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Anionic Ring-Opening Polymerization of Small Phosphorus Heterocycles and Their Borane Adducts: An Ab Initio Investigation

Michelle L. Coote, Jennifer L. Hodgson, Elizabeth H. Krenske, and S. Bruce Wild

Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

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ABSTRACT: *The kinetics and thermodynamics of anionic ring-opening reactions of phosphiranes, phosphetanes, and phospholanes and their borane adducts have been studied by high-level ab initio procedures. For the free heterocycles, model propagation reactions involving nucleophilic attack by Me_2P^- at the ring α-carbon were found to be feasible for the three- and four-membered rings, but not for the five-membered ring. For the borane adducts, nucleophilic attack by $Me_2(BH_3)P^-$ was only facile for the three-membered ring, despite an increased thermodynamic tendency toward ring opening for the borane adducts of both the three- and four-membered rings. The formation constants of the borane adducts of methylphosphirane and methylphosphetane were $K = 2.6 \times 10^{13}$ L mol^{-1} and $K = 1.2 \times 10^{20}$ L mol^{-1}, respectively. A Marcus analysis of the ring-opening reactions of methylphosphirane, methylphosphetane, and their borane adducts showed that the release of ring strain and an "additional factor" contribute to rate enhancement compared with their strain-free analogues. The additional factor was larger for the three-membered rings than for the four-membered rings and was larger in the free heterocycles than in their borane adducts. The additional factor is complex in origin and appears to reflect an increase in the separation between the bonding and antibonding orbitals of the breaking bond on going from the three-membered rings to the four-membered rings, and on going from the free heterocycles to the borane adducts.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:118–128, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20323

Correspondence to: Michelle L. Coote; e-mail: mcoote@rsc.anu.edu.au.
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INTRODUCTION

Polymers containing an inorganic element in their backbone are well known to show interesting and unique properties, including metal ion-binding characteristics and flameretardancy [1]. Stereoregular polyphosphines have many potential applications, one of which is the self-assembly of supramolecular polynuclear metal complexes in which linear arrays of metal ions are surrounded by two polyphosphine strands in helical arrangements. Univalent copper, silver, and gold complexes having these structures have been isolated with use of configurationally pure tetraphosphines and hexaphosphines as the helicating agents [2–4]. Longer polyphosphines would facilitate the self-assembly of complexes that could be considered as "metal-ion wires" in which the polyphosphines are the insulating material. To achieve this goal, however, a stereocontrolled synthesis of long-chain polyphosphines is needed. The current approach [2–4], in which stereoregular polyphosphines are isolated by the fractional crystallization or chromatographic separation of statistical

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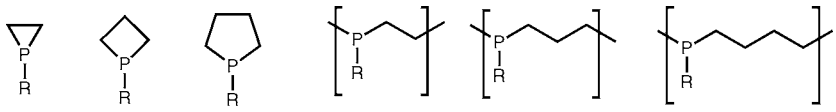
mixtures of diastereomers produced in nonstereoselective syntheses, is a laborious and expensive procedure that becomes increasingly less feasible as the polyphosphine becomes longer (each added chiral phosphorus center doubles the number of possible stereoisomers of a constitutionally unsymmetrical polyphosphine). In the present work, we use ab initio calculations to examine the feasibility of a possible synthetic route to *stereoregular* polyphosphines, with a view to directing future experimental studies.

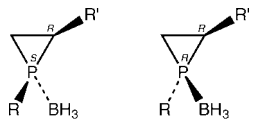
Polyphosphines can be formed by the ring-opening polymerization of phosphiranes (**1**), phosphetanes (**2**), and possibly phospholanes (**3**), which give rise to the polymers **4,** **5**, and **6**, respectively.



1 2 3 4 5 6

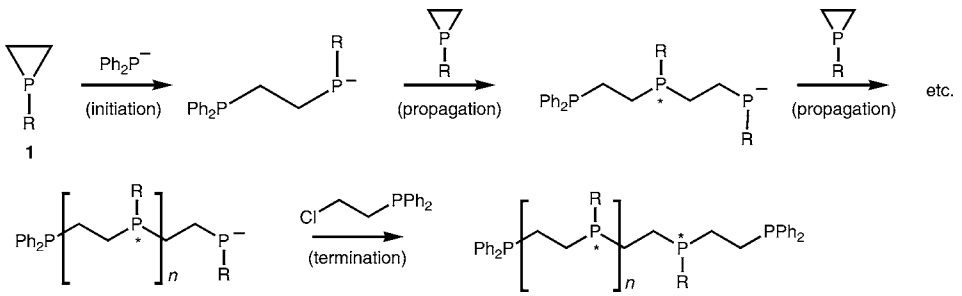
The reactions can be initiated by UV light or heat [5–8], or by ionic initiators [9,10]. Recently, we used theoretical calculations to suggest that a radical ring-opening polymerization process may also be possible for the phosphetanes [11]. Of these processes, the anion-initiated route is likely to provide the most important opportunities for the synthesis of stereoregular polyphosphines and related compounds [12,13]. In this work, we will focus on anionic ring-opening polymerization in which the anion attacks at the ring carbon **α** to phosphorus. The polymerization of **1** by the diphenylphosphide anion is shown in Scheme 1. It can be seen from the scheme that the propagating species is prochiral in that the propagation step creates a chiral center at phosphorus that will be of left- or right-handed configuration with respect to the arrangement of the four different substituents (including the lone pair of electrons) around the tetrahedral phosphorus. The next propagation step produces a second chiral phosphorus center in which the new R group at phosphorus will be on the same or opposite side of the first P-*R* group (with respect to the plane of the phosphorus–carbon chain). Unless there are steric effects operating in the propagating system that cause the R groups to lie on the same side (isotactic polymer) or on alternating sides (syndiotactic polymer) of the phosphorus–carbon chain, polymerization of the phosphiranes **1** will lead to products in which the *P*-substituents are randomly disposed above and below the phosphorus–carbon chain of the polymer (atactic polymer).

