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Exchange and insertion reactions involving borane adducts of phosphirane and phosphirene: a G2(MP2) ab initio investigation

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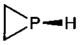
Abstract

Ab initio molecular orbital calculations at the G2(MP2) level have been employed to investigate the insertion and exchange reactions between unsaturated hydrocarbons and borane adducts of three-membered phosphorus heterocycles. Exchange is predicted to be energetically highly preferred over insertion, despite a large thermodynamic driving force for the latter. However, the present results suggest that the barriers for exchange are too high for the reaction to be observed experimentally. The barriers for exchange and insertion are considerably greater than those for the corresponding reactions of the related phosphiranium and phosphirenium ions. The higher barriers for exchange in the borane adducts can be rationalized in terms of the characteristic principal electronic interaction of exchange transition structures. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ab initio; Borane adducts; Exchange; Insertion; Phosphirane; Phosphirene

1. Introduction

In 1967 Wagner et al. reported the first synthesis of phosphirane (**1**) [1]. Since then, the chemistry of phosphirane and substituted phosphiranes has been widely investigated [2]. Unsubstituted phosphiranes are prone to polymerization, but this can be circumvented by coordination of the phosphirane to a Lewis acid, in particular $W(CO)_5$ [2,3]. Several investigations of the chemistry of coordinated phosphiranes have been reported [2,4]. The first synthesis of *phosphirenes* was reported more recently by Marinetti et al. [5]; the phosphirenes were isolated as adducts, for example **2**. The chemistry of such compounds has also been the subject of several investigations [2,6].



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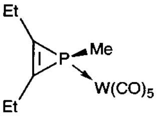

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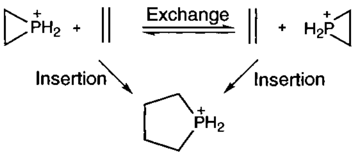
In a recent theoretical study of alkene and alkyne exchange and insertion in phosphiranium and phosphirenium ions (e.g. 1):



(1)

we found that exchange is energetically highly preferred over insertion, despite the large thermodynamic driving force for the latter [7]. These results are consistent with the facile and exclusive experimental observation of exchange in such ions [8]. Experimental data for coordinated phosphiranes and phosphirenes, however, suggest that the situation is somewhat different for these systems. Insertion reactions have been observed in coordinated phosphiranes; for example, intramolecular insertion reactions are observed in coordinated 2-alkenylphosphiranes [9,10], and vinyl ethers insert into coordinated 2-alkoxyphosphiranes [10]. However, exchange continues to be the preferred reaction for cer-

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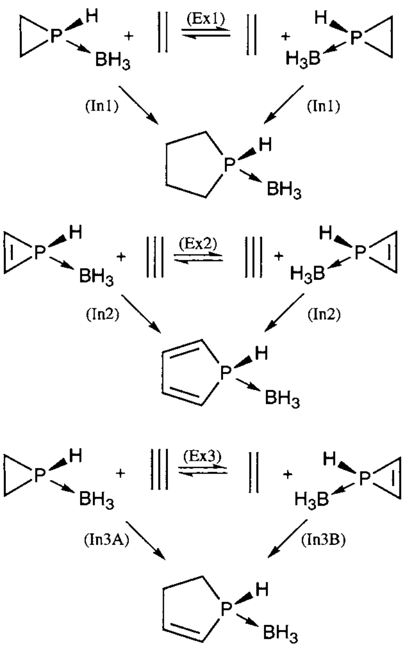
tain coordinated phosphiranes and alkynes [11]. In contrast, only insertion has been observed between coordinated phosphirenes and alkynes, the reaction being found to proceed under mild conditions and in reasonable yields [12]. The comparison between the results for exchange and insertion in ionic three-membered heterocycles [7,8,13,14] and those for the neutral adducts of phosphirane and phosphirene [2,9–12] suggests that the positive charge on the phosphiranium and phosphirenium ions has a significant influence on the energy barriers for exchange and insertion reactions. Accordingly, we have now employed high level ab initio molecular orbital calculations to map the energy barriers for exchange and insertion reactions in neutral borane adducts of phosphirane and phosphirene. As well as being of interest in their own right, the borane adducts were examined as possible cost-effective models for the related tungsten carbonyl compounds, for which exchange and insertion have been reported. Exchange and insertion have yet to be observed in borane adducts of phosphirane and phosphirene, but the present study may provide an indication of their feasibility.

