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Structural properties of azaphosphirane and its $W(CO)_5$ complex. A density functional study

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Abstract

Properties and ring opening reactions are investigated for azaphosphirane and its *P*-phenyl and $W(CO)_5$ complex using density functional theory (B3LYP). Azaphosphirane has a relatively small N-inversion barrier of 10.8 kcal mol^{-1} and a high 56.8 kcal mol^{-1} 'turnstile' P-inversion barrier. Its strain energy is 26.5 kcal mol^{-1} at G3(MP2). The P–C bond is the weakest bond. Only 27.4 kcal mol^{-1} is needed to break it, which is half that needed for both the C–N and P–N bonds. This P–C ring opening to the *P*,*N*-ylide is endothermic by 8.5 kcal mol^{-1}. *P*-phenyl substitution has little effect neither on the geometries nor on the energy of the ring opening. Complexation by $W(CO)_5$ leads to a tighter ring but the energy for breaking the P–C bond still requires 27.8 kcal mol^{-1}. The resulting *P*,*N*-ylide is only 3.9 kcal mol^{-1} less stable than azaphosphirane. Cleaving either the C–N or P–N bond remain much more demanding processes. The calculations suggest that the reactivity of azaphosphirane may well have its origin in the readily accessible *P*,*N*-ylide. Its influence on the reaction of phosphinidenes with imines is discussed.

Keywords: Azaphosphirane; Three-membered rings; Ring opening; Effect of complexation

1. Introduction

Azaphosphiranes are hardly investigated structures. This is rather surprising in light of the importance of three-membered ring structures in chemistry. Until two decades ago, the reason for this deficiency may have been the difficulty in generating small organophosphorus ring systems. However, since Mathey and coworkers developed a synthetic route to electrophilic phosphinidene complexes, such as $R–P{=}W(CO)_5$, many new phosphorus containing heterocycles have become accessible [1]. The most simple ones are phosphiranes and phosphirenes, which are formed from the addition of the in-situ generated carbene-like synthon to olefins and acetylenes, respectively [2]. Subsequently, many 1,2-additions have been reported for a variety of C=X bonds, where X is O [3], S [4], Si [5], or P [6]. Still, only as recently as 1994 did Streubel et al. [3b] report on the first 1,2-addition to a C=N bond. This was accomplished by thermal decomposition of a 2*H*-azaphosphirene complex in the presence of an imine (Scheme 1). More recently, Mathey and coworkers [7] showed that $PhPW(CO)_5$ reacts with an excess of imine to give 1,4,2-diazaphospholanes. Using instead $MePW(CO)_5$ they also obtained a 1,2,3-azadiphosphetidine (Scheme 2). The formation of these products was considered to result from insertion of a second imine and phosphinidene, respectively, into the presumably weak P–N bond of the undetected azaphosphirane intermediate. A CPN ring has also been proposed earlier as an intermediate in the reaction of phosphenium ions with imines that likewise yield five-membered ring compounds [8]. Synthetic routes to uncomplexed azaphosphiranes have also been reported [9]. Recently, we isolated a complexed azaphosphirane, which, as Mathey [7] described, converts with excess imine into 1,4,2-diazaphospholanes [10]. In the same study we also found that additions to diimines give heterocycles via *P*,*N*-ylide intermediates instead of azaphosphiranes (Scheme 3).

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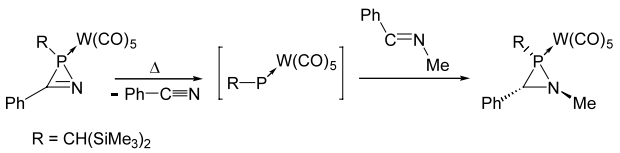
Whereas unsaturated $W(CO)_5$-complexed azaphosphirenes are used as precursors for phosphane ylides and complexed phosphinidenes (see, e.g. Scheme 1) [3,11], apparently little is known about the chemical and structural properties of the saturated system. We now present a theoretical study on azaphosphirane, its ring opening reactions, inversion barriers, and strain energy. The effect of phenyl substitution and $W(CO)_5$-complexation to phosphorus on opening of the ring structure will also be discussed.

