.3)	27.5 (32.0)	28.4 (27.1)	50.4 (52.5)
6M	26.8 (31.7)	27.4 (32.2)	27.7 (26.3)	49.2 (52.9)
7M	25.6	25.5	23.0	46.1
8M	25.2	25.0	22.5	45.1
9M	25.8	26.1	23.7	46.2
10M	22.7 (25.5)	22.6 (26.1)	21.5 (21.3)	42.2 (45.9)
11M	23.8	31.2	24.5	46.7
12M	23.5	33.6	25.2	45.8
13M	23.8 (25.9)	30.8 (32.9)	24.4 (23.4)	45.0 (48.3)
14M	27.4	31.1	25.2	50.7
4V	26.5 (34.8)	–	27.7 (27.0)	47.5 (54.7)
5V	32.3 (37.7)	27.1 (32.9)	29.4 (28.6)	51.3 (55.5)
6V	24.2 (29.9)	28.8 (34.2)	28.7 (27.3)	47.9 (51.7)
7V	23.8	26.0	23.9	44.6
8V	25.8	24.0	22.5	44.4
9V	27.2	30.4	25.6	48.5
10V	23.0 (25.8)	22.4 (26.1)	22.0 (21.5)	41.8 (45.0)
11V	26.4	27.7	23.1	49.0
12V	23.4	36.7	25.8	46.7
13V	23.8 (24.7)	30.8 (32.7)	24.5 (22.9)	45.7 (47.7)
14V	32.1	28.6	26.6	54.3

are 'late' compared with 2H- and 3H-phospholes and their substituted analogs.

FMO analysis

E_{HOMO} and E_{LUMO} values of parent and methyl- and vinyl-substituted phospholes and the HOMO–LUMO and LUMO–HOMO energy difference between the diene and ethylene along with the quantum of charge transfer values from diene to dienophile at the transition state (q_{CT}) are given in Table 3. The reactions of the parent phospholes with ethylene follow the inverse electron demand. Similarly, those of methyl- and vinyl-substituted phospholes follow the inverse electron demand. Therefore, the substitution of phospholes does not affect the electron demand on Diels–Alder reactions with ethylene. The normal and inverse electron demands represent the flow of electrons from diene to dienophile and from dienophile to diene, respectively. The FMO energy gaps obtained for 2H-phospholes are lower than those for 1H- and 3H-phospholes. The reactivity of 1H-, 2H- and 3H-phospholes and their substituted analogs based on the FMO energy gap decreases in the order 2H-phospholes > 3H-phospholes > 1H-phospholes. In case of phospholes,

Scheme 2. The designation of bond lengths and nomenclature for transition states and products of 1H-, 2H- and 3H-phospholes and their methyl- and vinyl-substituted analogs

Table 3. Frontier molecular orbital energies (E_{HOMO} and E_{LUMO} in eV), FMO energy gaps between the diene and dienophile (E_N and E_I in eV) and the quantum of charge transfer from diene to dienophile at the transition state (q_{CT}) for all the dienes considered in this study[a]

Diene	E_{HOMO}	E_{LUMO}	E_N	E_I	q_{CT}[b]
1	−6.25	−1.02	6.76	6.24	−0.011 (0.007)
2	−5.91	−1.61	6.42	5.65	0.009
3	−6.19	−1.40	6.70	5.86	−0.022
4M	−6.08	−0.97	6.59	6.29	−0.017 (0.027)
5M	−5.97	−0.88	6.48	6.38	(0.024)
6M	−6.10	−0.86	6.61	6.40	−0.001 (0.017)
7M	−5.73	−1.43	6.24	5.83	0.018
8M	−5.80	−1.51	6.31	5.75	0.016
9M	−5.67	−1.51	6.18	5.75	0.029
10M	−5.87	−1.62	6.38	5.64	0.009 (0.009)
11M	−6.08	−1.32	6.59	5.94	−0.015
12M	−5.96	−1.33	6.47	5.93	−0.008
13M	−6.15	−1.42	6.66	5.84	−0.019 (−0.020)
14M	−5.88	−1.30	6.39	5.96	−0.005
4V	−6.11	−1.02	6.62	6.24	−0.020 (0.026)
5V	−5.73	−1.43	6.24	5.83	−0.010 (0.002)
6V	−5.97	−1.26	6.48	6.00	−0.018 (0.001)
7V	−5.68	−1.87	6.19	5.39	0.008
8V	−5.78	−1.71	6.29	5.55	0.002
9V	−5.52	−1.94	6.03	5.32	0.017
10V	−5.94	−1.74	6.45	5.52	0.007 (−0.001)
11V	−6.0	−1.49	6.51	5.77	−0.023
12V	−5.77	−1.63	6.28	5.63	−0.030
13V	−6.20	−1.49	6.71	5.77	−0.022 (−0.032)
14V	−5.56	−1.89	6.07	5.37	−0.022