A possible route to stereoregular polyphosphines is to fix the configuration at phosphorus by the addition of borane and adding a carbon substituent, as in **7a** or **7b**.

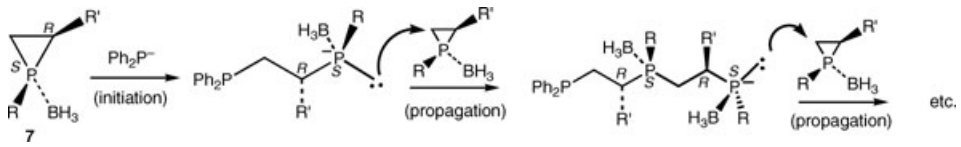


7a 7b

The configurationally pure phosphine–borane center should effectively transmit the chiral information from the carbon, through the phosphorus, to the propagating species. The configuration at phosphorus should be preserved during the propagation step, consistent with established knowledge on the stereoselectivity of alkylation of chiral phosphido–borane groups [14–16]. Deboranation of the stereoregular phosphine–borane polymer can then be effected, following an established procedure [4]. One cycle of the



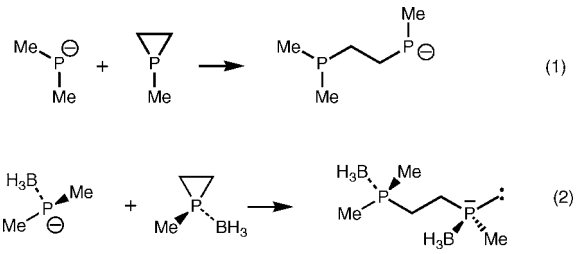
SCHEME 1



SCHEME 2

polymerization of **7** is shown in Scheme 2. For this strategy to be successful, however, it is essential that the formation of the borane adduct (both in the propagating species and on the monomer) does not interfere with the polymerization process itself. The purpose of the present work is to use theoretical calculations to examine whether this is the case.

Ring-opening polymerization of phosphorus heterocycles is also of interest from a theoretical viewpoint. In particular, Wolk et al. [17] noted that the parent PH phosphirane is much more reactive than the corresponding phosphetane, despite their nearly identical stain energies and similar reaction exothermicities. This behavior has also been observed for the parent cyclopropane and cyclobutane molecules and has caused much debate [18–23]. Hoz and coworkers have speculated that the increase in reactivity is due to there being less orbital rehybridization needed to form the transition state in the case of the three-membered ring, compared with the four-membered ring [17,22,23]. This is because the orbitals on the carbon atoms of the three-membered ring are distorted from sp^3 character. It is generally thought that the three-membered phosphiranes, unlike the four- and five-membered counterparts, have a bonding arrangement that it is intermediate between the cyclopropane analogue and an alkene-transition metal type π-complex [24]. Houk and coworkers have instead used molecular orbital arguments to show that odd-numbered rings may have higher reactivities than even-numbered rings because the breaking ring bond has additional antibonding character in the former case [18–20]. We recently noted that the three-membered phosphiranes were unusually reactive to *radical* ring opening when propagation occurs via attack of a *P*-centered propagating radical at a ring carbon, but that the reverse was true when propagation occurs via attack of a *C*-centered propagating radical at phosphorus [11]. On this basis, we suggested that the unusually high reactivity of the three-membered rings was associated with the site of attack, rather than the nature of the breaking bond, although the antibonding character of the breaking P—C bond may still play a role. In the present work, we further probe these unusual reactivity preferences by investigating the effects of ring size on the nucleophilic ring-opening reaction in the presence and absence of the borane group.



SCHEME 3

In what follows, high level ab initio calculations have been used to investigate the feasibility of the anionic ring-opening polymerization of the borane adducts of phosphorus heterocycles. The propagation rate coefficients for the anionic ring opening of methylphosphirane, methylphosphetane, and methylphospholane have been calculated using small models of the propagation step in the presence and absence of the borane group. The propagation steps for the phosphirane are illustrated in Scheme 3. We have also examined stabilities of the borane adducts in order to determine if the borane will dissociate during the reactions (and thereby lead to racemic polymers). In this investigation, we focus on the *P*-methyl adducts, to serve as simple models for subsequent extension to systems containing more experimentally important substituents, such as phenyl or *t*-butyl.