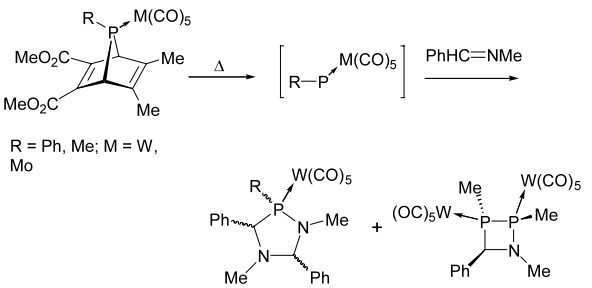
2. Computational details

All calculations were performed with the GAUSSIAN 98 suite of programs [12]. Closed-shell optimizations, frequency calculations, and intrinsic reaction coordinate (IRC) following were carried out with density functional theory using Becke's three-parameter hybrid exchange functional [13] and the Lee et al. correlation functional [14] (B3LYP). For the ring atoms the 6-31 + G** basis set was used, while the smaller 6-31G* basis was used for the C and O non-ring atoms (i.e. the $W(CO)_5$ and phenyl groups). The Hay and Wadt effective core potential, which incorporates relativistic effects implicitly, with the LANL2DZ basis set was used for tungsten. The ring strain energy of azaphosphirane was determined with Pople's G3(MP2) method [15].

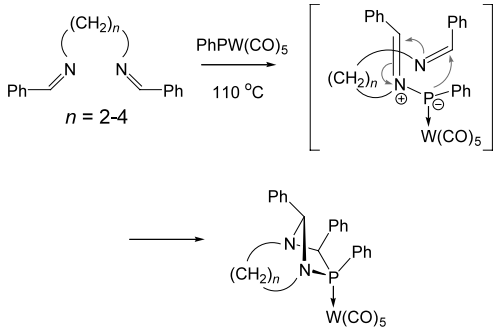
All transition structures were verified by vibrational analysis to have one and only one imaginary frequency, the nature of which was confirmed by IRC calculations to relate them to either bond breaking or N- or P-inversion processes.



Scheme 1.



Scheme 2.



Scheme 3.

3. Results and discussion

We start with the parent azaphosphirane (CH_4NP) by evaluating the inversion barriers of its heteroatoms and by comparing its strain energy with other three-membered ring structures. Next, we establish the strength of each of its three bonds through ring opening reactions. This is followed by considering the influence of both *P*-phenyl substitution and *P*-complexing the $W(CO)_5$ group on the ring opening reactions.

3.1. Azaphosphirane, CH_4NP

Azaphosphirane prefers an *anti*-configuration (Fig. 1). Its P–N bond is 0.042 Å shorter than the 1.852 Å P–C bond, which is of normal length as is the 1.456 Å C–N bond.

Conversion of the *anti* isomers to the 1.1 kcal mol^{-1} less stable *syn* form can occur via inversion at both the P- and N-atoms. The transition structures for both are also depicted in Fig. 1. Inversion at the N-center is favored by far. Its barrier of 10.8 kcal mol^{-1} is considerably less than the 16.1 kcal mol^{-1} for aziridine; similar aziridine inversion barriers have been reported at other levels of theory [16]. Compared to carbon the more electropositive and more distant phosphorus has apparently a stabilizing effect on the trigonal nitrogen.

Inversion at the phosphorus center of phosphirane can occur either by a trigonal or a T-shaped mechanism (Scheme 4). Heavier elements show an increased tendency for T-type or 'turnstile' inversions because of their preferred orthogonal bonding angles. However, an earlier theoretical study suggested a trigonal inversion for C_2H_5P, but a 'turnstile' inversion for halogen derivatives [17]. We find both pathways accessible to phosphirane with a preference for the 'turnstile' (50.6 kcal mol^{-1}) over the trigonal inversion (65.4 kcal mol^{-1}). Inversion at phosphorus in azaphosphirane also occurs via a 'turnstile' rotation of the PH group, but with a higher barrier of 56.8 kcal mol^{-1} due to repulsion by the nitrogen's lone pair. The PH rotation causes major elongations of both the C–P and P–N bonds, suggesting a conversion from a σ- to a π-type interaction with the imine base.

