Inorg. Chem. **1999,** *38,* 6049−6054 **6049**

A G2 Ab Initio Investigation of Ligand-Exchange Reactions Involving Mono- and Bis-Adducts of the Phosphenium Ion

Theis I. Sølling,[†] S. Bruce Wild, and Leo Radom*

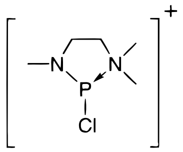
Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

Received September 8, 1999

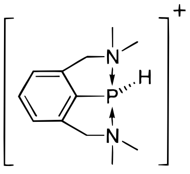
Ab initio calculations at the G2 level have been employed to investigate the ligand-exchange reactions between mono-adducts of the phosphenium ion (e.g., $[H_3N{-}PH_2]^+$) and simple first- or second-row Lewis bases (e.g., NH_3). We have found virtually all the reactions to proceed without an intermediate barrier via a bis-adduct of the phosphenium ion with two Lewis bases (e.g., $[H_3N{-}PH_2{-}NH_3]^+$). The ligand-exchange reactions are predicted to be experimentally feasible and the bis-adducts of the phosphenium ion to be experimentally observable in appropriate cases. The energetics of the ligand-exchange reactions may be rationalized using qualitative orbital interaction arguments in terms of the electronegativity of the ligand in the mono-adducts and the donor ability of the reacting Lewis base. Comparisons with previous investigations of corresponding ligand-exchange reactions involving π-ligands reveal that the electronic characteristics of the bis-adduct resemble those of the transition structures for π-ligand exchange.

Introduction

The phosphenium ion (PH_2^+) is a highly reactive species,[1] and substantial attention, theoretical[2] as well as experimental,[1] has been devoted to the investigation of factors that influence the stabilities of such ions. Since the pioneering work by Fleming et al.[3] in which the first stabilized phosphenium ion was spectroscopically characterized, it has been established that π-donor substituents on the phosphorus atom strongly stabilize phosphenium ions.[1,2] Coordination of Lewis bases to the positively charged phosphorus atom defines an alternative approach to stabilizing phosphenium ions, and experimental evidence supports the existence of mono- and bis-adducts of phosphenium ions with Lewis bases formed in this manner (e.g., **1** and **2**).[4,5] In most cases, the phosphenium ion in question is coordinated in an intramolecular fashion, as in **1** and **2**. However, experimental results that can be interpreted in terms of a phosphenium ion coordinated by two distinct donors have been reported.[6] The adducts $[X_2P(PMe_3)_2]^+X^-$ (where X = Cl or Br) have been isolated at −20 °C.[6]



1



2

We have recently carried out studies of reactions that can be formulated as the exchange of a π-ligand coordinated to a phosphenium ion for another π-ligand.[7,8] We found such π-ligand-exchange reactions to be low-energy processes, which proceed from reactants to products via transition structures that resemble phosphenium ions coordinated by two π-ligands.[8] The experimental observation of adducts between phosphenium ions and Lewis bases[4,5] could be taken to indicate that ligand-exchange reactions between mono-adducts of phosphenium ions and Lewis bases may proceed via intermediate bis-adducts[5] and, thus, differ from the corresponding reactions involving π-donors.[8] In the present work, we have employed high-level ab initio calculations to study such exchange reactions for a broad range of mono-adducts and Lewis bases. We make predictions regarding the feasibility of such reactions and the stabilities of the associated bis-adducts of the phosphenium ion.

Computational Methods

Ab initio molecular orbital calculations[9] were carried out using a slightly modified form of G2 theory[10] with the GAUSSIAN 94[11] and

---

[†] Present address: Department of Chemistry, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark.

(1) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367−382.

(2) See for example: (a) Hutchins, L. D.; Paine, R. T.; Campana, C. F. *J. Am. Chem. Soc.* **1980**, *102*, 4521−4523. (b) Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789−797. (c) Zhang, C.-J.; Zhan, C.-G.; Huang, T.-B. *J. Mol. Struct.: THEOCHEM* **1995**, *357*, 9−18.

(3) Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534−2540.

(4) (a) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046−3050. (b) Bartsch, R.; Sanchez, M.; Wolf, R. *Phosphorus Sulfur* **1988**, *35*, 89−92. (c) Becker, W.; Schmutzler, R. *Phosphorus Sulfur* **1988**, *36*, 231−239. (d) Becker, W.; Schomburg, D.; Schmutzler, R. *Phosphorus, Sulfur Silicon* **1989**, *42*, 21−35. (e) Lamandé, L.; Munoz, A. *Tetrahedron Lett.* **1991**, *32*, 75−78. (f) Reed, R.; Réau, R. Dahan, F.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 339−401. (g) Sanchez, M.; Cosledan, F.; Sotiropoulos, J. M.; Lamandé, L.; Drapailo, A. B.; Gudima, A. O.; Romanenko, V. D. *Tetrahedron Lett.* **1995**, *36*, 2085−2088.