2. Computational methods

Ab initio molecular orbital calculations [15] were performed using a slightly modified form of G2(MP2) theory [16] with the GAUSSIAN 94 [17] and MOLPRO 96 [18] systems of programs. G2(MP2) theory corresponds effectively to single-point energy calculations at the QCISD(T)/6-311 + G(3df,2p) level on MP2(full)/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point vibrational energies (ZPVEs) and a so-called higher level correction. It has been shown to perform well for the calculation of several thermodynamic properties, e.g. proton affinities [19,20], enthalpies of formation [21–23] and atomization energies [16]. G2(MP2) theory was developed by Curtiss et al. as a cost-effective alternative to the computationally more demanding G2 theory in studies of molecules for which G2 theory is not feasible [16]. It is well established that G2 theory predicts several thermochemical properties (including reaction barriers) very accurately [24]. To conform with established practice in recent theoretical investigations of exchange and insertion reactions in related systems [7,13,14], ZPVEs were calculated using MP2(full)/6-31G(d) harmonic vibrational frequencies scaled by 0.9646 [25] rather than the standard scaled HF/6-31G(d) frequencies. We shall refer to this procedure throughout as G2(MP2) for the sake of brevity and the relative energies within the text correspond to 0 K values calculated using this method. The G2(MP2) total energies of all the species investigated in the present work are presented in Table S1 of the supplementary material. The transition structures reported in this work have in each case been confirmed by an intrinsic reaction coordinate analysis and by the calculation of vibrational frequencies (one imaginary frequency).



Scheme 1.

3. Results and discussion

The exchange (Ex1–Ex3) and insertion (In1, In2, In3A and In3B) reactions investigated in the present work are depicted in Scheme 1. The pathways for exchange and insertion are discussed in the following sections, and comparisons are made between the exchange and insertion reactions investigated herein (Table 1) and the corresponding reactions in related phosphiranium and phosphirenium ions investigated previously [7]. Finally, we discuss the

Table 1
Calculated barriers and reaction energies for exchange (Ex) and insertion (In) reactions[a]

Reaction[b]	Barrier	Reaction energy
Ex1	128.0	0.0
Ex2	150.1	0.0
Ex3	143.4	8.7
In1	311.6	−204.3
In2	275.8	−324.5
In3A	293.2	−255.6
In3B1	206.5	−264.3
In3B2	204.4	−264.3

[a] G2(MP2) values in kJ mol^{-1} at 0 K.

[b] See Scheme 1.

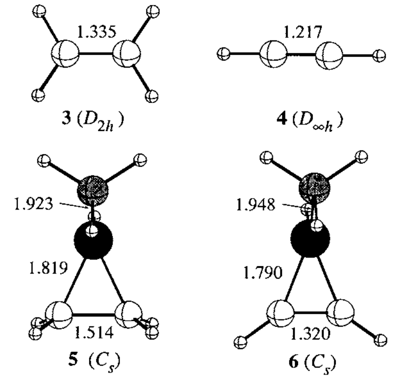


Fig. 1. Selected MP2(full)/6-31G(d) geometrical parameters of reactant molecules involved in the Ex1–Ex3 exchange and In1–In3 insertion reactions. Bond lengths in Å.

feasibility of exchange and insertion in borane adducts of phosphiranes and phosphirenes and also examine in detail the transition structures for exchange. Figs. 1, 2, 4 and 6 depict MP2(full)/6-31G(d) optimized structures, including selected optimized geometric parameters, for all the species involved in the present investigation. Complete geometries in the form of GAUSSIAN archive entries are presented in Table S2 of the supplementary material.

