CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200701077

A Promising Method for Phosphinidene Generation: Complexes of Phosphinidenes with N-Donor ligands

Zoltán Benkõ,[a] Dietrich Gudat,*[b] and László Nyulászi*[a]

Abstract: 1,3,2-diazaphospholenes and related compounds can formally be regarded as complexes of phosphinidenes (R–P) with 1,4-diazabutadienes. The dissociation Gibbs free energies of these "complexes" were calculated by using density functional theory (B3LYP/3-21G(*) and B3LYP/6-311+G**). The dissociation Gibbs free energies show systematic dependence on the phosphorus substituent as well as on the stability of the N-donor ligand formed as a byproduct. The thermodynamics and kinetics of the dissociations were thoroughly examined. The results allow us to conclude that novel routes of phosphinidene generation can be developed.

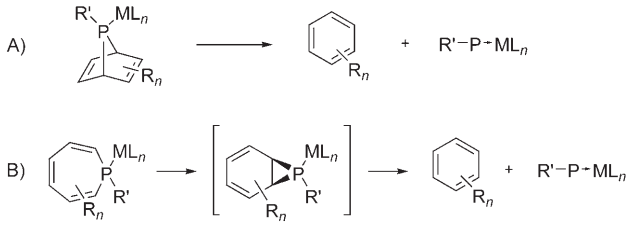
Keywords: aromaticity · density functional calculations · dissociation · N-donor ligands · phosphinidene

Introduction

The synthetic and theoretical investigations of low coordinated compounds have become an amazing and rapidly expanding field of main group chemistry during the last few decades. A large number of carbenes,[1] silylenes[2] and germylenes[3] have already been synthesised and their availability has prompted structural and reactivity studies. Some of them have been applied in a wide range of synthetic reactions as the reagent or catalyst.[4]

Phosphinidenes (R–P) are phosphorus analogues of carbenes. So far no stable free phosphinidenes have been synthesised;[5] although, based on the diagonal relationship between carbon and phosphorus, it can be surmised that it is possible to stabilise phosphinidenes as well. In our previous work,[6] we have shown computationally that $(Me_3Si)_2C{=}N\text{-}P$ has a singlet ground state, and as it is stable against dimerisation, it is a likely synthetic target. No facile synthetic route has been found, however, to access this compound.[7]

For the generation of free phosphinidenes, several methods have been developed. The application of phosphiranes[5a–b] (three-membered rings containing phosphorus), diphosphenes[8] (R′–P=P–R) or phosphanylidene–phosphoranes (R′–P=PR_3)[9] has remained quite limited. Two widely applicable preparative methods are known, however, for the in situ synthesis of phosphinidene complexes. The first of them was reported by Marinetti, Mathey et al. in 1982,[10] who generated a transient phosphinidene complex by thermal decomposition of a phosphanorbornadiene complex (Scheme 1A).[11] Later on, Lammertsma and co-workers applied (benzo)phosphepine as viable phosphinidene source, which released the phosphinidene complex via a phosphanorcaradiene intermediate (a bicyclic isomer of the seven-membered-ring phosphepine; Scheme 1B).[12] The driving force in both types of reactions is the formation of an aromatic ring. Recently, the generation of a stabilised amino-



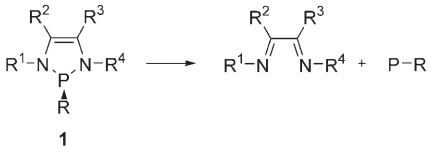
Scheme 1.

[a] Dipl.-Chem. Z. Benkõ, Prof. Dr. L. Nyulászi
Department of Inorganic and Analytical Chemistry
Budapest University of Technology and Economics
Szent Gellért tér 4, 1111 Budapest (Hungary)
Fax: (+36) 1463-36-42
E-mail: nyulaszi@mail.bme.hu

[b] Prof. Dr. D. Gudat
Institute of Inorganic Chemistry
University of Stuttgart, Pfaffenwaldring 55
70569 Stuttgart (Germany)
Fax: (+49) 711-685-64241
E-mail: gudat@iac.uni-stuttgart.de

phosphinidene from triphosphabenzene and its trapping by a second molecule of triphosphabenzene has also been reported.[13]