COMPUTATIONAL PROCEDURES

Standard ab initio molecular orbital theory [25] and density functional theory [26] calculations were carried out using GAUSSIAN 98 [27], GAUSSIAN 03 [28], and MOLPRO 2000.6 [29]. Barriers, enthalpies, rates, and equilibrium constants were calculated for the propagation step in the nucleophilic ring-opening polymerization of methylphosphirane (**1**), methylphosphetane (**2**), and methylphospholane (**3**) and of the borane adducts of **1** and **2**. We have also calculated the rates and equilibrium constants for the formation of the borane adducts of **1** and **2**.

The geometries of the reactants, products, and transition structures were optimized at the B3-LYP/6-31+G(d) level of theory, and frequency calculations were also carried out at this level [30]. Since scale factors were not available for the B3-LYP/6-31+G(d) frequencies, those for the B3-LYP/6-31G(d) level [30] were used instead. Significant effort was taken to ensure that the optimized structure was the global (rather than merely the local) minimum energy structure by performing extensive conformational searches at this level. Improved energies were obtained via a modified G3(MP2)-RAD [31] procedure, which we denote as G3(MP2)-RAD(+). G3(MP2)-RAD is a high-level procedure that attempts to reproduce coupled-cluster [CCSD(T)] energies with a large triple zeta basis set using additivity corrections carried out at the RMP2 level. It has been demonstrated to provide accurate absolute values of the heats of formation for a large test set of radical and nonradical species (MAD 4.7 kJ mol^{-1}) [31]. In our modified version of the method, *all* calculations involving the 6-31G(d) basis set were replaced with calculations using the 6-31+G(d) basis set, the extra diffuse functions being included in order to improve the treatment of the anionic species.

The calculated geometries, frequencies, and barriers were then used to evaluate the rate and equilibrium constants for the propagation reactions at 298.15 K via standard transition state theory [32,33]:

$$k(T) = \kappa(T)\frac{k_B T}{h}(c^\circ)^{1-m} e^{(-\Delta G^\ddagger/RT)} = \kappa(T)\frac{k_B T}{h}(c^\circ)^{1-m}\frac{Q_\ddagger}{\prod_{\text{reactants}} Q_i} e^{(-\Delta E^\ddagger/RT)} \quad (1)$$

where $\kappa(T)$ is the tunneling correction factor (assumed to be unity for the present reactions), T is the temperature (298.15 K), k_B is Boltzmann's constant (1.380658×10^{-23} J $molec^{-1}$ K^{-1}), h is Planck's constant ($6.6260755 \times 10^{-34}$ J s), c° is the standard unit of concentration (mol L^{-1}), m is the molecularity of the reaction, R is the universal gas constant (8.3142 J mol^{-1} K^{-1}), $Q_\ddagger$ and Q_i are the molecular partition functions of the transition structure and reactant i, respectively, $\Delta G^\ddagger$ is the Gibbs free energy of activation, and $\Delta E^\ddagger$ the 0 K, zero-point energy corrected energy barrier for the reaction. The value of c° depends on the standard-state concentration assumed in calculating the thermodynamic quantities (and translational partition function). In the present work, these quantities were calculated for 1 mol of an ideal gas at 298.15 K and 1 atm, and hence c° = 0.040876 mol L^{-1}. The partition functions and associated thermodynamic quantities (H and S) were evaluated from the calculated geometries, frequencies, and energies, using standard formulae based on the statistical thermodynamics of an ideal gas, under the rigid-rotor/harmonic oscillator approximation [32,33].

In the case of the ring-opening reactions, standard transition state theory was used, as described above. However, the formation of the adducts was a barrierless process, and so variational transition state theory was required [34]. The minimum energy path for forming the adduct was approximated as a relaxed scan along the forming P···B bond length, as calculated at the B3-LYP/6-31+G(d) level of theory. At each point along the scan, a frequency calculation was performed at the B3-LYP/6-31+G(d) level, and the geometries, energies, and frequencies were then used to calculate Gibbs free energy under the rigid rotor/harmonic oscillator approximation, as described above. The variational transition state was then identified as the geometry having the maximum value of the Gibbs free energy. At this point, the energies were then improved to the G3(MP2)-RAD(+) level of theory, and the resulting value of $\Delta G^\ddagger$ was used to calculate the rate coefficient, via Eq. (1).

A Marcus analysis [35], analogous to that adopted previously [17], was also performed. Under Marcus theory, the barrier is said to depend on the reaction enthalpy (ΔE_0) and the intrinsic barrier (Ea_{int}), as follows:

$$Ea_{\text{Marcus}} = Ea_{\text{int}} + \frac{\Delta E_0}{2} + \frac{\Delta E_0^2}{16 Ea_{\text{int}}} \quad (2)$$

The intrinsic barrier is defined as the barrier of the corresponding reaction in the absence of a thermodynamic driving force, which in the case of the nonboranated species is modeled as

$$Me_2P^- + Me_3P \rightarrow Me_3P + Me_2P^-$$

In the case of the borane adducts, the corresponding reaction is

$$Me_2(BH_3)P^- + Me_3(BH_3)P \rightarrow Me_3(BH_3)P + Me_2(BH_3)P^-$$

For each reaction, the Marcus barrier (Ea_{Marcus}) was calculated at the G3(MP2)-RAD(+) level of theory and compared with the corresponding observed (i.e., ab initio calculated) barrier at the same level. The "additional factor" is defined as the difference between the Marcus barrier and the observed barrier; the "strain contribution" is defined as the enthalpic component of the Marcus barrier (i.e., $\Delta E_0/2 + \Delta E_0^2/16 Ea_{\text{int}}$). It should be noted that the "strain contribution" and "additional factors" are sometimes reported as their absolute values; however, in the present work, we will retain their signs, so as to avoid confusion.