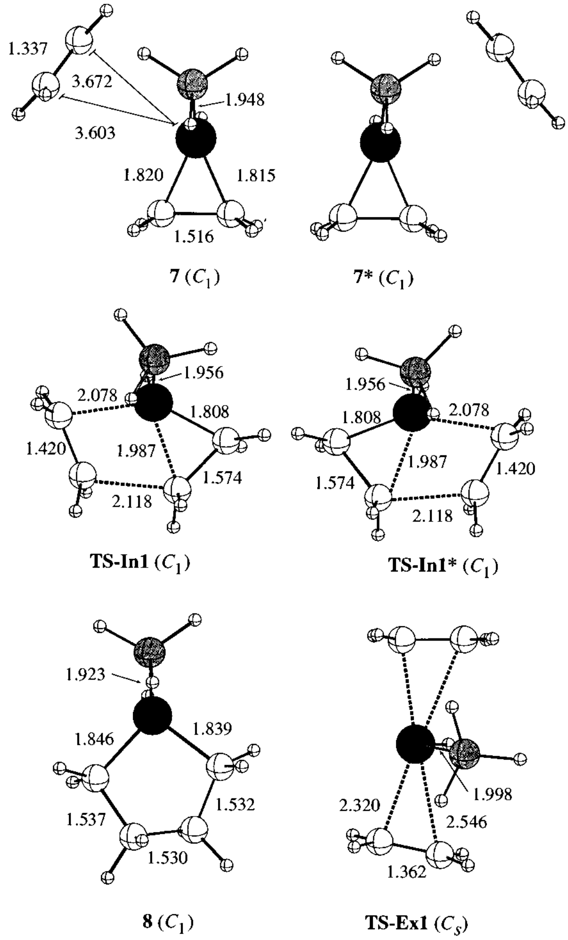


Fig. 2. Selected MP2(full)/6-31G(d) geometrical parameters of species involved in the Ex1 and In1 reactions. Bond lengths in Å.

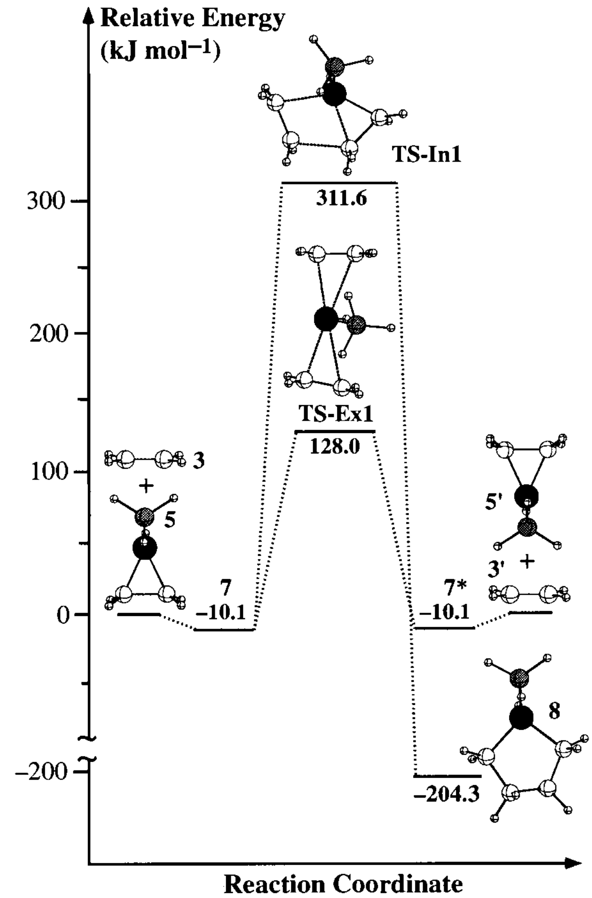


Fig. 3. Schematic energy profiles for the Ex1 and In1 reactions.

3.1. Exchange reactions

In exchange reaction Ex1, the borane adduct of phosphirane **5** reacts with ethylene to form the initial C_1 complex **7**, bound relative to the reactants by 10.1 kJ mol^{-1} (Fig. 3). Reactant complex **7** and product complex **7*** are enantiomers (Fig. 2). The C_s transition structure **TS-Ex1** at 128.0 kJ mol^{-1} connects the reactant and product complexes. There is a symmetry-related pathway which proceeds from reactants to complex **7*** and then to complex **7** via **TS-Ex1**. This is omitted from the schematic energy diagram in Fig. 3 for simplicity.

Reaction Ex2 proceeds from acetylene and the borane adduct of phosphirene **6** to an initial C_s complex **9** (Fig. 5). This complex is bound by 10.4 kJ mol^{-1} relative to the reactants. In this identity reaction, reactant and product complexes are equivalent. They are connected by the C_s transition structure **TS-Ex2** at 150.1 kJ mol^{-1}.