[a] E_{HOMO} and E_{LUMO} of ethylene are − 7.26 and 0.51 eV, respectively. All values were obtained at B3LYP/6–31G* level.
[b] The quantum of charge transfer values for the *anti* form are given in parentheses.

while the FMO analysis indicates that a vinyl group may be treated as an electron-withdrawing group, Hansch's R and F values do not support such a classification.[32] Thus caution should exercised in employing FMO analysis for cycloaddition reactions involving vinyl substituents. The difference in E_I values among the positional isomers in each type of phosphole is insignficant in the case of both methyl- and vinyl-substituted phospholes, so the regioselectivity in cycloaddition may be less. The quantum of charge transfer values from diene to dienophile at the transition state (q_{CT}) for 1H- and 3H-phospholes are in agreement with the electron demand, but positive q_{CT} values are obtained for parent and substituted 2H-phospholes.

Activation and reaction energies with thermo-chemical data

Table 4 gives the activation energies, enthalpies, entropies and Gibbs free energies of activation for the reactions of parent and methyl- and vinyl-substituted phospholes with ethylene. The activation energy required for 2H-posphole (**2**) is 10.3 kcal mol^{-1}, which is 10.1 and 13.1 kcal mol^{-1} lower compared with 1H- and 3H-phospholes respectively. For either methyl- or vinyl-

substituted phospholes, the substituted 2H-phospholes require lower activation energies than substituted 1H- and 3H-phospholes. Except for **8V** and **11V**, other substituted phospholes require slightly higher activation energies than the corresponding parent phospholes. The dienes **8V** and **11V** require 1.5 and 1.3 kcal mol^{-1} lower activation energies than the parent phospholes **2** and **3**, respectively. Spino *et al.* reported that the conjugating substituents at the C(2) or C(3) position significantly stablitizes the transition state through extended π-conjugation with the diene portion.[33] Hence the dienes **6V** in vinyl-1H-phospholes, **7V** and **8V** in vinyl-2H-phospholes and **11V** in vinyl-3H-phospholes have lower activation energies than the rest. As expected, the effect is more predominant for vinyl substitution. The computed activation energies obtained for vinyl-substituted phospholes further validate Spino *et al.*'s proposal that substitution on inner sp^2 centers selectively stabilizes the transition-state region in the reaction coordinate.[33] Lower entropies of activation are observed for vinyl-substituted phospholes than their corresponding methyl-substituted phospholes. The reactivity based on activation energies for parent and substituted phospholes decreases in the order 2H-phospholes > 3H-phospholes > 1H-phospholes. The computed results reproduce excellently the experimental findings of Mathey and

Table 4. Activation energy ($\Delta E^{\ddagger}$), enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$) and Gibbs free energy ($\Delta G^{\ddagger}$) of activation obtained for the Diels–Alder reactions of parent phospholes (**1–3**) and methyl-substituted (**4M–14M**) and vinyl-substituted (**V–14V**) phospholes with ethylene at the B3LYP/6–31G* level (values in parentheses correspond to the *anti* form; all values are in kcal mol^{-1})

Diene	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
1	24.4 (24.6)	25.3 (25.5)	−12.5 (−12.6)	37.7 (38.1)
2	10.3	11.4	−12.4	23.8
3	20.4	21.5	−12.4	33.9
4M	25.3 (25.4)	25.9 (26.1)	−12.7 (−12.8)	38.6 (38.9)
5M	25.1 (25.4)	25.9 (26.4)	−12.7 (−12.8)	38.6 (39.2)
6M	25.0 (25.0)	25.9 (25.9)	−12.1 (−12.1)	37.9 (38.0)
7M	11.5	12.5	−12.0	24.5
8M	10.9	11.8	−11.7	23.6
9M	11.7	12.6	−12.7	25.3
10M	11.3 (10.7)	12.3 (11.5)	−12.5 (−12.7)	24.8 (24.2)
11M	21.2	22.3	−12.0	34.3
12M	21.4	22.5	−12.6	35.1
13M	21.5 (21.9)	22.6 (22.7)	−12.6 (−12.7)	35.2 (35.4)
14M	21.9	23.0	−12.7	35.7
4V	24.4 (24.9)	25.1 (25.7)	−12.8 (−12.9)	37.9 (38.6)
5V	25.2 (26.2)	26.0 (27.1)	−12.5 (−12.5)	38.5 (39.6)
6V	24.8 (24.9)	25.7 (25.9)	−12.3 (−12.5)	38.0 (38.3)
7V	11.4	12.3	−12.2	24.5
8V	8.8	9.9	−12.4	22.4
9V	11.7	12.6	−13.0	25.6
10V	12.4 (11.5)	13.4 (12.2)	−12.6 (−12.9)	26.0 (25.1)
11V	19.1	20.2	−12.4	32.6
12V	20.9	21.9	−14.2	36.1
13V	21.8 (20.6)	22.9 (21.3)	−12.6 (−12.7)	35.5 (34.1)
14V	22.3	23.4	−14.0	37.3