(5) (a) Balitzky, Y. V.; Pipko, S. E.; Sinitsa, A. D.; Chernega, A. N.; Gololobov, Y. G. *Phosphorus, Sulfur Silicon* **1993**, *75*, 167−170. (b) Pipko, S. E.; Balitzky, Y. V.; Sinitsa, A. D.; Gololobov, Y. G. *Tetrahedron Lett.* **1994**, *35*, 165−168. (c) Carré, F.; Chuit, C.; Corriu, R. J. P.; Monforte, P.; Nayyar, N. K. *J. Organomet. Chem.* **1995**, *499*, 147−154. (d) Carré, F.; Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reyé, C. *J. Organomet. Chem.* **1997**, *529*, 59−68. (e) Bezombes, J.-P.; Carré, F.; Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reyé, C. *J. Organomet. Chem.* **1997**, *535*, 81−90.

(6) Summers, J. C.; Sisler, H. H. *Inorg. Chem.* **1970**, *9*, 862−869.

(7) Hockless, D. C. R.; McDonald, M. A.; Pabel, M.; Wild, S. B. *J. Organomet. Chem.* **1997**, *529*, 189−196.

(8) Sølling, T. I.; McDonald, M. A.; Wild, S. B.; Radom, L. *J. Am. Chem. Soc.* **1998**, *120*, 7063−7068.

10.1021/ic991080e CCC: $18.00

MOLPRO 96[12] program packages. The aim of G2 theory is to approximate QCISD(T)/6-311+G(3df,2p) energies for MP2(full)/6-31G(d) optimized geometries, with the incorporation of scaled HF/6-31G(d) zero-point vibrational energies (ZPVEs) and a so-called higher level correction. G2 theory has been shown to perform well in the calculation of thermodynamic properties such as atomization energies, heats of formation, and reaction barriers.[10,13] In the present study, we have used a slightly modified version of G2 theory in which the ZPVEs were calculated using MP2(full)/6-31G(d) harmonic vibrational frequencies scaled by 0.9646.[14] This approach was used in order to be consistent with several recent studies of ligand-exchange reactions involving the phosphenium ion or related isoelectronic species.[8,15] This modified version of G2 theory is formally referred to as G2-(ZPE=MP2),[16] but we use the G2 label here in the interests of brevity. The transition structures reported in the present work have been confirmed in each case by the calculation of vibrational frequencies (one imaginary frequency) and an intrinsic reaction coordinate analysis. Calculated G2 total energies and GAUSSIAN archive entries for the MP2(full)/6-31G(d) optimized geometries are presented in Tables S1 and S2 of the Supporting Information. Relative energies within the text correspond to G2 values at 0 K.

Results and Discussion

For virtually all the systems that we have studied, the exchange reactions involving mono-adducts of the phosphenium ion ($[X-PH_2]^+$) and Lewis bases (Y) follow the pattern shown in Figure 1. The reactant ion ($[X-PH_2]^+$) combines with the neutral donor molecule (Y) to form, without a barrier, a bis-adduct of the phosphenium ion ($[X-PH_2-Y]^+$). This ion dissociates without a reverse barrier to give the product donor molecule (X) and the product mono-adduct ($[H_2P-Y]^+$). Thus, there is no intermediate barrier in these reactions

A possible complicating reaction that the mono-adduct $[X-PH_2]^+$ might undergo is unimolecular rearrangement to a more stable isomeric ion. For example, $[H_2O-PH_2]^+$ could perhaps rearrange to $[HO-PH_3]^+$. We have examined this possibility through G2 calculations and find that, despite an exothermicity of 85.6 kJ mol^{-1}, the rearrangement is impeded by a large barrier of 195.0 kJ mol^{-1}. Such reactions are therefore not likely to play a significant role in the present study.

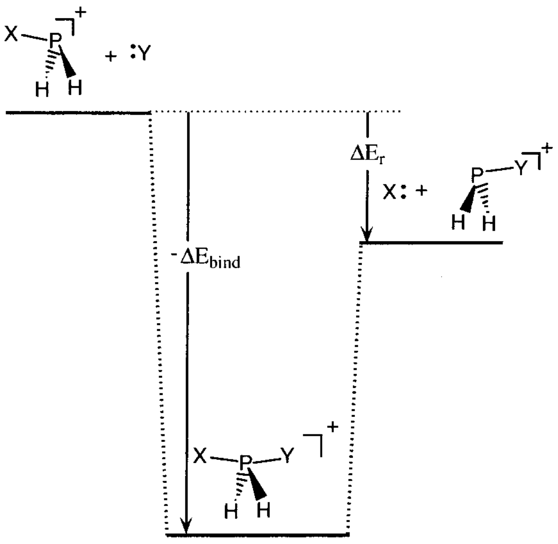
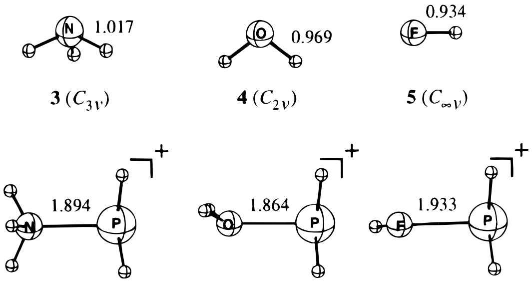


Figure 1. Generalized energy profile for the $[X-PH_2]^+ + Y \rightarrow X + [PH_2-Y]^+$ exchange reactions. X and Y are chosen from first- and second-row donors (NH_3, H_2O, HF, PH_3, H_2S, or HCl).