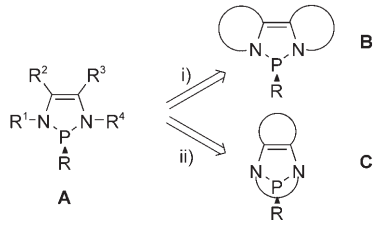
A hitherto unexplored method for the generation of phosphinidenes is the decomposition of a five-membered diazaphospholene ring **1** by means of formation of a diazabutadiene as a byproduct (Scheme 2). The formal consideration



Scheme 2.

of **1** in this context as a diazabutadiene complex of a phosphinidene parallels a description that has been used for carbenes and carbene analogues[14] and the fragmentation of **1** is further related to the known decomposition of N-heterocyclic stannylenes to give a diazadiene and tin.[15] Although **1** is known as a stable compound,[16] it can be conceived that by varying the substituent pattern of the complexing diazabutadiene moiety, appropriately substituted 1,3,2-diazaphospholenes might be utilised as phosphinidene sources (Scheme 2).

As a possible approach to this target, we wanted to consider not only the dissociation of diazaphospholenes with an isolated ring **A** (with $R_i = H$ atoms), but also of their congeners with fused ring systems, such as **B** and **C** shown in Scheme 3.



Scheme 3.

The fused ring framework in heterocycles **B** was chosen in such a way that the fission of the phosphinidene is accompanied by the formation of 2,2′-bipyridine or 1,10-phenanthroline. These species are widely used bidentate chelating ligands in coordination chemistry[17] and supramolecular chemistry[18] and are expectedly aromatic which ought to contribute to the driving force for the dissociation shown in Scheme 2. Fragmentation of the bicyclic 1,4,7-diazaphosphanorbornadiene framework in compounds of type **C** is similar to the currently used synthetic approaches of phosphinidene complexes reported by Mathey[10] and Lammertsma.[12]

The aim of this study is to investigate computationally the possible formation of phosphinidenes by means of decomposition of the N-heterocyclic precursors mentioned above. The influence of benzannelation pattern and substituent effects will be discussed in detail.

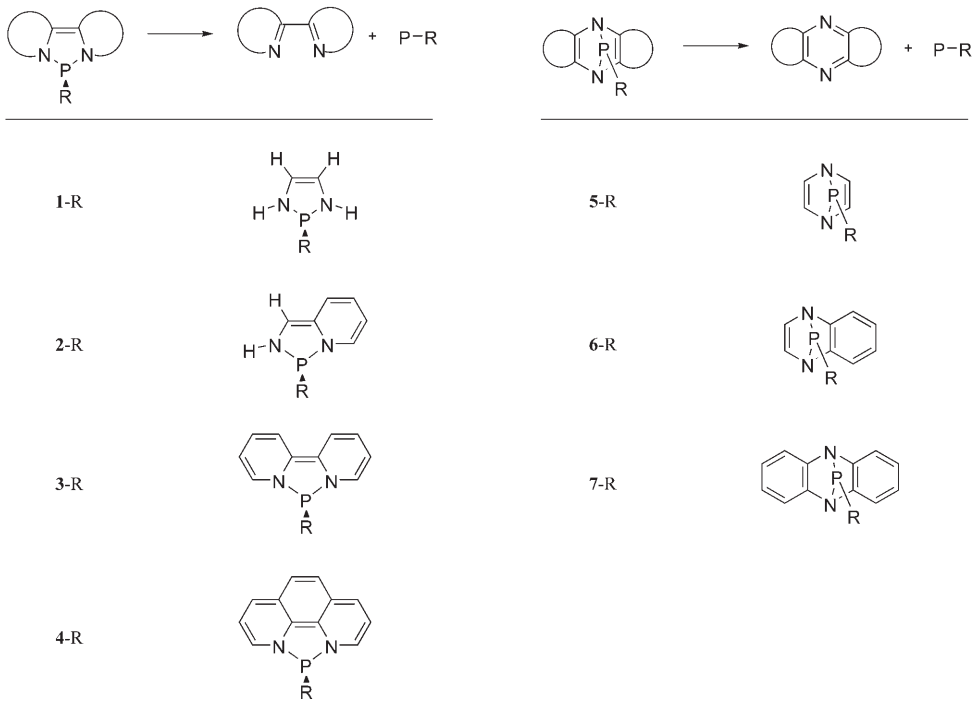
Calculations

DFT calculations were carried out with the Gaussian 03 program package.[19] All structures were calculated with two different basis sets (B3LYP/3-21G(*) and B3LYP/6-311+G**).[20] At each of the optimised structures, vibrational analysis was performed to check whether the stationary point located is a minimum or a transition structure (TS) characterised as a first-order saddle point of the potential energy hypersurface. The Gibbs free energies were calculated by utilising the B3LYP/6-311+G** harmonic frequencies at 298 K. The NICS values[21] were calculated at the B3LYP/6-311+G** level at the ring centre (NICS(0)), and also at 1.0 Å above the ring plane (NICS(1)). In case of any TS located, IRC calculations were carried out to find the minima, which are connected by the transition structures. The stability of the wavefunction was tested for all the optimised structures. In certain cases, higher level calculations were also performed to test the reliability of the results (see the Results and Discussion section). For the visualisation of the molecules, the Molden program was used.[22]