co-workers that 1H- and 2H-phospholes are in equilibrium, with selective trapping of 2H-species in Diels–Alder reactions where the substituted acetylene was used as dienophile.[3]

The reaction energy, enthalpy, entropy and Gibbs free energy of reaction for all the reactions considered in this study are presented in Table 5. Although the difference in activation energies between 2H- and 3H-phospholes is substantial (ca 10 kcal mol^{-1}), the reaction exothermicities are virtually identical. Except for four dienes for methyl- and five dienes for vinyl-substituted phospholes, the reaction energies obtained for other substituted phospholes do not vary to a great extent compared with the corresponding parent phospholes. The diene **5**, **9**, **12** and **14**, which have the methyl or vinyl group attached to the reactive sp^2 carbon, are predicted to be less exothermic than the parent and other substituted phospholes in the corresponding phosphole types. The decrease in exothermicity is very small, within 2–3 kcal mol^{-1}, for the dienes **5M**, **9M**, **12M** and **14M** compared with the corresponding parent phospholes. However, the decrease in exothermicity is significantly higher (by about 5–6 kcal mol^{-1}) in vinyl-substituted isomers. The reaction of diene **11V** with ethylene is the

most exothermic among all the reactions considered in this study. In general, *anti* products formed are more stable than *syn* products.

Distortion energies

The distortion energies of diene and ethylene, the total distortion energies of reactants and the interaction energies were calculated and are given in Table 6. The interaction energies were obtained by subtracting the total distortion energies from the activation energies. Parent 2H-phosphole (**2**) has the least distortion energy and the lowest activation energy; the trend is unchanged with methyl or vinyl substitution. These results are in agreement with the high reactivity and early transition state for 2H-phospholes.

CONCLUSIONS

We have reported quantitatively reliable B3LYP/6–31G* calculations in delineating the effect of substitution by methyl and vinyl group on geometries, relative stabilities and Diels–Alder reactivities of 1H-, 2H- and 3H-phospholes. The relative stabilities of phospholes and substituted phospholes predict that 2H-phospholes are more stable than 1H- and 3H-phospholes and the substituents prefer phosphorus sites over carbon. Diels–Alder reactions of substituted phospholes, except **8V** and **11V**, require slightly higher activation energies than the reactions of the corresponding parent phospholes. The reactivity of phospholes based on activation energy decreases in the order 2H-phospholes > 3H-phospholes > 1H-phospholes, and this order is in agreement with the FMO analysis. Although 2H-phospholes require very low activation energy compared with 3H-phospholes, the difference in reaction energies between these types is not very high. The reactions of dienes, which yield products possessing the substituent at the bridgehead carbon, are predicted to be less exothermic than other dienes in each type of phosphole. 2H-phospholes are less distorted from their equilibrium geometries to form the transition states compared with 1H- and 3H-phospholes. The Diels–Alder strategy is a promising route to access novel phosphorus-containing polycyclic compounds.

Supplementary material

Tables of the transition state and product geometries of all the reactions considered, the group charges accumulated for the substituents in the phospholes and the B3LYP/6–31G* optimized Cartesian coordinates for all the reactants, transition states and products are available at the epoc website at http://www.wiley.com/epoc.