3 (C_{3v}) **4** (C_{2v}) **5** ($C_{\infty v}$)

6 (C_s) **7** (C_1) **8** (C_s)

Figure 2. Optimized (MP2(full)/6-31G(d)) geometries of first-row Lewis bases and of the mono-adducts of the phosphenium ion with first-row Lewis bases. Bond lengths are in Å.

In the following sections, we discuss in detail the energetics of the exchange reactions as well as the properties of the bis-adducts of the phosphenium ion, and we present a qualitative rationalization of the results. Also, we shall draw a parallel with the exchange reactions between three-membered ionic heterocycles and unsaturated hydrocarbons[8,15] and discuss possible experimental consequences of the present results.

Exchange Reactions Involving First-Row Donors. Optimized structures of the species involved in the possible exchange reactions between ammonia, water, or hydrogen fluoride (Y) and the adducts of the phosphenium ion with any of these molecules ($[X-PH_2]^+$) are shown in Figures 2 and 3. The reaction energies (ΔE_r) and the binding energies (ΔE_{bind}) of the associated bis-adducts (Figure 3) are presented in Table 1.

When a particular mono-adduct ($[X-PH_2]^+$) reacts with first-row donors (Y), the binding energies of the associated bis-adducts decrease with the electronegativity of the donor atom, i.e., in the order $[X-PH_2-NH_3]^+ > [X-PH_2-OH_2]^+ > [X-PH_2-FH]^+$ (Table 1). In contrast, when a particular donor (Y) reacts with an adduct between the phosphenium ion and either ammonia, water, or hydrogen fluoride, the most strongly bound bis-adduct is formed from the mono-adduct with the most electronegative ligand. Thus, the binding energies, which lie between 28.3 and 265.4 kJ mol^{-1}, increase in the order $[H_3N-PH_2-Y]^+ < [H_2O-PH_2-Y]^+ < [HF-PH_2-Y]^+$. Consistent with the above discussion, the most strongly bound bis-adduct is formed from $[HF-PH_2]^+$ (**8**) and ammonia, whereas $[H_3N-$

---

(9) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(10) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221−7230.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*; Gaussian Inc.: Pittsburgh, PA, 1995.

(12) MOLPRO 96 is a package of ab initioprograms written by H. J. Werner and P. J. Knowles with contributions from J. Almlof, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hempel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, and R. Lindh.

(13) For recent reviews on G2 theory, see: (a) Curtiss, L. A.; Raghavachari, K. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995. (b) Raghavachari, K.; Curtiss, L. A. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995. (c) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063−1079.

(14) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345−350.

(15) (a) Sølling, T. I.; Wild, S. B.; Radom, L. *Chem. Eur. J.* **1999**, *5*, 509. (b) Sølling, T. I.; Radom, L. *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 263−270. (c) Sølling, T. I.; Wild, S. B.; Radom, L. *J. Organomet. Chem.* **1999**, *580*, 320−327.

(16) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1995**, *103*, 4192−4200.

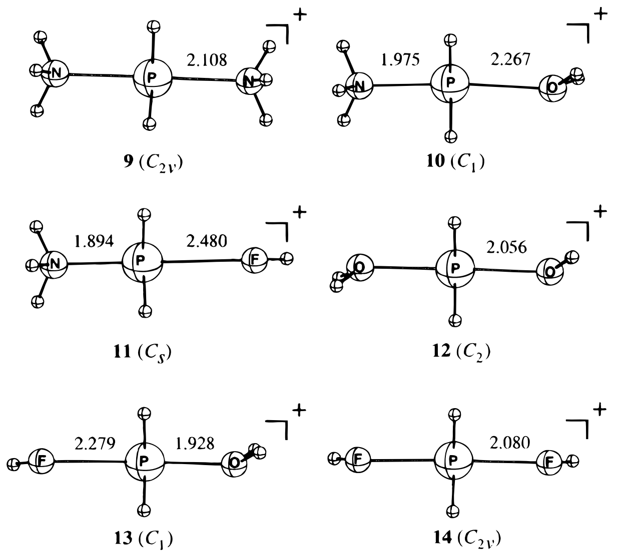


Figure 3. Optimized (MP2(full)/6-31G(d)) geometries of the bis-adducts of the phosphenium ion with two first-row Lewis bases. Bond lengths are in Å.