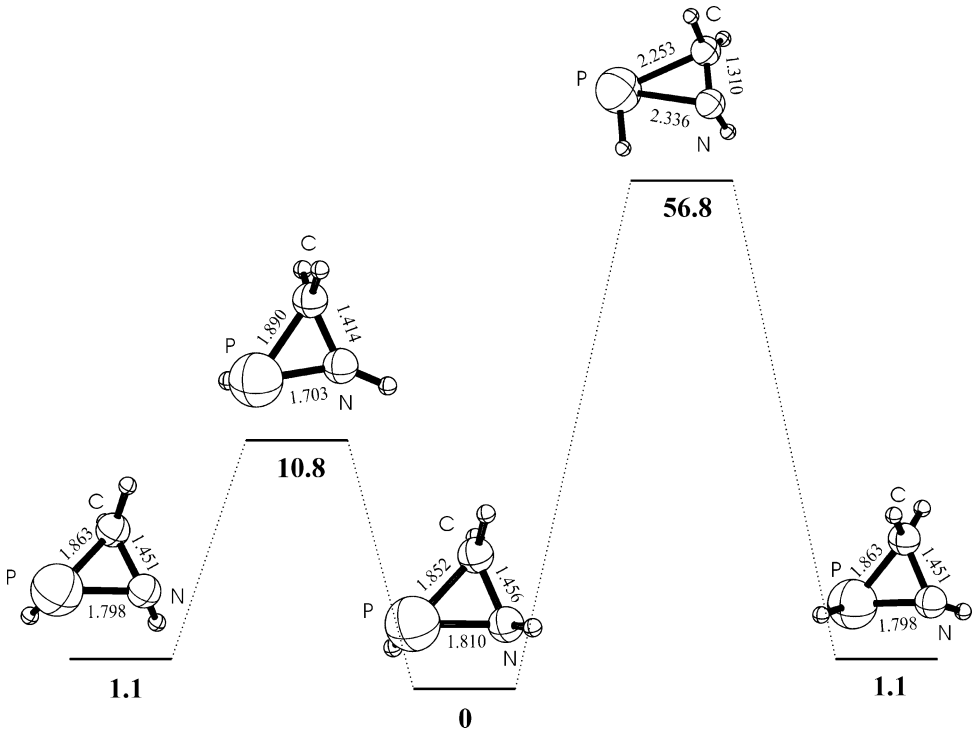


Fig. 1. N- and P-inversions for azaphosphirane. Relative energies are in kcal mol^{-1} and bond lengths are in Å.

These calculations indicate that P-epimerization at the phosphorus center itself is not feasible in three-membered rings without a ring opening process. However, in the case of azaphosphiranes, the low N-inversion barrier may lead to an apparent P-epimerization. Of course, substituents will influence this process.

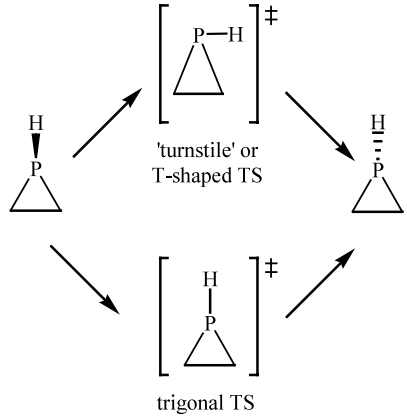
Three-membered rings are highly strained and azaphosphirane is no exception. To quantify its strain energy (SE), we calculated the reaction energy for homodesmotic Eq. (1) [18] using G3(MP2) heats of formation for all of its components. The resulting SE of 26.5 kcal mol^{-1} is much higher than that of phosphirane (21.4 kcal mol^{-1}) and, surprisingly, only slightly less than that of aziridine (28.2 kcal mol^{-1}) [19].

$$\textit{cyclo}\text{-}CH_2NHPH + CH_3NH_2 + CH_3PH_2 + NH_2PH_2 \rightarrow CH_3NHPH_2 + CH_3PHNH_2 + NH_2CH_2PH_2 \quad (1)$$