RESULTS AND DISCUSSION

The kinetics and thermodynamics of the model propagation reactions in the anionic ring-opening polymerization of methylphosphirane, methylphosphetane, and methylphospholane are shown in Table 1. The corresponding values for the borane adducts of the monomers are listed in Table 2. In Table 3 are listed the kinetic and thermodynamic parameters for the formation of the phosphirane and phosphetane adducts themselves. The Marcus analysis parameters for anionic ring opening of the three- and four-membered heterocycles and their borane adducts are given in Table 4. Because of the low reactivity of methylphospholane toward anionic ring opening, no calculations were performed on the borane adduct of this monomer. B3-LYP/6-31+G(d) optimized geometries of all species are shown in Figs. 1 and 2, and complete geometries in the form of GAUSSIAN archive entries are available from the author on request. In what follows, we first examine whether a ring-opening polymerization process is feasible for borane adducts; we then discuss the effect of ring size on the kinetics and thermodynamics of the process.

TABLE 1 Kinetics and Thermodynamics (298 K)[a] of the Nucleophilic Ring Opening of Methylphosphirane, Methylphosphetane and Methylphospholane: $MeP(CH_2)_n + Me_2P^- \rightarrow Me_2P(CH_2)_nPMe^-$

	Phosphirane $n = 2$	*Phosphetane* $n = 3$	*Phospholane* $n = 4$
$\Delta H^{\ddagger}$ (kJ mol^{-1})	8.6	33.0	87.0
$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	−131.7	−137.8	−136.3
$\Delta G^{\ddagger}$ (kJ mol^{-1})	47.9	74.1	127.7
k_{298} (L mol^{-1} s^{-1})	6.2×10^{5}	1.6×10^{1}	6.5×10^{-9}
ΔH (kJ mol^{-1})	−123.5	−119.0	−43.5
ΔS (J mol^{-1} K^{-1})	−145.8	−139.1	−125.8
ΔG (kJ mol^{-1})	−80.1	−77.6	−6.0
K (L mol^{-1})	2.6×10^{15}	9.4×10^{14}	2.7×10^{2}

[a]Calculated at the G3(MP2)-RAD(+)//B3-LYP/6-31+G(d) level of theory in conjunction with the harmonic oscillator approximation (see text).

TABLE 2 Kinetics and Thermodynamics (298 K)[a] of the Nucleophilic Ring Opening of the Borane Adducts of Methylphosphirane and Methylphosphetane: $Me_3(H_3B)P(CH_2)_n + Me_2(H_3B)P^- \rightarrow Me_2(H_3B)P(CH_2)_nP(BH_3)Me^-$

	Phosphirane $n = 2$	*Phosphetane* $n = 3$
$\Delta H^{\ddagger}$ (kJ mol^{-1})	19.3	60.1
$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	−114.1	−136.4
$\Delta G^{\ddagger}$ (kJ mol^{-1})	53.3	100.8
k_{298} (L mol^{-1} s^{-1})	6.8×10^{4}	3.4×10^{-4}
ΔH (kJ mol^{-1})	−191.4	−142.6
ΔS (J mol^{-1} K^{-1})	−157.1	−139.5
ΔG (kJ mol^{-1})	−144.6	−101.0
K (L mol^{-1})	5.2×10^{26}	1.2×10^{19}

[a]Calculated at the G3(MP2)-RAD(+)//B3-LYP/6-31+G(d) level of theory in conjunction with the harmonic oscillator approximation (see text).

TABLE 3 Kinetics and Thermodynamics (298 K)[a] of the Formation of Borane Adducts of Methylphosphirane and Methylphosphetane: $MeP(CH_2)_n + BH_3 \rightarrow Me(H_3B)P(CH_2)_n$

	Phosphirane $n = 2$	*Phosphetane* $n = 3$
$\Delta G^{\ddagger}$ (kJ mol^{-1})	21.2	23.5
k (L mol^{-1} s^{-1})	2.9×10^{10}	1.1×10^{10}
ΔG (kJ mol^{-1})	−68.6	−106.8
K (L mol^{-1})	2.6×10^{13}	1.2×10^{20}

[a]Calculated at the G3(MP2)-RAD(+)//B3-LYP/6-31+G(d) level of theory in conjunction with the harmonic oscillator approximation (see text).

Is Polymerization Feasible?