Table 1. Reaction Energies (ΔE_r) for Exchange Processes Involving First-Row Donors and Binding Energies (ΔE_{bind}) of the Associated Bis-Adducts of the Phosphenium Ion[a]

ion ($[X-PH_2]^+$)	Y	ΔE_{bind}[b]	ΔE_r[b]
$[H_3N-PH_2]^+$ (**6**)	NH_3	99.4	0.0
	H_2O	55.9	117.3
	HF	28.3	237.1
$[H_2O-PH_2]^+$ (**7**)	NH_3	173.2	−117.3
	H_2O	92.3	0.0
	HF	38.3	119.8
$[HF-PH_2]^+$ (**8**)	NH_3	265.4	−237.1
	H_2O	158.1	−119.8
	HF	64.9	0.0

[a] G2 values in kJ mol^{-1} at 0 K. [b] See Figure 1.

$PH_2]^+$ (**6**) and hydrogen fluoride combine to give the most weakly bound bis-adduct of the phosphenium ion.

The reaction energies for exchange have values up to 237.1 kJ mol^{-1} in magnitude. The formation of a mono-adduct from $[X-PH_2]^+$ and ammonia, water, or hydrogen fluoride becomes energetically more demanding in the order $NH_3 < H_2O < HF$ (Table 1). This result reflects the fact that the product mono-adduct becomes less strongly bound as the donor ability of the new ligand decreases.

Exchange Reactions Involving Second-Row Donors. The structures of the species involved in the possible exchange reactions between second-row donors and the mono-adducts $[H_3P-PH_2]^+$, $[H_2S-PH_2]^+$, or $[HCl-PH_2]^+$ are depicted in Figures 4 and 5. The calculated reaction energies and binding energies of the associated bis-adducts of the phosphenium ion with second-row donors are presented in Table 2.

The trends in Table 2 parallel those for the exchange reactions involving first-row donors. Thus, the most strongly bound bis-adduct is formed from $[HCl-PH_2]^+$ (**20**) and phosphine (199.8 kJ mol^{-1}), whereas the most weakly bound bis-adduct is formed from $[H_3P-PH_2]^+$ (**18**) and hydrogen chloride (18.3 kJ mol^{-1}).

The reaction energies have values up to 181.4 kJ mol^{-1} in magnitude, and the trends for the reaction energies in Table 2 parallel those for the exchange reactions involving first-row donors.

The only formal exception to the qualitative form of the general potential energy diagram depicted in Figure 1 is found for the identity reaction between phosphine and the phosphenium ion coordinated by phosphine, which has a double-well rather than a single-well potential energy surface. The reactants $[H_3P-PH_2]^+$ (**18**) and PH_3 (**15**) combine to form the bis-adduct of the phosphenium ion with two phosphine molecules $[H_3P-PH_2-PH_3]^+$ (**21**) (Figure 5), in which the P−P bond lengths are not equal. However, the symmetric C_{2v} transition structure **TS: 21 → 21′** lies just 1.0 kJ mol^{-1} higher in energy than **21**.

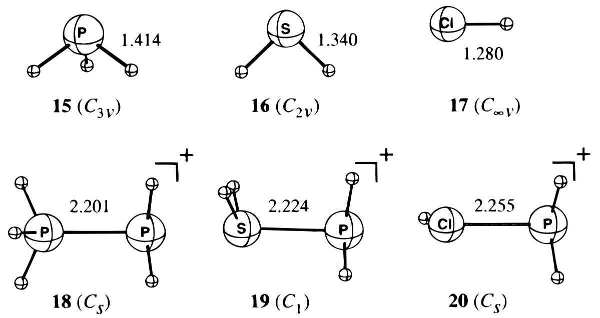


Figure 4. Optimized (MP2(full)/6-31G(d)) geometries of second-row Lewis bases and of the mono-adducts of the phosphenium ion with second-row Lewis bases. Bond lengths are in Å.

Table 2. Reaction Energies (ΔE_r) for Exchange Processes Involving Second-Row Donors and Binding Energies (ΔE_{bind}) of the Associated Bis-Adducts of the Phosphenium Ion[a]

ion ($[X-PH_2]^+$)	donor	ΔE_{bind}[b]	ΔE_r[b]
$[H_3P-PH_2]^+$ (**18**)	PH_3	34.7	0.0
	H_2S	29.5	77.3
	HCl	18.3	181.4
$[H_2S-PH_2]^+$ (**19**)	PH_3	106.8	−77.3
	H_2S	57.6	0.0
	HCl	26.3	104.2
$[HCl-PH_2]^+$ (**20**)	PH_3	199.8	−181.4
	H_2S	130.4	−104.2
	HCl	51.0	0.0

[a] G2 values in kJ mol^{-1} at 0 K. [b] See Figure 1.