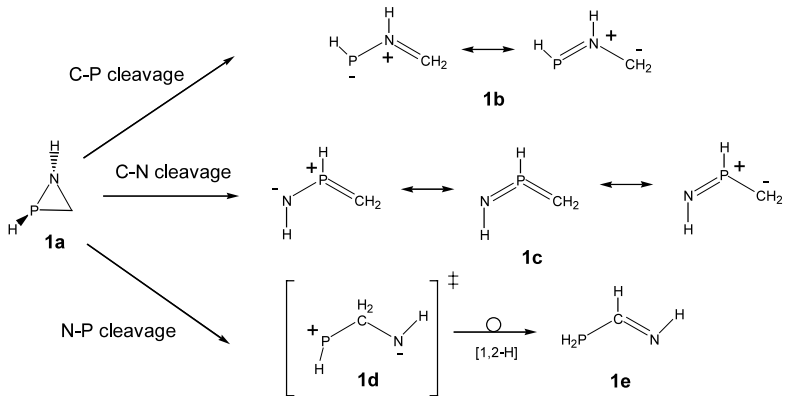
3.2. Ring opening

Does the high strain energy of azaphosphirane heighten its reactivity? We explore this by means of three ring-opening reactions, i.e. cleavage of the carbon–phosphorus, the carbon–nitrogen, and the nitrogen–phosphorus bonds. These processes are schematically depicted in Scheme 5, which also shows resonance structures of the ring-opened products. The energy profiles are given in Fig. 2 and selected bond distances are listed in Table 1.

Rupture of the C–P bond to give *syn*-**1b** is endothermic by only 8.5 kcal mol^{-1} and has a surprisingly small barrier of 27.4 kcal mol^{-1}. The ylide character of this structure is evident from the P–N bond distance of 1.568 Å. It reflects a strong interaction of ^{1}PH with the nitrogen atom of the imine. The barrier for cleavage of the C–N bond to give *anti*-**1c** is much higher (57.1 kcal mol^{-1}) and also more endothermic (16.5 kcal mol^{-1}). Its N–P and N–C bond distances illustrate ylene instead of ylide character [20]. As expected, the C–N bond of azaphosphirane is much stronger the C–P bond. The higher stability of ylide **1b** over ylene **1c** reflects their



Scheme 4.



Scheme 5.

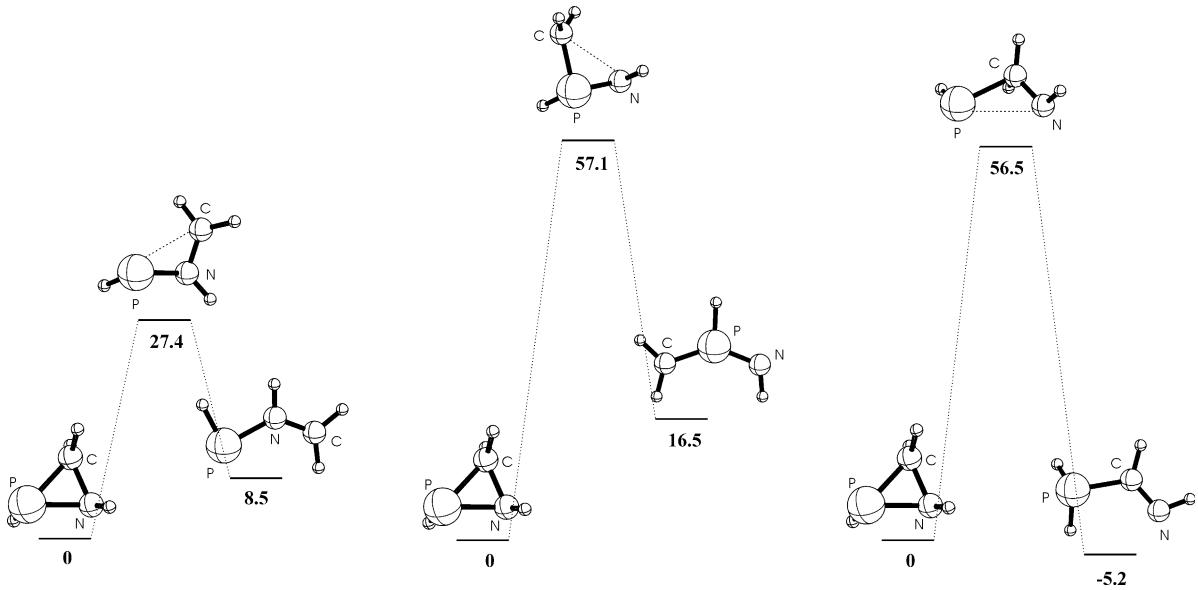


Fig. 2. Ring opening pathways for azaphosphirane. Relative energies are in kcal mol^{-1}.