Results and Discussion

The fragmentation reactions of the two types of ring mentioned above (Schemes 2 and 3) were studied for compounds with different numbers of fused rings and R groups (see Scheme 4). The complexes can be divided into two groups: compounds **1**–**4** containing type **B** (including bipyridine or phenanthroline derivatives) and compounds **5**–**7** with type **C** (pyrazine derivatives) ring systems.

Both dissociation energies and Gibbs free energies calculated at the B3LYP/6-311+G** level with different R substituents are listed in Table 1 (the two sets of values are in excellent correlation: $R^2 = 0.999$), whereas the results of computations at the B3LYP/3-21G(*) level are given as Supporting Information. The deviations between the two levels of theory are rather large for all of the complexes. The larger basis set gave systematically lower values (average difference 19.2 kcal mol^{-1} with a standard deviation of 2.5 kcal mol^{-1}); however, the trends of the values are the same with respect to the number of ring annelations and R substituents. The basis set superposition error (*BSSE*) was calculated by using the counterpoise method,[23] and was found to range between 19.1 and 22.6 kcal mol^{-1} for calculations performed with the smaller basis set (B3LYP/3-21G*) and between 2.3 and 2.6 kcal mol^{-1} only for calculations performed with the larger basis set (B3LYP/6-311+G**). This indicates that the difference of the dissociation energies is mainly attributable to the *BSSE*. To estimate the reliability of our data, in the case of **1**-R, CBS-QB3 energy calcula-



Scheme 4. Reactions and complexes (nR, n = 1–7) studied. R denotes the substituent R on the P atom: R = H (**a**), NH_2 (**b**), $N=CH_2$ (**c**), and $N=C(SiH_3)_2$ (**d**); for example, **1a** corresponds to compound **1** with R = H.

Table 1. Dissociation energies (ΔE_{dissoc}(nR)) and Gibbs free energies (ΔG_{dissoc}(nR)) at 298 K of the complexes nR (n = 1–7 see Scheme 4; in kcal mol^{-1}, B3LYP/6-311+G**//B3LYP/6-311+G**).

R =	H (**a**)		NH_2 (**b**)		$N=CH_2$ (**c**)		$N=C(SiH_3)_2$ (**d**)	
	ΔE_{dissoc}	ΔG_{dissoc}	ΔE_{dissoc}	ΔG_{dissoc}	ΔE_{dissoc}	ΔG_{dissoc}	ΔE_{dissoc}	ΔG_{dissoc}
1-R	88.0	74.0	62.4	49.1	42.1	27.5	28.9	13.5
2-R	65.7	51.9	40.8	27.5	20.5	5.6	7.2	−8.4
3-R	43.3	31.0	20.8	8.3	−1.4	−16.0	−16.2	−29.4
4-R	40.8	28.7	18.3	6.1	−4.1	−17.5	−18.5	−33.8
5-R	7.5	−4.2	−15.1	−26.6	−39.3	−51.7	−52.7	−64.8
6-R	21.2	8.4	−2.1	−14.6	−26.1	−39.7	−39.9	−53.3
7-R	36.7	23.6	11.9	−0.7	−11.7	−25.7	−25.5	−41.2

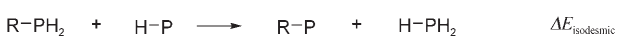
tions were also performed. The differences are between −2.1 and +3.0 kcal mol^{-1} with respect to B3LYP/6-311+G**, indicating that this level is reasonably accurate.

The reliability of our computations can also be estimated by comparison with available information from previous experimental studies: Derivatives of **1a** and **1b** with bulky *t*Bu and Mes* substituents at the ring nitrogens[24] as well as analogous compounds with chlorine (R = Cl)[16c,25] and bromine (R = Br)[26] substituents have been reported as stable entities and the +82.5 and +81.0 kcal mol^{-1} dissociation Gibbs free energy values computed for **1a** and **1b**, respectively, are in good accordance with the stabilities of these compounds (the energetic effect of the substituents at nitrogen should be far less than the computed stability discussed above).