Table 5. Reaction energy (ΔE_r), enthalpy (ΔH_r), entropy (ΔS_r) and Gibbs free energy (ΔG_r) of reaction obtained for the Diels–Alder reactions of parent phospholes (**1–3**) and methyl-substituted (**4M–14M**) and vinyl-substituted (**4V–14V**) phospholes with ethylene at the B3LYP/6–31G* level (values in parentheses correspond to the *anti* form; all values are in kcal mol^{-1})

Diene	ΔE_r	ΔH_r	ΔS_r	ΔG_r
1	−19.3 (−21.5)	−15.5 (−17.6)	−13.7 (−13.7)	−1.8 (−3.9)
2	−27.7	−24.3	−13.5	−10.8
3	−27.0	−22.7	−13.7	−9.0
4M	−18.9 (−20.3)	−15.4 (−16.8)	−13.8 (−13.7)	−1.6 (−3.1)
5M	−17.4 (−19.5)	−13.9 (−16.0)	−14.1 (−14.2)	0.2 (−1.8)
6M	−19.9 (−22.2)	−16.1 (−18.4)	−13.7 (−13.8)	−2.3 (−4.6)
7M	−28.1	−24.6	−13.5	−11.1
8M	−28.7	−25.2	−13.6	−11.6
9M	−24.9	−21.7	−14.0	−7.7
10M	−28.3 (−28.3)	−25.1 (−25.0)	−13.6 (−13.7)	−11.5 (−11.4)
11M	−28.1	−23.8	−13.8	−10.0
12M	−24.6	−20.7	−14.1	−6.6
13M	−26.3 (−26.6)	−22.3 (−22.6)	−13.9 (−13.9)	−8.5 (−8.7)
14M	−24.9	−20.9	−14.1	−6.8
4V	−19.4 (−20.9)	−15.8 (−17.3)	−13.9 (−13.8)	−1.9 (−3.5)
5V	−14.7 (−16.3)	−11.2 (−12.8)	−13.9 (−13.9)	2.7 (1.1)
6V	−18.7 (−20.6)	−14.9 (−16.8)	−13.5 (−13.5)	−1.4 (−3.3)
7V	−25.9	−22.6	−13.3	−9.3
8V	−29.3	−25.7	−13.6	−12.1
9V	−21.1	−18.0	−14.3	−3.7
10V	−27.4 (−27.3)	−24.2 (−24.0)	−13.8 (−13.9)	−10.3 (−10.1)
11V	−32.2	−27.7	−14.1	−13.6
12V	−21.6	−17.6	−15.8	−1.8
13V	−28.5 (−28.8)	−24.4 (−24.7)	−13.8 (−13.8)	−10.6 (−10.8)
14V	−21.7	−17.7	−15.5	−2.2

Table 6. Reactants and total distortion energies and the interaction energies obtained for the Diels–Alder reactions of parent (**1–3**) and methyl-substituted (**4M–14M**) and vinyl-substituted (**4V–14V**) phospholes obtained at the B3LYP/6–31G* level (values in parenthesis are for the *anti* form; all values are in kcal mol^{-1})

Diene	Distortion energy			Interaction energy
	Diene	Ethylene	Total	
1	20.7 (17.6)	8.9 (8.7)	29.5 (26.3)	−5.2 (−1.8)
2	10.6	6.1	16.7	−6.4
3	16.0	7.2	23.2	−2.8
4M	20.5 (18.9)	8.7 (8.9)	29.2 (27.8)	−3.9 (−2.4)
5M	20.9 (18.1)	9.2 (8.9)	30.1 (27.0)	−5.0 (−1.6)
6M	21.3 (18.3)	8.9 (8.9)	30.2 (27.2)	−5.2 (−2.2)
7M	11.1	6.4	17.5	−6.0
8M	10.8	6.2	17.0	−6.1
9M	11.3	6.7	18.0	−6.3
10M	11.2 (11.0)	5.8 (5.6)	17.0 (16.6)	−5.7 (−5.9)
11M	16.5	7.2	23.7	−2.5
12M	16.3	7.6	23.9	−2.5
13M	16.1 (17.4)	7.2 (6.6)	23.3 (24.0)	−1.8 (−2.1)
14M	17.0	7.5	24.5	−2.6
4V	19.9 (18.6)	8.7 (8.7)	28.6 (27.3)	−4.2 (−2.4)
5V	20.6 (18.2)	9.7 (9.3)	30.2 (27.6)	−5.1 (−1.4)
6V	20.4 (17.3)	9.1 (8.9)	29.5 (26.2)	−4.7 (−1.3)
7V	10.8	6.8	17.6	−6.2
8V	8.9	6.0	14.9	−6.1
9V	11.1	7.5	18.6	−6.9
10V	12.4 (12.4)	5.9 (5.6)	18.3 (18.0)	−5.9 (−6.5)
11V	15.1	6.4	21.5	−2.4
12V	15.7	7.6	23.4	−2.5
13V	16.5 (17.3)	7.2 (6.4)	23.7 (23.6)	−1.9 (−3.0)
14V	17.0	7.9	24.9	−2.6

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