different ability to accommodate charge polarization. The electropositive phosphinidene (^{1}PH) is much more stabilized by the imine than the nitrene (^{1}NH) is by the phosphaalkene. Heterolytic cleavage of the P–N bond is nearly as demanding (56.5 kcal mol^{-1}) as breaking the C–N bond. However, no 1,3-dipolar intermediate could be identified. Instead, the IRC shows that when the P–N distance elongates beyond the 1.648 Å in transition structure **1d**, stabilization results from transfer of a hydride from the neighboring carbon to the terminal phosphorus. The resulting *C*-phosphinoimine **1e** is 5.2 kcal mol^{-1} more stable than azaphosphirane.

These theoretical results illustrate that the barrier for breaking the C–P bond is about half that of both the C–N and P–N bonds. The primary product of this process is a *P*,*N*-ylide. We next address how P-substitution influences the energetics of these processes.

3.3. The effect of phenyl substitution

The three ring openings are evaluated for the *P*-phenyl substituted azaphosphirane. The optimized structures, having the same conformations as the unsubstituted system, are displayed in Fig. 3 together with their relative energies. Selected geometrical parameters are listed in Table 1.

The phenyl group has little if any influence on the geometry of the three-membered ring. It lengthens the distal bond slightly (0.005 Å) with similar shortenings of both vicinal bonds. The effect is opposite to that in cyclopropane [21]. Evidently, the π-acceptor ability of the phenyl group is not prominent in the heterocyclic structure.

The phenyl group has likewise little influence on the energy barriers for breaking any of its bonds. The largest effect is found for the weaker C–P bond (25.8 kcal mol^{-1}). In comparison to the parent system, the

barrier for formation of the *P*,*N*-ylide (cf. **1b**) is reduced by 1.6 kcal mol^{-1} while the endothermicity increases to 11.6 kcal mol^{-1}. This indicates a destabilizing effect of the phenyl group on the ylide. The much higher barriers of about 57 kcal mol^{-1} for breaking both the C–N and P–N bonds are similar to those of the parent system. Even the endothermicity for formation of the ylene (17.2 kcal mol^{-1}) is similar to that of **1c**. The phenyl group has a small destabilizing effect on the formation of the phosphino-imine (cf. **1e**).

3.4. Effect of P → W(CO)$_5$ complexation

Transition metal groups typically stabilize low valent structures. This is particularly evident for phosphinidenes (R–P:) but also for the three-membered phosphiranes [2]. Azaphosphirane is no exception. On W(CO)$_5$ complexation it shortens both vicinal bonds substantially, the P–C bond by 0.031 to 1.822 Å and the N–P bond by 0.046 to 1.478, and elongates the distal C–N bond by 0.022 Å. Geometrical parameters for the W(CO)$_5$ structures are summarized in Table 1. The

Table 1
Bond lengths (Å) in the ring and the three ring opening transition structures for azaphosphirane (P–H), W(CO)$_5$-complexed phosphirane (P → W(CO)$_5$), and *P*-phenyl azaphosphirane (*P*-phenyl) calculated at the B3LYP level of theory

Structure	**1a**								
	C–P	C–N	N–P						
P–H	1.853	1.456	1.810						
P-phenyl	1.850	1.461	1.791						
P → W(CO)$_5$	1.822	1.478	1.764						
	[C N P]TS (**1a** → **1b**)			[C P N]TS (**1a** → **1c**)			[N C P]TS (**1a** → **1e**)		
	C–P	C–N	N–P	C–P	C–N	N–P	C–P	C–N	N–P
P–H	2.399	1.344	1.791	1.790	2.499	1.648	1.926	1.350	2.595
P-phenyl	2.415	1.353	1.760	1.787	2.459	1.648	1.928	1.365	2.832
P → W(CO)$_5$	2.355	1.329	1.871	1.764	2.716	1.640	1.987	1.299	2.847
	1b			**1c**			**1e**		
	C–P	C–N	N–P	C–P	C–N	N–P	C–P	C–N	N–P
P–H	2.847	1.318	1.744	1.652	3.017	1.568	1.849	1.275	2.746
P-phenyl	2.856	1.316	1.754	1.656	2.971	1.571	1.849	1.276	2.751
P → W(CO)$_5$	2.826	1.297	1.806	1.646	2.976	1.586	1.848	1.271	2.720