It should be noted that the dissociation reactions of **1a**–**7a** were calculated under the assumption that a singlet phosphinidene is formed, although the singlet in the case of the parent PH phosphinidene is less stable than the triplet[6,27] (by 30,1 kcal mol^{-1} at CCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G**).[6] The dissociation reactions for NH_2-substituted derivatives (**1b**–**7b**) were also calculated with singlet phosphinidene; however in this case, the triplet is more stable than the singlet[6,28] by only 2.3 kcal mol^{-1} at CCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G**.[6]

In our previous study,[6] we have shown by using the isodesmic reaction (Scheme 5) that the stability of the (singlet) phosphinidenes is as follows: $P-H \ll P-NH_2 < P-N=CH_2 < P-N=C(SiH_3)_2$. A plot of the energies of the isodesmic reaction ($\Delta E_{isodesmic}$) against the dissociation Gibbs free energies (ΔG_{dissoc}) of **1**-R–**7**-R (Figure 1) gives a good correlation for all types of heterocycles studied, and allows us to conclude that—as expected—the more stable the (singlet) phosphinidene is, the less stable the reactant complex.

Comparing the two basic routes of phosphinidene generation from type **B** (**1**-R–**4**-R) and **C** (**5**-R–**7**-R, Scheme 3) compounds revealed different tendencies which are, however,



Scheme 5.

independent of the nature of R: With bipyridine- or phenanthroline-like ligands (type **B** compounds, **1**-R–**4**-R), the dissociation Gibbs free energy decreases with increasing number of fused rings in the direction from **1**-R to **4**-R. Type **C** compounds with a pyrazine unit (**5**-R–**7**-R), however, show a different trend: here, **7**-R compounds with phenazine ligands with two benzannelated rings exhibit the largest stability, whereas the 1,4,7-diazaphosphanorbornadienes **5**-R are predicted to be unstable even when R = H (Figure 2).

To check further the reliability of our calculations, the phosphinidene precursors reported in earlier studies have also been computed with the substituent R: $-N=C(SiH_3)_2$, which has the largest stabilising effect on the phosphinidenes (compounds **8d**–**10d**). Compounds **8d** and **9d** are the

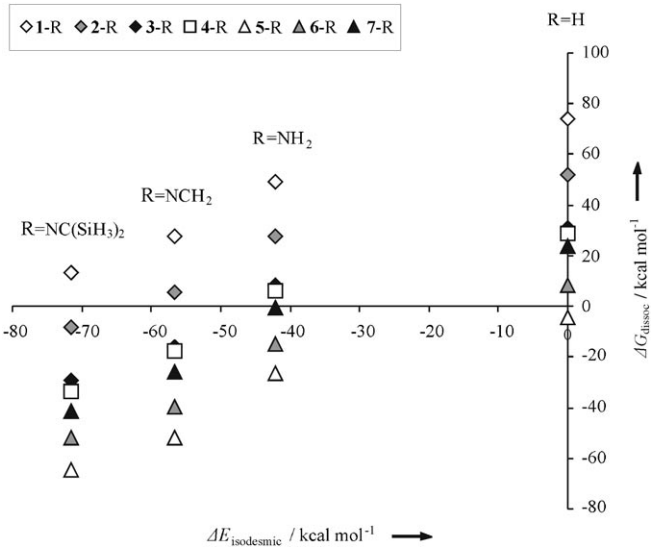


Figure 1. Relationship between the dissociation Gibbs free energies (ΔG_{dissoc}) and the energies of the isodesmic reaction ($\Delta E_{isodesmic}$)[6] at the B3LYP/6-311+G** level.