The data in Table 1 suggest that nucleophilic ring-opening polymerization may be possible for both methylphosphirane and methylphosphetane, but not for methylphospholane. The nucleophilic ring-opening reactions of methylphosphirane and methylphosphetane exhibit comparable thermodynamic parameters and lie strongly in favor of the ring-opened products. The rate constant for ring opening of the phosphirane ($k_{298} = 6.2 \times 10^{5}$ L mol^{-1} s^{-1}) suggests that polymerization is likely to proceed on a useful timescale. The kinetic barrier for the phosphetane is much higher, but its rate constant ($k_{298} = 1.6 \times 10^{1}$ L mol^{-1} s^{-1}) is still of a magnitude that will allow polymerization to take place. In contrast, for methylphospholane, the anionic ring opening is only weakly exergonic and its calculated rate constant ($k_{298} = 6.5 \times 10^{9}$ L mol^{-1} s^{-1}) suggests that nucleophilic ring-opening polymerization is not feasible. For this reason, only the three- and four-membered rings were included in the examination of the borane adducts.

The formation of the borane adducts from the free heterocycles and BH_3 displayed equilibrium constants of 2.6×10^{13} L mol^{-1} (phosphirane) and 1.2×10^{20} (phosphetane). The phosphetane–borane adduct was much more stable than its phosphirane counterpart, which is in agreement with experimental precedent: on the one hand, it has been reported that the borane adduct of *t*-butylphosphirane releases borane upon mild heating [36], whereas the borane adducts of various phosphetanes are

TABLE 4 Kinetic and Thermodynamic Parameters (0 K)[a] for Marcus Analysis of Ring Opening of Phosphiranes and Phosphetanes and Their Borane Adducts

	ΔE_0 (kJ mol^{-1})	*Ea* (kJ mol^{-1})	Ea_{Marcus} (kJ mol^{-1})	*Strain contribution* (kJ mol^{-1})	*Additional factor* (kJ mol^{-1})
$Me_3P + Me_2P^-$	0	102.8	–	–	–
$Me_3(H_3B)P + Me_2(H_3B)P^-$	0	127.0	–	–	–
1 $+ Me_2P^-$	−123.9	7.2	50.1	−52.6	−43.0
2 $+ Me_2P^-$	−120.1	31.7	51.5	−51.3	−19.8
1$(BH_3) + Me_2(H_3B)P^-$	−191.4	16.8	49.4	−77.7	−32.6
2$(BH_3) + Me_2(H_3B)P^-$	−144.2	58.0	65.2	−61.9	−7.2

[a]Calculated at the G3(MP2)-RAD(+)//B3-LYP/6-31+G(d) level of theory (see text).