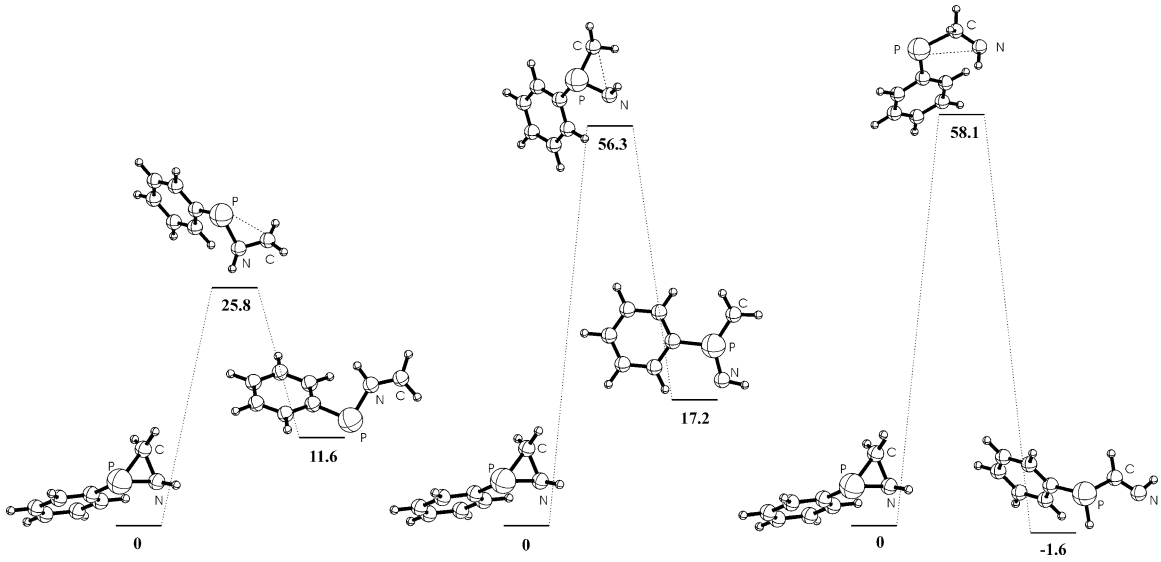


Fig. 3. Ring opening pathways for *P*-phenyl substituted azaphosphirane. Relative energies are in kcal mol^{-1}.