The bis-adducts of the phosphenium ion with second-row Lewis bases are more weakly bound than the bis-adducts of the phosphenium ion with first-row Lewis bases (Tables 1 and 2). The reaction energies are also smaller in magnitude.

Exchange Reactions Involving both First- and Second-Row Donors. Figure 6 depicts the possible bis-adducts of the phosphenium ion which can be formed when the exchange reaction involves both a first- and a second-row donor. Reaction energies of the possible exchange reactions between a first-row donor and a phosphenium ion coordinated by a second-row ligand and the binding energies of the associated bis-adducts are presented in Table 3 while corresponding values for the reactions between a second-row donor and a phosphenium ion coordinated by a first-row ligand are presented in Table 4.

It can be seen from Tables 3 and 4 that the binding energies of the bis-adducts are related to donor electronegativity in the same manner as described in the previous two sections. Thus, the two most strongly bound bis-adducts are formed from $[HCl-PH_2]^+$ (**20**) plus ammonia and $[HF-PH_2]^+$ (**8**) plus phosphine, these species being bound by 210.8 and 256.0 kJ mol^{-1}, respectively (Tables 3 and 4). Moreover, the two most weakly bound bis-adducts are those formed from $[H_3N-PH_2]^+$ (**6**) plus hydrogen chloride and $[H_3P-PH_2]^+$ (**18**) plus hydrogen fluoride, the binding energies being 22.6 and 25.7 kJ mol^{-1}, respectively (Tables 3 and 4).

The reaction energies have values up to 230.3 kJ mol^{-1}. The most favorable reaction energies are associated with the transformation of mono-adducts with the least effective donor

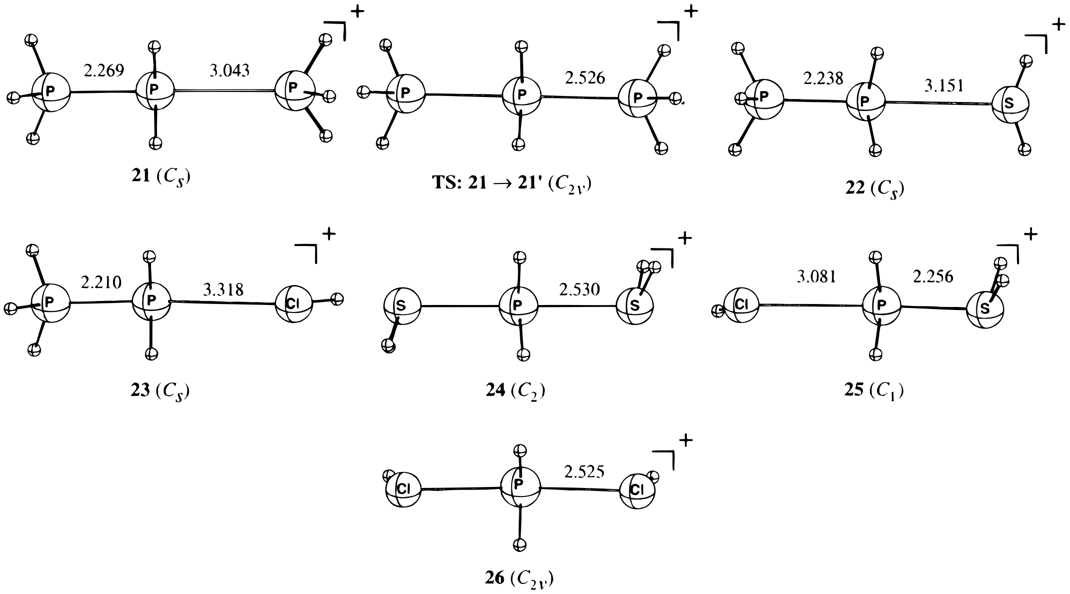


Figure 5. Optimized (MP2(full)/6-31G(d)) geometries of the bis-adducts of the phosphenium ion with two second-row Lewis bases. Bond lengths are in Å.