The exchange reaction Ex3 is a non-identity reaction. The coordinated phosphirane **5** and acetylene initially form the C_s complex **12**, which is bound relative to the reactants by 11.2 kJ mol^{-1} (Fig. 7). In the reverse direction, the coordinated phosphirene **6** and ethylene combine to give the C_1 complex **13**, which is bound by 10.1 kJ mol^{-1} relative to these species. Reactant complex **12** and product complex **13** are connected by the C_1 transition structure **TS-Ex3** at 143.4 kJ mol^{-1}. The product complex and the transition structure in this reaction are chiral. Reactant complex **12** and the enantiomer of the product complex **13** are connected by the enantiomer of **TS-Ex3** in a distinct pathway. Again this pathway is omitted from the schematic energy diagram for simplicity (Fig. 7). Reaction Ex3 is endothermic by 8.7 kJ mol^{-1}, thus there is no significant thermodynamic driving force.

3.2. Insertion reactions

In a previous investigation of exchange and insertion reactions in phosphiranium and phosphirenium ions [7], we found the barriers for exchange to be substantially lower than for insertion, despite the large thermodynamic driving force for the latter. This result was consistent with the experimental observation of exclusive exchange. On the other hand, insertion has been observed for phosphiranes and phosphirenes coordinated to W(CO)$_5$. To this end, we have investigated whether the energy barriers for insertion are significantly reduced for phosphiranes and phosphirenes coordinated to borane.

In the reaction In1, ethylene inserts into a C–P bond of the borane adduct of phosphirane **5** to form the C_1 borane adduct of phospholane **8** (Fig. 3). This reaction involves the same initial complex (**7**) as the corresponding exchange reaction. The initial complex and the five-membered heterocycle **8** are connected by the C_1 transition structure **TS-In1**. Theory predicts a barrier of 311.6 kJ mol^{-1} and an exothermicity of 204.3 kJ mol^{-1} for this reaction. The transition structure and the initial complex are chiral. In a distinct pathway, **7*** is connected with a conformer of **8** via **TS-In1*** (the enantiomer of **TS-In1**, Fig. 2). The latter pathway is omitted from the schematic energy diagram in Fig. 3 for simplicity.

Reaction In2 proceeds in a manner very similar to In1. The borane adduct of phosphirene (**6**) and acetylene initially combine to give the C_1 complex **10**, bound by 13.7 kJ mol^{-1} relative to the reactants (Fig. 5). This complex and the C_s symmetric borane adduct of 1*H*-phosphole (**11**) are connected by the C_1 transition structure **TS-In2**. The insertion of acetylene into a C–P bond of **6** requires a high barrier (275.8 kJ mol^{-1}), despite the significant exothermicity of 324.5 kJ mol^{-1}. Again the initial complex and the transition structure are chiral. As for reaction In1, there is a distinct pathway that connects the enantiomer of the initial complex with the five-membered heterocycle via the enantiomer of **TS-In2**. This is omitted in Figs. 4 and 5 for simplicity.

Reaction In3A represents insertion of acetylene into a C–P bond of the coordinated phosphirane **5** to form the C_1 five-membered heterocyclic borane adduct **15** (Fig. 7). Initially the reactants combine to give the C_1 complex **14**, which is bound by 11.7 kJ mol^{-1} relative to the reactants. This complex and the five-membered heterocycle **15** are connected by the C_1 transition structure **TS-In3A**. Here also, the barrier is high (293.2 kJ mol^{-1}) despite the large exothermicity (255.6 kJ mol^{-1}). As for reactions In1 and In2, the initial complex and the transition structure are chiral, although in this case the five-membered heterocycle is also chiral. In a pathway that is stereochemically related to the one in Fig. 7 (not depicted), **TS-In3A*** connects the complex **14*** with the heterocycle **15***.