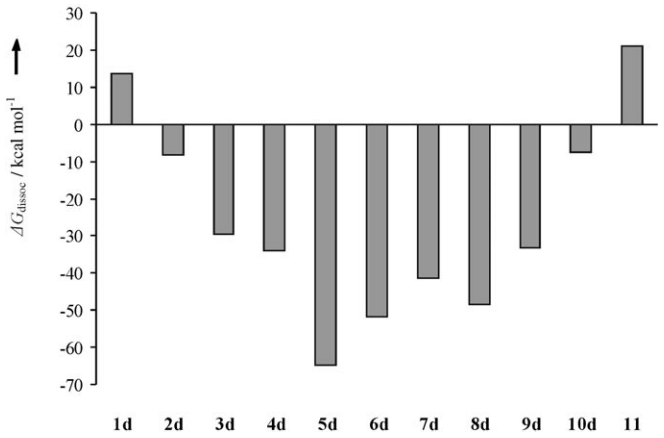
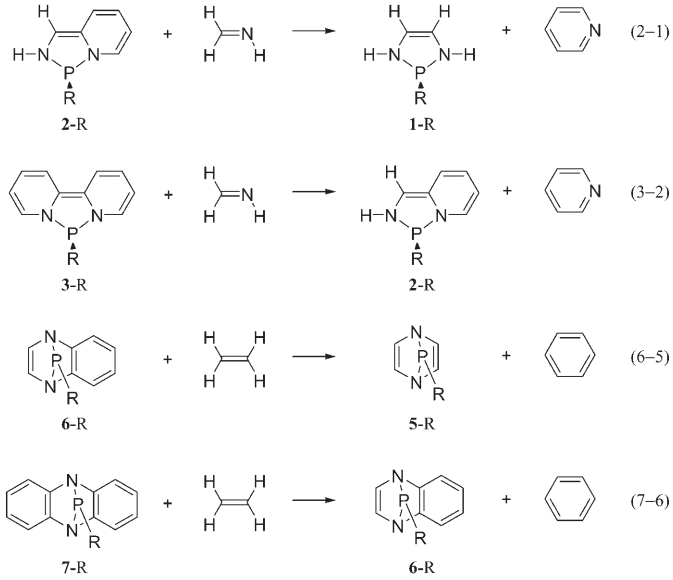


Figure 2. The dissociation Gibbs free energies (ΔG_{dissoc}) with R = $-N{=}C(SiH_3)_2$ substituents at 298 K (B3LYP/6-311+G**//B3LYP/6-311 +G**).

analogues of the norbornadiene and norcaradiene compounds reported by Mathey[10] and Lammertsma,[12] **10d** is the $-N{=}C(SiH_3)_2$ analogue of the phosphirane **11** the decomposition of which has afforded mesityl phosphinidene previously.[5]

The quite negative B3LYP/6-311+G** dissociation Gibbs free energies of **8d** and **9d** (-33.6 and -48.5 kcal mol^{-1}, respectively) suggest that the norbornadiene and norcaradiene compounds can dissociate easily. For **10d** (with R = $-N{=}C(SiH_3)_2$), the dissociation Gibbs free energy is -7.6 kcal mol^{-1}, suggesting that the phosphirane compounds are less prone to behave as phosphinidene sources than the norbornadiene type precursors. *trans*-2,3-Dimethyl-1-mesitylphosphirane (**11**) was reported to be stable at room temperature and its decomposition could only be initiated by photolysis or pyrolysis at 190 °C.[5a–b] The calculated Gibbs free energy of the dissociation reaction (Mes-$PC_2H_2Me_2$ (**11**) = ^{3}(Mes-P) + $C_2H_2Me_2$) calculated at the B3LYP/6-311+G** level (with triplet mesityl-phosphinidene) is +20.9 kcal mol^{-1} at 298 K, which agrees with the former experimental observations.

To understand the different tendencies in the dissociation energies, we have investigated possible factors leading to the stabilisation of the starting materials by calculating the energies of the isodesmic reactions shown in Scheme 6.



Scheme 6.

The energies of the similar isodesmic reactions were also calculated for the bare ligands resulting after the cleavage of the phosphinidene moiety (marked with **L** in Table 2), and all isodesmic reaction energies are collected in Table 2. The computed energies of reactions 2–1 (Scheme 6) are around -25 kcal mol^{-1} for all R groups. This suggests that compounds **2**-R experience an extra destabilisation as compared with **1**-R. The second benzannelation (reactions 3–2) results in a similar destabilisation to the first one (reactions 2–1). The destabilisation is attributable to the loss of aromaticity (which is present in the reference compound pyridine, but is significantly reduced in the annelated N-containing ring of **2**-R or **3**-R with 7π electrons). A recent estimation[29] of the aromatic stabilisa-

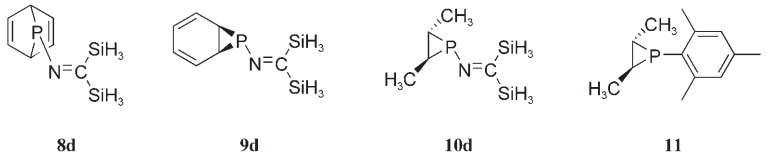


Table 2. Isodesmic reaction energies (*IE*(R) and *IE*(L)) in kcal mol^{-1} (B3LYP/6-311+G**). L denotes energies of isodesmic reactions in the case of the bare "ligands" remaining after cleavage of P–R in Scheme 6; note that in these cases, the double-bond positions differ from those shown in Scheme 6.