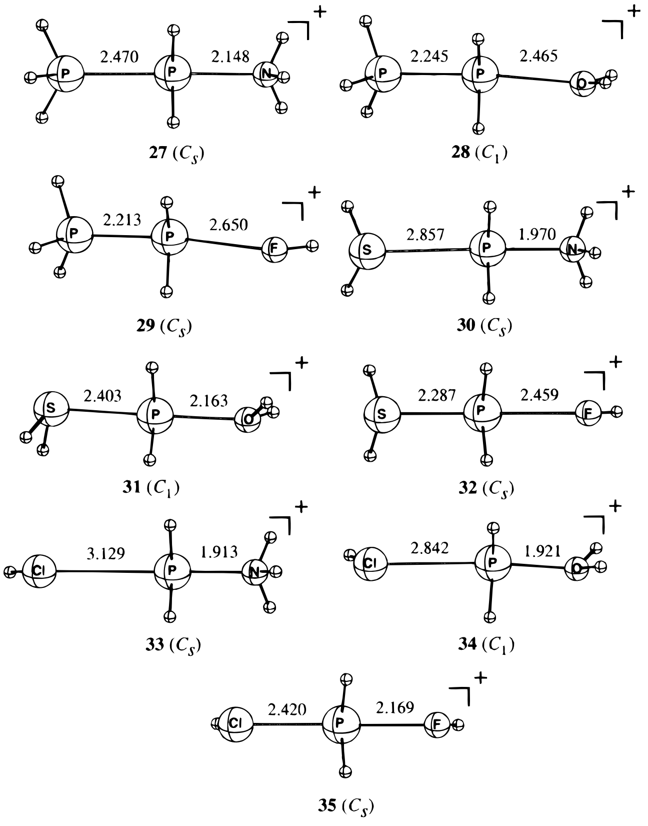


Figure 6. Optimized (MP2(full)/6-31G(d)) geometries of the bis-adducts of the phosphenium ion with one first-row and one second-row Lewis base. Bond lengths are in Å.

Table 3. Reaction Energies (ΔE_r) for Exchange Processes between First-Row Donors and Phosphenium Ions Coordinated by a Second-Row Ligand and Binding Energies (ΔE_{bind}) of the Associated Bis-Adducts of the Phosphenium Ion[a]

ion ($[X-PH_2]^+$)	donor	ΔE_{bind}[b]	ΔE_r[b]
$[H_3P-PH_2]^+$ (**18**)	NH_3	68.8	−6.8
	H_2O	45.1	110.6
	HF	25.7	230.3
$[H_2S-PH_2]^+$ (**19**)	NH_3	127.1	−84.0
	H_2O	60.8	33.3
	HF	30.5	153.1
$[HCl-PH_2]^+$ (**20**)	NH_3	210.8	−188.2
	H_2O	108.6	−70.9
	HF	40.2	48.9

[a] G2 values in kJ mol^{-1} at 0 K. [b] See Figure 1.

Table 4. Reaction Energies (ΔE_r) for Exchange Processes between Second-Row Donors and Phosphenium Ions Coordinated by a First-Row Ligand and Binding Energies (ΔE_{bind}) of the Associated Bis-Adducts of the Phosphenium Ion[a]

ion ($[X-PH_2]^+$)	donor	ΔE_{bind}[b]	ΔE_r[b]
$[H_3N-PH_2]^+$ (**6**)	PH_3	62.0	6.8
	H_2S	43.1	84.0
	HCl	22.6	188.2
$[H_2O-PH_2]^+$ (**7**)	PH_3	155.6	−110.6
	H_2S	94.1	−33.3
	HCl	37.7	70.9
$[HF-PH_2]^+$ (**8**)	PH_3	256.0	−230.3
	H_2S	183.6	−153.1
	HCl	89.1	−48.9

[a] G2 values in kJ mol^{-1} at 0 K. [b] See Figure 1.

ligands (e.g., HF, HCl) to mono-adducts with the most effective donor ligands (e.g., NH_3, PH_3).

Binding Energies of the Bis-Adducts of the Phosphenium Ion. The present results for the binding energies of the bis-adducts $[X-PH_2-Y]^+$ (Tables 1-4) can readily be rationalized using qualitative molecular orbital theory, noting initially that the magnitude of the interaction between two orbitals is inversely proportional to the energy gap between them.[17] In addition, we note that (a) the donor ability of Y decreases to the right of a period and (b) the acceptor ability of mono-adducts $[X-PH_2]^+$ increases as the electronegativity of X is increased. Hence, when a particular mono-adduct reacts with a sequence of donors (Y), the binding energies of the associated bis-adduct would be expected to decrease as Y moves to the right of the period. On the other hand, when a particular donor reacts with mono-adducts $[X-PH_2]^+$, the binding energies of the associated bis-adducts would be expected to increase as X moves to the right of the period. These qualitative predictions are consistent with

---

(17) See, for example: Pross, A. *Theoretical and Physical Principles of Organic Reactivity*; Wiley: New York, 1995.