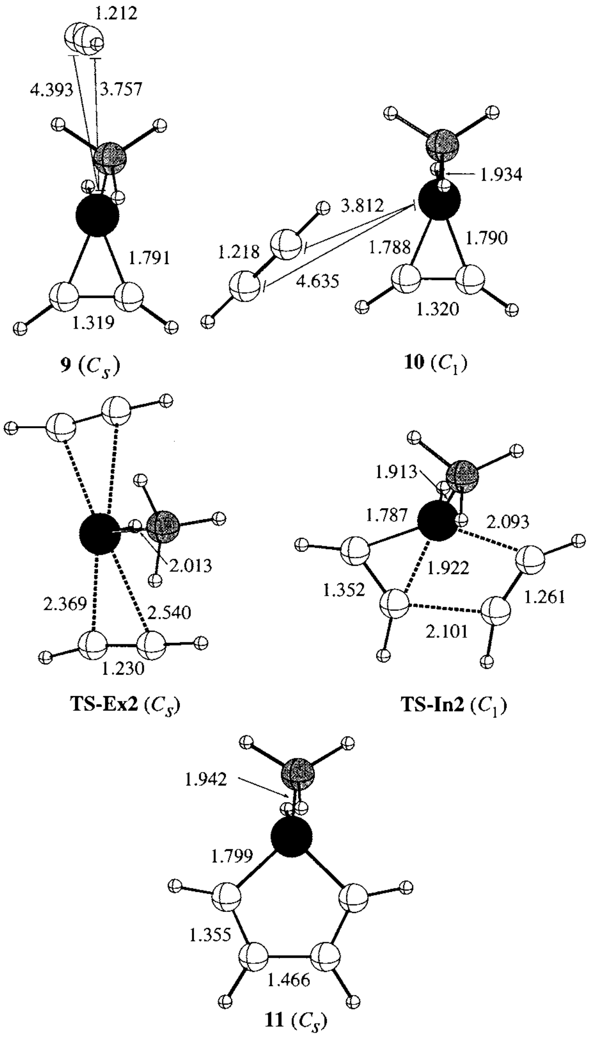


Fig. 4. Selected MP2(full)/6-31G(d) geometrical parameters of species involved in the In2 and Ex2 reactions. Bond lengths in Å.

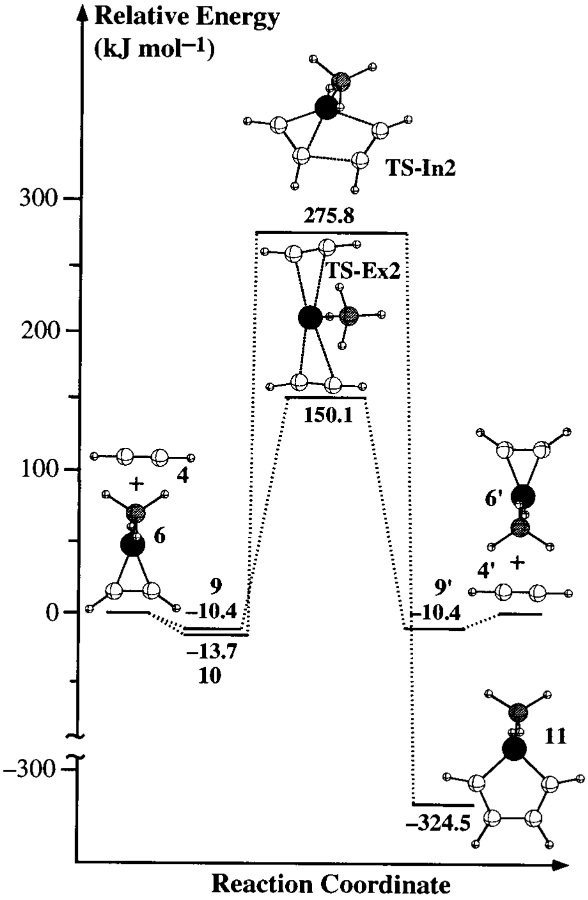


Fig. 5. Schematic energy profiles for the Ex2 and In2 reactions.