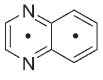
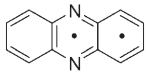
Isodesmic reaction	H *IE*(**a**)	NH_2 *IE*(**b**)	$N{=}CH_2$ *IE*(**c**)	$N{=}C(SiH_3)_2$ *IE*(**d**)	Ligand *IE*(L)
2–1	−23.6	−22.9	−22.9	−23.0	−1.3
3–2	−24.8	−22.4	−24.3	−25.8	−2.4
6–5	5.2	4.5	4.6	4.3	−8.5
7–6	3.2	1.6	2.0	3.0	−12.3

tion in pyridine is 31–33 kcal mol^{-1}, which is not far from the 25 kcal mol^{-1} obtained for reactions 2–1 and 3–2, respectively. The NICS(0)[21,30] and NICS(1) values for the six-membered rings of **2a** are +4.1 and +1.6 ppm, respectively. These small positive values indicate non-aromaticity (at the slight antiaromatic side). To the contrary, the corresponding NICS(0) and NICS(1) values for the pyridine imine obtained after the loss of the phosphinidene in reaction of **2**-R are −6.3 and −9.9 ppm which indicates—as expected—a significant aromaticity in the pyridine ring.

In case of the reactions of **4**-R, the increased aromatic stabilisation of the product phenanthroline (in comparison to bipyridine) shifts the dissociation energies and Gibbs free energies even further to the negative direction, although the difference is not substantial. It should be noted that phenanthroline has a rigid structure and is not able to undergo conformational isomerisation, whereas in case of the 2,2′-bipyridine, the *cis–trans* conformational change lowers the energy by 7.7 kcal mol^{-1} at the B3LYP/6-311+G** level (for the other two bipyridine-type ligands, similar conformational energy changes of 7.5 and 5.4 kcal mol^{-1} have been computed).

For type **C** compounds (**5**-R–**7**-R), an opposite trend than for type **B** compounds is observed: the dissociation energy (and Gibbs free energy) increases with the number of benzannelations. This suggests that the aromaticity of the ligands might decrease in the order pyrazine (in **5**-R) > quinoxaline (in **6**-R) > phenazine (in **7**-R). The NICS(0) and NICS(1) values for these compounds in Table 3 (in good accordance with former studies[30]) reveal that the central ring of the phenazine system shows the largest and the pyrazine the smallest aromaticity, although the differences are only minor.

Table 3. NICS(0) and NICS(1) values of benzene, pyrazine, quinoxaline and phenazine (in ppm, at B3LYP/6-311+G** level on geometries optimised at B3LYP/6-311+G**).

			 A B		 A B	
			A	B	A	B
NICS(0)	−8.0	−5.3	−6.1	−8.8	−9.2	−7.4
NICS(1)	−10.2	−10.2	−10.5	−10.9	−12.8	−10.0

Nevertheless, the isodesmic reaction energies in Table 2 show that the stability of the quinoxaline ring is 8.5 kcal mol^{-1} less than that of pyrazine plus benzene (the energy of the corresponding isodesmic reaction for naphthalene and benzene is of similar value: 11.3 kcal mol^{-1}), showing that the NICS values estimate the aromaticity of the pyrazine moiety only and not that of the entire fused ring system. While the stabilization of the ligands decreases somewhat with benzannelation, the energy of the isodesmic reactions 6–5 and 7–6 (Scheme 6), shows only a small stability enhancement with increasing number of benzannelated rings. This effect (which is again not sensitive to the substituent R) may be associated with the 0.01 Å shorter C–N bond lengths in case of benzannelated rings.

The activation energy of the phosphinidene loss was calculated for compounds **3a–d** and **5a–d**, which could be the most promising phosphinidene-generating targets, and **8a–d**, which are the analogues of the already applied phosphinidene sources (Table 4). Interestingly, in the case of compounds **8c** and **8d**, concerted reaction paths could only be found (see Figure 3 for **8c**). For compounds **8a** and **8b**, a stepwise mechanism with norcaradiene-type intermediates was obtained. All the other compounds (with nitrogen het-

Table 4. Energies of the transition states (E_{TS1}) and intermediates (E_{IM}) compared to the energies of complex compounds (**3a–d**, **5a–d**, **8a–d**) and reaction energies in the phosphinidene elimination reactions (in kcal mol^{-1}, B3LYP/6-311+G**).