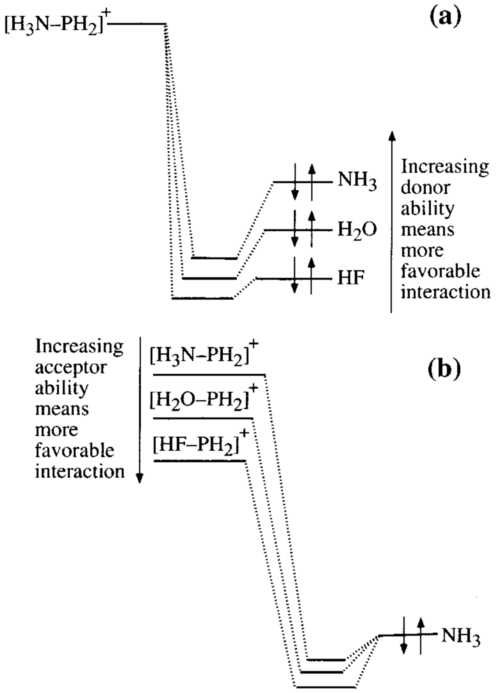
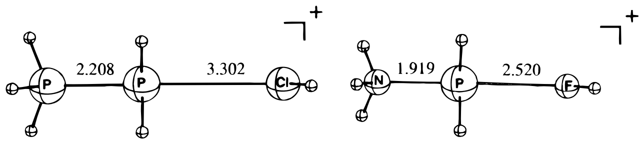


Figure 7. Orbital interaction diagrams corresponding to the formation of $[X-PH_2-Y]^+$ showing (a) more favorable interaction accompanying increasing donor ability of the Lewis base Y or (b) more favorable interaction accompanying increasing electronegativity of X and hence improved acceptor ability of $[X-PH_2]^+$.

the data in Tables 1–4 and are illustrated in Figure 7 for the binding energies presented in Table 1.

When a particular donor reacts with a phosphenium ion coordinated by a first- or a second-row donor from the same group, the more strongly bound bis-adduct results from the phosphenium ion with the first-row ligand (compare Table 1 with Table 3 and Table 2 with Table 4). This may be attributed to the fact that the electronegativity decreases in going from the first to the second row and that the mono-adduct with the more electronegative ligand is the more effective acceptor.

In addition to the dependence on the energy gap, the magnitude of the interaction between two orbitals is also directly proportional to their overlap.[17] Comparisons of the binding energies of the bis-adducts formed from a particular mono-adduct and either a first- or a second-row donor (from the same group) reveal that overlap can become important in certain cases. For example, despite the fact that phosphine is a slightly better donor than ammonia,[18] the latter forms the more strongly bound bis-adducts, presumably due to more effective overlap (compare Table 1 with Table 4 and Table 2 with Table 3). On the other hand, hydrogen sulfide forms more strongly bound bis-adducts than water with the stronger acceptors, $[H_2O-PH_2]^+$, $[HF-PH_2]^+$, $[H_2S-PH_2]^+$, and $[HCl-PH_2]^+$, indicating that the donor ability is the dominant factor in these cases.[18] Similar results are found for the hydrogen chloride/hydrogen fluoride pair. The very small difference in lone-pair energies for the phosphine/ammonia pair and the much larger differences for hydrogen sulfide/water and hydrogen chloride/hydrogen fluoride are consistent with the relative donor abilities generally playing a greater role in the last two cases.[18] The overlap factor becomes dominant for the weaker acceptors $[H_3N-PH_2]^+$ and $[H_3P-PH_2]^+$, e.g., water forms more strongly bound bis-adducts than hydrogen sulfide with these species, because of the larger energy gap in such circumstances. The proton affinities (PA) of the donors reveal trends that are consistent with the binding energies calculated for the stronger acceptors, i.e., PA(NH_3) > PA(PH_3) whereas PA(H_2O) < PA(H_2S) and PA(HF) < PA(HCl).[19]

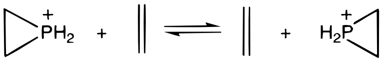


23a (C_s) (0.6) **TS: 11 → 11′** (C_s) (0.4)

Figure 8. Alternative conformations of the bis-adducts. The energy relative to the favored conformer is given in parentheses in kJ mol^{-1}.

Conformational Factors. The discussion in the previous sections is based on bis-adducts in their lowest energy conformations. We note that there are other shallow conformational minima in phosphenium ions coordinated by two second-row ligands or by one first-row and one second-row ligand (e.g., **23a**). On the other hand, in the case of bis-adducts of the phosphenium ion with two first-row Lewis bases, the alternative conformers of the favored structure correspond in most cases to low-lying transition structures connecting either chiral forms or equivalent forms of the favored conformer (e.g., **TS: 11 → 11′** in Figure 8).

Comparisons with Other Exchange Reactions Involving the Phosphenium Ion. In a previous investigation, we characterized a low-energy pathway for π-ligand exchange in phosphiranium and phosphirenium ions:[8]



(1)

It is tempting to consider such reactions as "π-ligand" equivalents of the ligand-exchange reactions investigated in the present work.

More recently, we have provided a detailed electronic description of the central transition structure in reaction 1 and similar reactions.[8,15] The principal interaction can be considered as that occurring between an empty p-orbital on phosphorus and the filled π-orbitals of the two hydrocarbons.[15b] It resembles the triple-ion configuration ($X^-\cdots CH_3^+\cdots X^-$) found in S_N2 transition structures[20] and what appears to be a similar interaction in the bis-adduct between SiH_3^+ and carbon monoxide. Such adducts have been characterized experimentally as well as theoretically.[21] The principal interaction is very similar to the bonding interaction in the bis-adducts of the phosphenium ion investigated herein (Figure 9). The species **36** and **37** (Figure 9) represent transition structures and (strongly bound) minima, respectively. This is consistent with the fact that the (filled) π-orbitals are less effective donors than are the (filled) lone pairs of the first- and second-row donors considered in the present work.