In reaction In3B, the five-membered heterocycle **15** is formed upon insertion of ethylene into the coordinated phosphirene **6**, via either of the C_1 transition structures **TS-In3B1** or **TS-In3B2**. The two transition structures, in which the borane group is respectively syn or anti to the incoming ethylene molecule (Fig. 6), are diastereomers. **TS-In3B1** lies slightly higher in energy and connects the initial C_1 complex **13** with the five-membered heterocycle. **TS-In3B2** connects the C_1 complex **16**, bound by 10.9 kJ mol^{-1} relative to ethylene plus **6**, with the five-membered heterocycle. The reaction exothermicity of In3B is 264.3 kJ mol^{-1} and the energy barriers are 206.5 kJ mol^{-1} and 204.4 kJ mol^{-1} when proceeding via **TS-In3B1** or **TS-In3B2**, respectively. For each of the pathways represented by **TS-In3B1** and **TS-In3B2**, there is a stereochemically related pathway similar to that described for In3A.

3.3. Insertion versus exchange

The results for the exchange and insertion barriers reported in the present work and in an earlier investigation of exchange and insertion in phosphiranium and phosphirenium ions [7] show several common features. For all systems investigated, the exchange barrier is predicted to be lower, despite the significant thermodynamic driving force for insertion. The barriers for the exchange and insertion reactions increase in the same order for the ionic and neutral systems: Insertion becomes energetically more expensive in the order In3B2 < In3B1 < In2 < In3A < In1 for the present neutral systems and for the analogous ionic systems (In3B1 and In3B2 correspond to a single reaction for the latter), whereas the barriers for exchange increase in the order Ex1 < Ex3 < Ex2. All the calculated barriers are higher in the neutral systems, however, the increase being most pronounced for exchange. Thus, the gaps between the insertion and exchange barriers are significantly smaller for the coordinated phosphiranes and phosphirenes. For the present systems the gaps are: 183.6 kJ mol^{-1} (In1–Ex1), 125.7 kJ mol^{-1} (In2–Ex2), 149.8 kJ mol^{-1} (In3A–Ex3), 71.8 kJ mol^{-1} (In3B1–Ex3) and 69.7 kJ mol^{-1} (In3B2–Ex3), whereas the corresponding values for the ionic systems are 230.2 kJ mol^{-1}, 177.0 kJ mol^{-1}, 201.4 kJ mol^{-1} and 186.9 kJ mol^{-1}. This indicates that the barriers for exchange in three-membered phosphorus heterocycles are considerably more sensitive to the extent of positive charge on phosphorus than are the barriers for insertion. Also it indicates that insertion is more likely to be observed in competition with exchange in reactions of neutral adducts of phosphirane and phosphirene than in the ionic systems, consistent with the experimental observation of insertion in certain pentacarbonyltungsten(0) phosphirane and phosphirene adducts [9,10,12].

3.4. Feasibility of exchange in borane complexes of phosphirane and phosphirene

The second-order rate constants for the reactions investigated herein can be roughly estimated at 298 K using transition state theory [26–28]. The estimated rate constants for exchange lie in the range from 3×10^{-16} to 4×10^{-19} M s^{-1}, whereas the insertion rate constants lie between 3×10^{-30} and 2×10^{-49} M s^{-1}. These small values suggest that borane adducts do not undergo exchange or insertion in the gas phase on a realistic time frame.

In the condensed phase, insertion and exchange reactions have been observed for certain pentacarbonyltungsten(0) phosphorane and phosphorene adducts [2,9–12]. Thus, it would seem that the borane adducts, although of interest in their own right, are not suitable models for the related transition-metal adducts. The alternative possibility of solvent effects of the magnitude necessary for the reactions to be observed is unlikely.