	E_{TS1}	E_{IM}		E_{TS1}	E_{IM}		E_{TS1}	E_{IM}
3a	12.1	−2.9	**5a**	15.3	−50.3	**8a**	25.6	−17.4
3b	17.2	7.5	**5b**	6.9	−39.7	**8b**	15.8	−8.0
3c	15.8	−0.5[a]	**5c**	8.5	−49.9	**8c**	12.0	–[b]
3d	10.1	−13.8	**5d**	4.5	−52.8	**8d**	5.4	–[b]

[a] Following the intermediate, a second transition state was found with an energy barrier of 1.7 kcal mol^{-1}. [b] The reaction proceeds by a concerted mechanism, no intermediate was found.

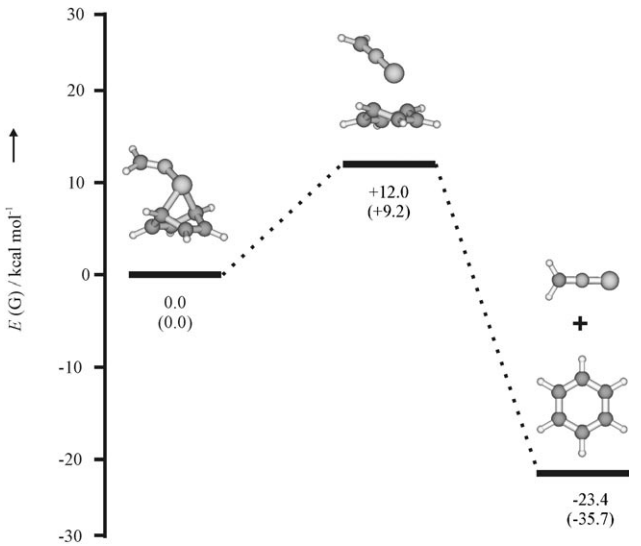


Figure 3. Reaction path along the reaction coordinate for **8c**. B3LYP/6-311+G** energies and Gibbs free energies (in brackets) in kcal mol^{-1}.

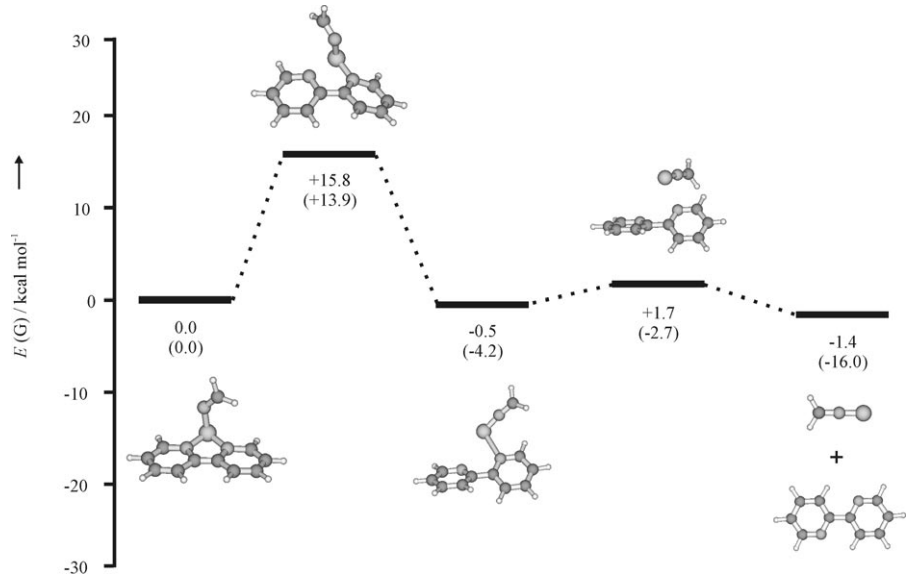


Figure 4. Reaction path along the reaction coordinate for **3c**. Energies and Gibbs free energies (in brackets) in kcal mol^{-1}. (B3LYP/6-311+G**//B3LYP/6-311+G**).