Experimental Consequences. The exchange reactions examined in the present study are predicted to proceed without

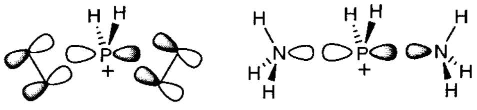
---

(18) Ionization energies (IE) of the donors in this work are 10.07 (NH_3), 9.87 (PH_3), 12.62 (H_2O), 10.46 (H_2S), 16.03 (HF), and 12.74 (HCl) (eV). These are taken to reflect the lone-pair energy, as suggested in ref 17. The IEs are obtained from: Hunter, E. P.; Lias, S. G. In *NIST Standard Reference Database Number 69, November 1998*; Mallard, W. G.; Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 1998 (http://webbook.nist.gov).

(19) Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 4885–4888.

(20) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1995**, *117*, 2024–2032.

(21) Hiraoka, K.; Katuragawa, J.; Sugiyama, T.; Minamitsu, A.; Yamabe, S.; Kouno, H. *Chem. Phys. Lett.* **1997**, *271*, 302–310.



36 **37**

Figure 9. Principal interaction in the central transition structure for π-ligand-exchange (e.g., **36**) resembling quite closely the bonding interaction in the bis-adduct of the phosphenium ion (e.g., **37**).

an intermediate barrier. Thus, all reactions that are not significantly endothermic should be experimentally feasible. As a rule of thumb, this is most likely to be the case when the more electronegative ligand is displaced. The bis-adducts are in some cases quite strongly bound, suggesting that species of this type should be experimentally observable.

To our knowledge there are no experimental data for the specific ligand-exchange reactions that we have examined. However, several groups have investigated the reactions of gaseous phosphenium ions with donor molecules[22] and have found that certain Lewis bases do coordinate to the phosphenium ion to form mono-adducts.[22d,e] We are unaware of any reported observations of bis-adducts of phosphenium ions in the gas phase, so this remains an experimental challenge. The formation of bis-adducts of phosphenium ions from reactions between mono-adducts and appropriate donors under conditions allowing collisional loss of excess energy would appear to offer a promising avenue for exploration.

Concluding Remarks

The present study contributes to the understanding of the factors that control the exchange reactions between mono-adducts of the phosphenium ion and either first- or second-row donors. We predict such reactions to proceed via an intermediate bis-adduct of the phosphenium ion without an intermediate barrier. The exchange reactions, as well as the associated bis-adducts themselves, should be experimentally observable in appropriate cases. The likelihood of observing the exchange reactions is largest when a more electronegative ligand is displaced. Relative binding energies of the bis-adducts can be rationalized using qualitative molecular orbital theory in terms of the donor ability of the reacting Lewis base and the electronegativity of the ligand in the mono-adduct of the phosphenium ion.

The binding interactions in the intermediate bis-adducts resemble quite closely the primary electronic interactions in the central transition structures in the corresponding exchange reactions involving π-ligands. The fact that the former are minima while the latter are transition structures is consistent with π-orbitals being less effective donors than lone pairs. An interesting question arises as to whether exchange reactions involving one π-ligand and one lone-pair ligand would proceed via an intermediate bis-adduct or a central transition structure. Work in this direction is in progress.

Acknowledgment. We gratefully acknowledge generous allocations of time on the Fujitsu VPP-300 supercomputer and the SGI-Power Challenge of the Australian National University Supercomputer Facility.

Supporting Information Available: Total G2 energies (Table S1) and GAUSSIAN archive entries for the MP2(full)/6-31G(d) optimized geometries (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

IC991080E

---

[22] (a) Holtz, D.; Beauchamp, J. L.; Eyler, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 7045−7055. (b) Wanczek, K.-P.; Hartmann, H.; Röschenthaler, G.-V. *Adv. Mass Spectrom.* **1978**, *7B*, 1301−1307. (c) Thorne, L. R.; Anicich, V. G.; Huntress, W. T. *Chem. Phys. Lett.* **1983**, *98*, 162−166. (d) Smith, D.; McIntosh, B. J.; Adams, N. G. *J. Chem. Phys.* **1989**, *90*, 6213−6219. (e) Thoen, K. K.; Gao, L.; Ranatunga, T. D.; Vainiotalo, P.; Kenttämaa, H. I. *J. Org. Chem.* **1997**, *62*, 8702−8707. (f) Gevrey, S.; Taphanel, M.-H.; Morizur, J.-P. *J. Mass Spectrom.* **1998**, *33*, 399−402.