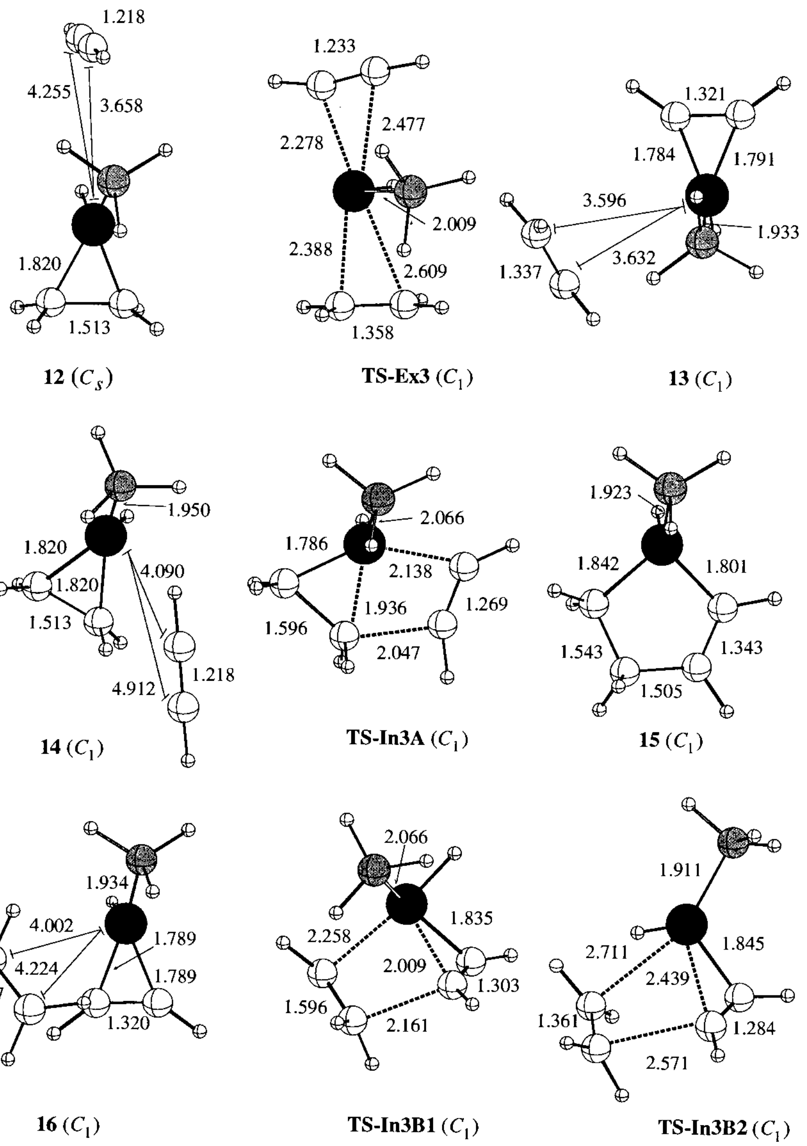


Fig. 6. Selected MP2(full)/6-31G(d) geometrical parameters of species involved in the In3A and In3B insertion reactions and the Ex3 exchange reaction. Bond lengths in Å.

3.5. Transition structures for exchange in ionic and neutral three-membered phosphorus heterocycles

The exchange transition structures reported herein are characterized by the rotation of the $PHBH_3$ moiety to an orientation almost parallel to the C–C bond, accompanied by the approach of the reactant hydrocarbon and elimination of the original hydrocarbon moiety from the ring (Figs. 2, 4 and 6). Exchange in borane adducts of phosphiranes and phosphirenes proceeds in a stereochemically defined manner which is dictated by the transition structure. Thus the reaction is stereospecific [29], as was the case for exchange in the related phosphiranium and phosphirenium systems investigated previously [7].

The hydrocarbon–$PHBH_3$–hydrocarbon arrangement found in the present exchange transition structures (Figs. 2, 4 and 6) is identical to the arrangement of hydrocarbon–ionic moiety–hydrocarbon found in investigations of exchange reactions in related ionic three-membered heterocycles [7,13,14]. This arrangement can be rationalized in terms of two interactions [14]: a principal interaction that closely resembles the triple-ion arrangement (e.g. $X^{-}\cdots CH_3^{+}\cdots X^{-}$) found in S_N2 transition structures [30] and a secondary backbonding interaction (Fig. 8).

The energy barriers for exchange in the present borane adducts are considerably higher than the barriers for exchange in the corresponding phosphiranium and phosphirenium ions. This observation can be rationalized in terms of a reduction in the principal interaction (the electron donation from the filled π-orbitals on the