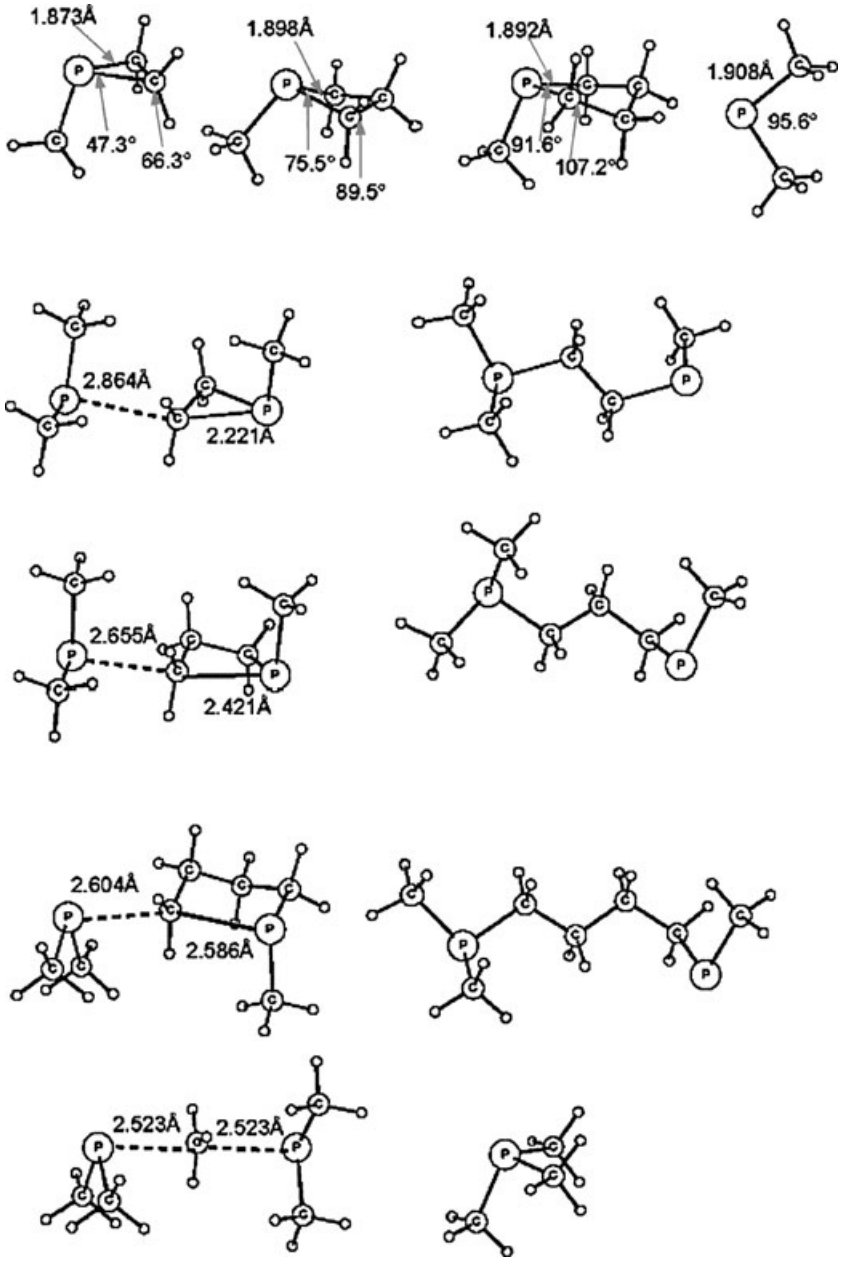


FIGURE 1 B3LYP/6-31+G(d) optimized geometries for the anionic ring opening of methylphosphirane, methylphosphetane and methylphospholane, together with the corresponding unstrained system.

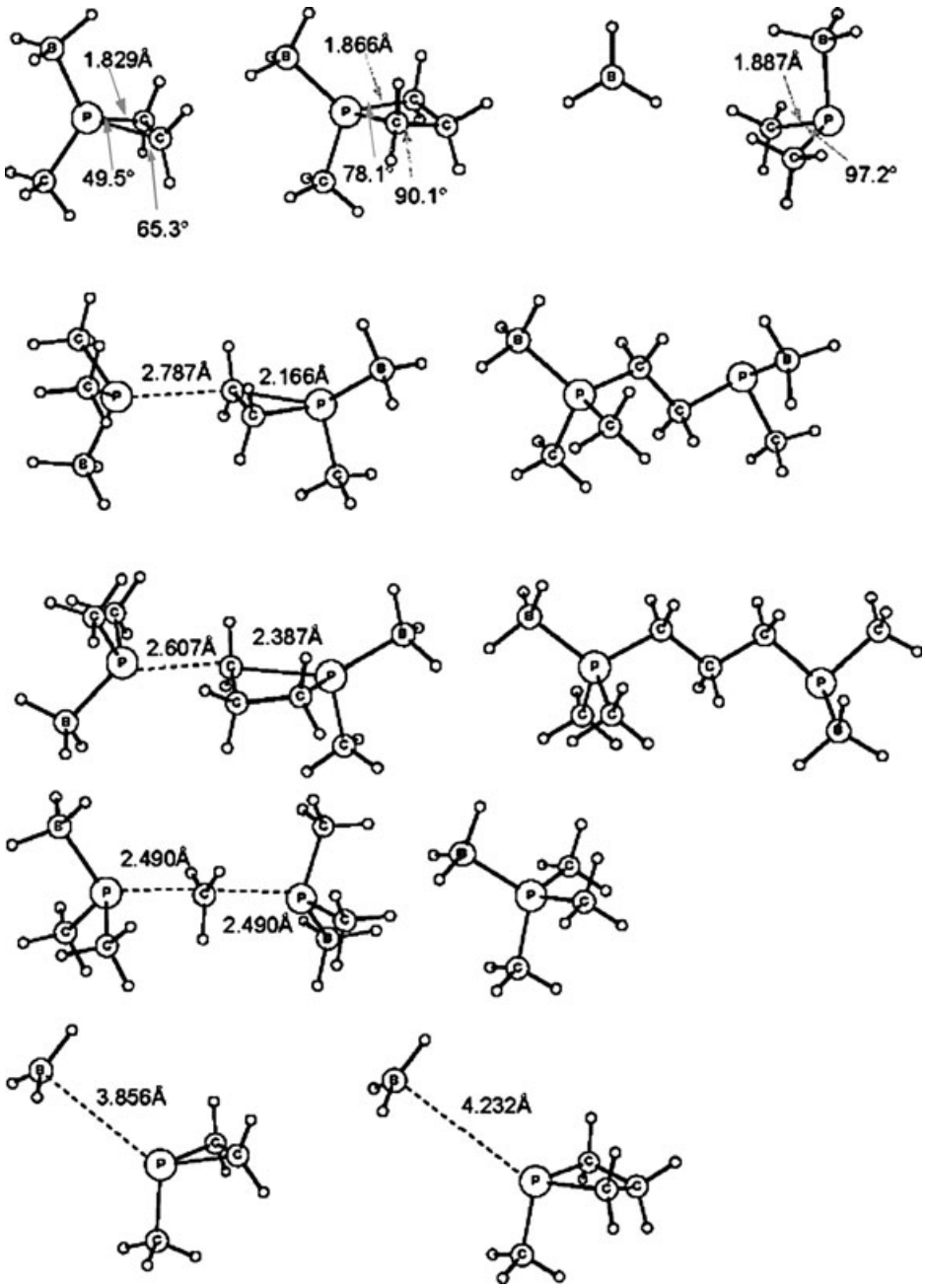


FIGURE 2 B3LYP/6-31+G(d) optimized geometries for the anionic ring opening of the borane adducts of methylphosphirane and methylphosphetane, together with the corresponding unstrained system. The (variationally optimized) transition states for the formation of the borane adducts of methylphosphirane and methylphosphetane are also shown.

useful as synthetic intermediates [37]. The lower stability of the phosphirane adduct, compared with the phosphetane adduct, is consistent with the poor donor capacity of phosphiranes in general, which results from the high s character of the phosphorus lone pair [38].