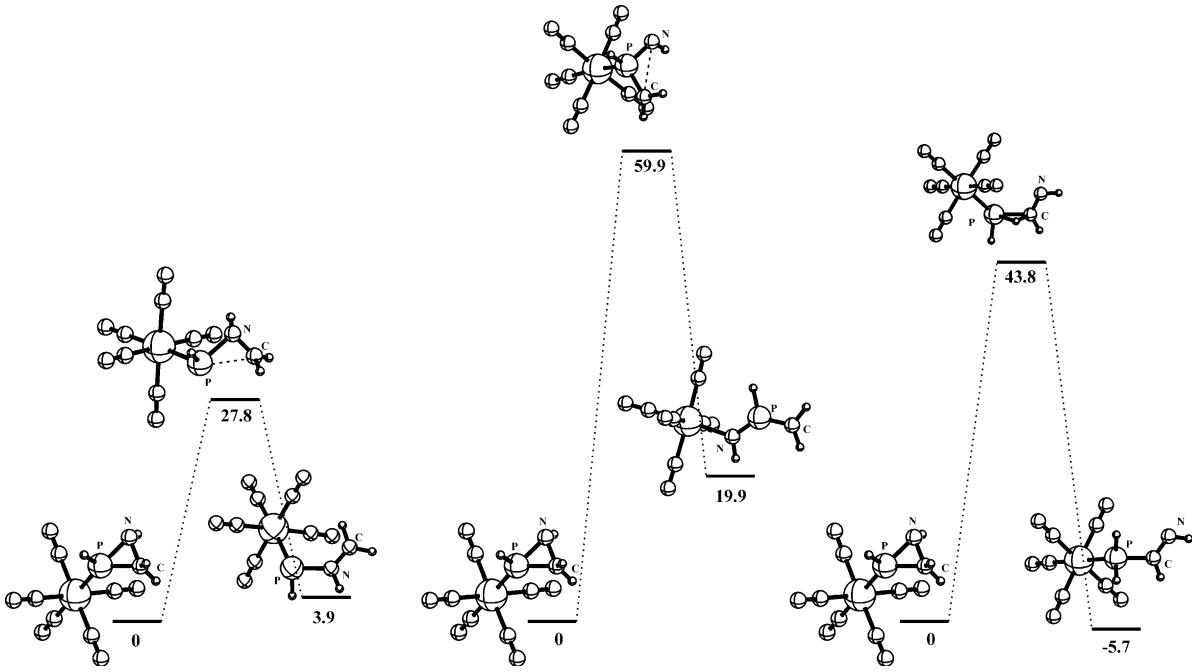


Fig. 4. Ring opening pathways for $P \rightarrow W(CO)_5$ complexed azaphosphirane. Relative energies are in kcal mol^{-1}.

structures and relative energies are displayed in Fig. 4.

Whereas the effect of the $W(CO)_5$ group is significant on the azaphosphirane structure, its impact on the three ring opening processes is hardly noticeable. Thus, cleaving the P–C bond requires 27.8 kcal mol^{-1}, which is virtually identical to that of the parent system, albeit that the reaction becomes less endothermic (3.9 kcal mol^{-1}), indicating a relative stabilization of 4.6 kcal mol^{-1} for the complexed ylide. The tremendous stabilization of the $W(CO)_5$ group on the singlet phosphinidene ^{1}PH has been recognized before and this is apparently also reflected in the *P*,*N*-ylide. The barrier for breaking the C–N is nearly twice that of the C–P bond, just as in the parent system, while the endothermicity for formation of the ylene has increased to 19.9 kcal mol^{-1}. The transition metal group has more influence on the barrier of the heterolytic P–N bond cleavage, which it reduces by 12.7 kcal mol^{-1} to a still significant 43.8 kcal mol^{-1}. The transition structure for this exothermic process shows also more clearly the transfer of a hydrogen from carbon to phosphorus during the ring opening. Related processes have not been observed experimentally.

4. Conclusion

Like all three-membered ring structures, azaphosphirane is a highly strained structure. Its strain energy, estimated with G3(MP2) theory at 26.5 kcal mol^{-1}, is similar to that of cyclopropane. DFT calculations at B3LYP/6-31 + G** show it to have a weak P–C bond (27.4 kcal mol^{-1}), which on cleavage results in a *P*,*N*-ylide. The ring opening is endothermic by 8.5 kcal mol^{-1}. *P*-Phenyl substitution and *P*-$W(CO)_5$ complexation have no influence on the ring opening process, although a relative stabilization of the ylide of 4.6 kcal mol^{-1} results on $W(CO)_5$ complexation. These calculations suggest that reaction of complexed phosphinidenes, such as R–P=$W(CO)_5$, with imines to give azaphosphiranes may occur via intermediate *P*,*N*-ylids. They further indicate that their interconversion is feasible. Thus, the formation of 1,4,2-diazaphospholanes from R–P=$W(CO)_5$ and imines (see Scheme 2) likely results from a 1,3-dipolar addition of an intermediate *P*,*N*-ylide to the imine.

Whereas *P*-phenyl substitution has little influence on the geometry of azaphosphirane the *P*-$W(CO)_5$ group condenses the structure, in accordance with experimental phosphirane structures. The parent structure CH_4NP prefers an *anti*-conformation. N-inversion requires 10.8 kcal mol^{-1}. P-inversion is much more demanding (56.8 kcal mol^{-1}) and proceeds preferably through a 'turnstile' process. This process is energetically compatible with the C–N and P–N ring opening reactions.

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