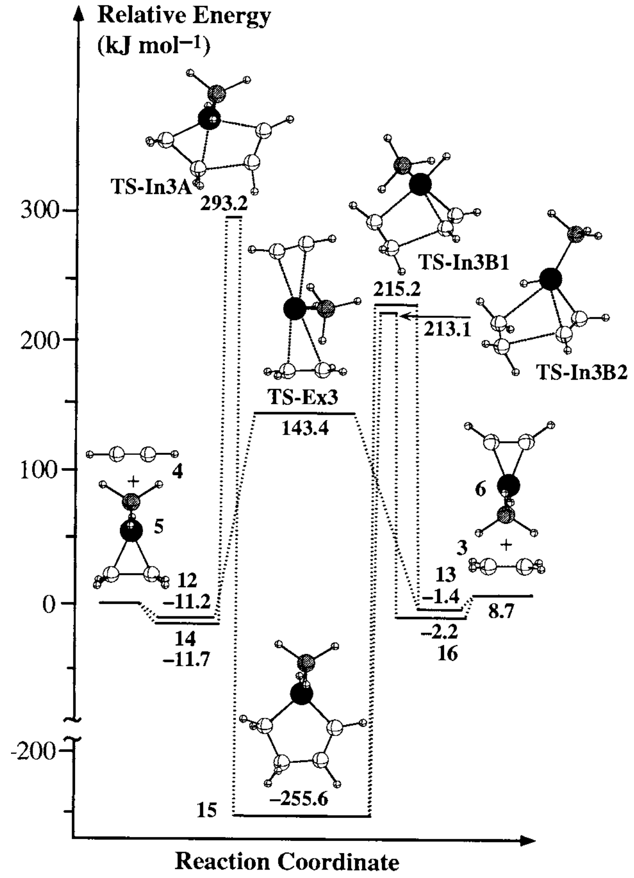


Fig. 7. Schematic energy profiles for the Ex3, In3A and In3B reactions.

two hydrocarbons to the empty p-orbital on the phosphorus atom) in the neutral transition structure. Since the slightly polarized $PHBH_3$ moiety is a less efficient acceptor than the positively charged PH_2^+ moiety (i.e. the energy of the vacant p-orbital lies higher in the neutral system), the neutral exchange transition structures are less strongly bound.

Exchange in uncoordinated phosphiranes and phosphirenes analogous to Ex1–Ex3 is found to require barriers of 144.8, 162.2 and 164.3 kJ mol^{-1}, respectively [31]. The results reported in the present paper suggest that such exchange is facilitated upon coordination to a Lewis acid, and that it becomes even more favorable as the amount of positive charge on phosphorus is increased.

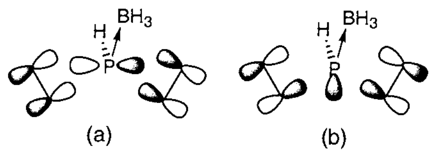


Fig. 8. The two characteristic electronic interactions in the exchange transition structures: (a) donation from filled π-orbitals to an empty p-orbital and (b) donation from a filled lone pair to empty π*-orbitals.

4. Concluding remarks

In this investigation of exchange and insertion reactions in borane adducts of phosphirane and phosphirene, we have found exchange to be strongly preferred over insertion, despite a considerable thermodynamic driving force for the latter. Nevertheless, exchange appears to be too slow to be feasible in the gas phase on a realistic time frame. The fact that exchange (and insertion) have been observed in certain pentacarbonyltungsten(0) adducts of phosphirane and phosphirene in the condensed phase appears to indicate that the borane adducts are not suitable models for the transition metal adducts.

Comparisons between the results for the borane adducts and the results for the corresponding reactions involving phosphiranium and phosphirenium ions reveal that insertion and exchange have higher barriers in the neutral systems, with the difference being larger for exchange. Thus, the gap between the barriers for exchange and insertion is reduced significantly for the borane adducts. This suggests that the barriers for exchange in three-membered phosphorus heterocycles are considerably more sensitive to the extent of positive charge on phosphorus than are the barriers for insertion, and it is consistent with the experimental observation of insertion in some pentacarbonyltungsten(0) phosphirane and phosphirene adducts.

The electronic characteristics of the exchange transition structures are closely similar to those that we have found in previous investigations of exchange in ionic three-membered heterocycles. The primary interaction between an empty p-orbital on the phosphorus atom and the filled π-orbitals of the two hydrocarbons involved in the exchange is weaker in the borane adducts, leading to higher exchange barriers for reactions involving the borane adducts.

5. Supplementary material

G2(MP2) total energies (Table S1) and Gaussian archive entries for the MP2(full)/6-31G(d) optimized geometries (Table S2) are available. Ordering information is given on any masthead page.

Acknowledgements

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