Nevertheless, the high-thermodynamic stabilities of the borane adducts suggest that they should be isolable species. The rate constants calculated for dissociation of BH_3 from the adducts are $k_{298} = 2.8 \times 10^{-2}$ mol L^{-1} s^{-1} (methylphosphirane) and $k_{298} = 2.3 \times 10^{-9}$ mol L^{-1} s^{-1} (methylphosphetane), which support this prediction, and are in good agreement with the experimental observations on the kinetic stabilities of the three- and four-membered adducts. In the context of a polymerization process, the adducts should be sufficiently kinetically stable, and there

should be no danger of losing the stereoinductive influence of the borane group on the monomer during the propagation step.

The data in Table 2 indicate that a borane group at phosphorus markedly increases the thermodynamic tendency toward anionic ring opening. Nevertheless, the presence of the borane group has little effect on the rate constant for ring opening of the phosphirane ($k_{298} = 6.8 \times 10^4$ L mol^{-1} s^{-1}) and its presence on the phosphetane reduces the rate constant by a factor of 10^4 ($k_{298} = 3.4 \times 10^{-4}$ L mol^{-1} s^{-1}). This result is explored in the following section. For practical purposes, it is likely that only phosphirane–borane adducts will undergo nucleophilic polymerization at a useful rate, provided that attack at the α-carbon is the primary mechanism and that side reactions are not significant. Under these circumstances, we expect that our objective of a stereocontrolled polymerization involving borane adducts will best be served by the three-membered-ring system. Our current investigations are now directed toward the effect of substituents (both at phosphorus and on the ring carbons) on the kinetics and stereochemistry of the propagation reaction.

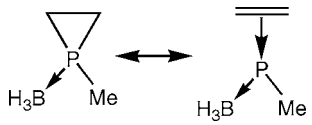
Effect of Ring Size

The variation of the ring-opening activation barrier as a function of ring size for the free heterocycles and their borane adducts has been quantified by the Marcus analysis (Table 4). As expected, the ab initio activation barriers for the ring-opening reactions are all much lower than those calculated for prototypical reactions in which ring strain plays no part. For the free heterocycles, the exothermicity of ring opening is essentially the same for the three- and four-membered rings, which indicates that they experience very similar ring strain. Despite this, however, the activation barrier for ring opening of the phosphirane is much lower than that for the phosphetane, implicating the contribution of an "additional factor." Although substantial for both the phosphirane (-43.0 kJ mol^{-1}) and phosphetane (-19.8 kJ mol^{-1}), the additional factor is significantly larger for the three-membered ring. The results show the same qualitative trend as those calculated previously at the lower HF/6-31+G(d) level by Wolk et al. [17] for the ring opening of parent PH-phosphirane (-73.6 kJ mol^{-1}) and PH-phosphetane (-18.0 kJ mol^{-1}), although, in the case of the phosphiranes, the additional factor is much more significant for the *P*-H substituted ring than the *P*-methyl substituted ring.

The ring-opening reactions of the borane adducts are considerably more exothermic than those of the free heterocycles. This indicates that coordination of the heterocycle to the borane unit induces an increase in ring strain. Inspection of the geometrical parameters of the rings (Figs. 1 and 2) reveals that the C_2 or C_3 unit is drawn closer to the phosphorus atom in the borane adducts, in order to compensate for the removal of electron density by coordination to BH_3. For example, in the phosphirane–borane adduct, the intracyclic P—C bonds are shortened by 0.04 Å and the PCC angles are decreased by 1.0° compared with the free phosphirane.

Despite providing the additional thermodynamic driving force for ring opening, however, the increased strain is not manifested in the rate parameters. Instead, the barrier to ring opening increases on forming the borane adducts. Based on the Marcus analysis (see Table 4), this appears to be the result of both an increase in the intrinsic barrier and a decrease in the "additional factor." The increased intrinsic barrier is likely to reflect the reduced electron density at phosphorus in the attacking $Me_2(H_3B)P^-$ anion, compared with the Me_2P^- anion. However, the decrease in the additional factor, which appears to be of similar magnitude in both the three- and four-membered heterocycles, is more complicated.

Some clues as to the nature of the additional factor are obtained by inspecting the molecular orbitals of the heterocycles and their borane adducts (Fig. 3). For the free phosphirane, the highest occupied molecular orbital (HOMO) consists of substantial C—C π character (as well as *P*-lone pair and P—C σ-bonding components). Coordination of the phosphirane to BH_3 results in an increase in the C—C π-type character, and a reorganization of orbital energies, such that the π-type orbital is lowered to HOMO-1. This indicates that the borane adduct (with its more electron-deficient phosphorus center) is characterized by a greater contribution by the alkene π-complex canonical form to the overall resonance structure (see below).



A relation can be drawn to the experimental work of Mathey [38], who has shown that the $W(CO)_5$ complexes of phosphiranes function as sources of the terminal phosphinidene complexes $RPW(CO)_5$ by elimination of an alkene unit. One may speculate that the elimination of an alkene unit from phosphirane–borane adducts may therefore provide similar useful synthetic opportunities. Previously, a theoretical investigation at the G2(MP2) level has

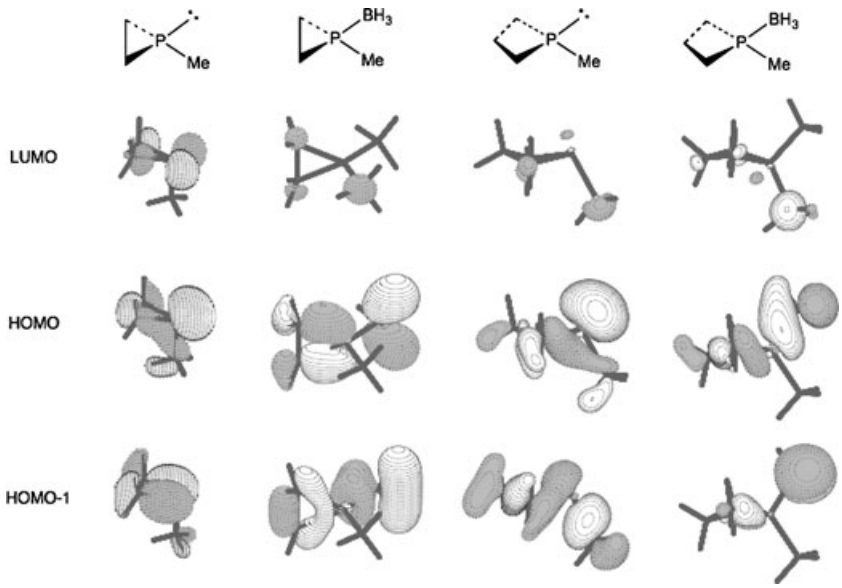


FIGURE 3 Molecular orbitals of methylphosphirane and methylphosphetane and their borane adducts.

suggested that alkene exchange is kinetically disfavored in the parent PH-phosphirane–borane adduct; however, substituted phosphiranes are yet to be examined. Moreover, that study described only a bimolecular mechanism of exchange and did not consider a mechanism involving the initial dissociation of the alkene from the phosphorus center.

The increased sp^2 character at the ring carbons in the phosphirane–borane adduct does not conform well with the proposal by Hoz and coworkers [17,22,23] that an increase in sp^2 character is responsible for a reduction in the additional factor, since the additional factor decreases (rather than increases) in the borane adducts. Likewise, the HOMOs of the free phosphetane and of the phosphetane–borane adduct both suggest a relatively conventional σ-bonding framework, which means that hybridization changes *per se* cannot be invoked as the principal component of the additional factor. An alternative theory is that proposed by Houk et al. [18–20], wherein the size of the additional factor is related to the degree of antibonding character that may be obtained by the orbital of the breaking bond by mixing with unoccupied orbitals of appropriate symmetry. This, in turn, is related to the HOMO–LUMO gap (or, more specifically, to the separation between the bonding and antibonding orbitals of the breaking bond). For the anionic ring opening of the phosphirane, the separation increases by approximately 41.5 kJ mol^{-1} on going to the borane adduct, whereas for the phosphetane, it increases by 96.5 kJ mol^{-1} [39]. The increase in the separation is, of course, consistent with the decrease in additional factor in the borane adducts.

It should be noted, however, that the energy separation between the bonding and antibonding orbitals of the breaking bond is ultimately a common factor in both explanations of the high reactivity of the three-membered rings. When comparing different systems, such as the free and complexed heterocycles, it is difficult to separate one influence (such as the orbital energies) from the other (orbital symmetries). This is further evidenced by our previous finding that, in the radical ring opening of phosphiranes and phosphetanes, the additional factor was more associated with site of attack than with the strength of the breaking bond [11]. It seems that aspects of both explanations may apply in different ways to different ring systems, and it is hoped that our current investigations into substituent effects in the ring-opening reactions will shed further light on the nature of the unusually high reactivity of these small phosphorus heterocycles.

CONCLUSIONS

Our ab initio calculations have suggested that anionic ring-opening polymerization should, in the absence of side-reactions, be feasible for phosphiranes, phosphetanes, and phosphirane–borane adducts, but not for phosphetane–borane adducts, phospholanes, or phospholane–borane adducts. The phosphirane–borane adducts are thus promising synthetic targets for a stereospecific ring-opening polymerization process. A Marcus analysis of the ring-opening reactions of the three- and four-membered heterocycles has revealed that although the coordination of the heterocycles to BH_3 results

in a large increase in strain energy, the effect of this extra exothermicity on the activation barrier for ring-opening is outweighed by the combination of a higher intrinsic barrier and a smaller additional factor. The former is due to the poorer nucleophilicity of the anion, whereas the latter is more complex in origin and reflects the separation between the bonding and antibonding orbitals of the breaking bond.

SUPPLEMENTARY INFORMATION

Information on B3-LYP/6-31+G(d) optimized geometries in the form of GAUSSIAN archive entries are available from the author on request (mcoote@rsc.anu.edu.au).

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