eroatoms) eliminate the phosphinidene by means of a stepwise mechanism (for an example, see Figure 4 for **3c**). In the latter case (compounds **3a–d** and **5a–d**), the intermediates formed (Figure 3) are best described as η^1-adducts of the phosphinidene (note that phosphinidenes are known to be stabilised by nucleophiles[7b,9,11,13,31]). Some η^1-adducts are similar in energy to the ligand+phosphinidene system; however, the entropy factor makes the dissociation reaction favourable. The phosphinidene loss from the η^1-adducts (**3a–d** and **5a–d**) and the norcaradienes (**8a** and **8b**) proceeds with a remarkably small barrier (except for **3c**). Examination of the values of the barrier heights reveals that the dissociation has no kinetic hindrance and the activation barriers of the complexes with N-donor ligands are not higher than those of the norbornadiene-type compounds.

Conclusion

1,3,2-Diazaphospholenes (**A**, Scheme 3) can be described as phosphinidene complexes with N-donor ligands and as such they may dissociate to form phosphinidenes. The dissociation Gibbs free energies for this fragmentation process were calculated at different levels of theory for a wide range of promising phosphinidene precursors which are distinguished by the presence of different substituents R at phosphorus and the embedding of the parent heterocycle into a bipyridine-like (**B**, Scheme 3) or a pyrazine-like (**C**, Scheme 3) fused ring system. The dissociation energy (and Gibbs free energy) decreases with the increasing stability of the singlet phosphinidene depending on R. A further systematic change can be observed for species with the same substituent R: the most important factor here is the aromatic stabilisation of the N-donor ligand formed upon releasing the phosphinidene, although stabilisation of the starting complex may have some influence as well. In type-**B** complexes, the increasing number of benzannelations promotes the dissociation, whereas in type-**C** complexes, ring fusion renders the dissociation thermodynamically less favourable. The energies of transition structures corresponding to the loss of phosphinidene for the different precursors studied are reasonably small, allowing the dissociation kinetically.

On the basis of our calculations, the phosphinidene complexes under study display a wide spectrum of dissociation Gibbs free energies and have thus different phosphinidene-generating power. The phosphinidene complexes with negative dissociation Gibbs free energies seem to be promising precursors for experimental studies directed to the generation of stable free phosphinidenes.

Acknowledgement

Financial support from OTKA T049258 is gratefully acknowledged.

[1] The first push, push carbene, the imidazol-2-ylidene has been reported by a) A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363; the first example of a push, pull carbene, the phosphono–silyl–carbene $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{P{-}C{-}SiMe}_3$ (also referred to as Bertrand-carbene) has been reported first by b) A. Igau, H. Gruetzmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1988**, *110*, 6463–6466; c) A. Igau, A. Baceiredo, G. Trinquier, G. Bertrand, *Angew. Chem.* **1989**, *101*, 617–618; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 621–622. For recent reviews see: d) D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92; e) W. Kirmse, *Angew. Chem.* **2004**, *116*, 1794–1801; *Angew. Chem. Int. Ed.* **2004**, *43*, 1767–1769; f) E. Hahn, *Angew. Chem.* **2006**, *118*, 1374–1378; *Angew. Chem. Int. Ed.* **2006**, *45*, 1348–1352.

[2] The first stable example reported by M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. L. Metzler, *J. Am. Chem. Soc.* **1994**, *116*, 2691–2692.

[3] The first bottleable example reported by W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki, M. Wagner, *Angew. Chem.* **1992**, *104*, 1489–1492; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1485–1488.

[4] D. Enders, T. Balensiefer, *Acc. Chem. Res.* **2004**, *37*, 534–541.

[5] The only phosphinidenes detected so far at low temperature were ground state triplets: a) X. Li, D. Lei, M. Y. Chiang, P. P. Gaspar, *J. Am. Chem. Soc.* **1992**, *114*, 8526–8531; b) X. Li, S. I. Weissman, T. S. Lin, P. P. Gaspar, A. H. Cowley, A. I. Smornov, *J. Am. Chem. Soc.* **1994**, *116*, 7899–7900; c) G. Bucher, M. L. G. Borst, A. W. Ehlers, K. Lammertsma, S. Ceola, M. Huber, D. Grote, W. Sander, *Angew.*

Chem. **2005**, *117*, 3353–3357; *Angew. Chem. Int. Ed.* **2005**, *44*, 3289–3293.

[6] Z. Benkõ, R. Streubel, L. Nyulászi, *Dalton Trans.* **2006**, *36*, 4321–4327.

[7] Similar to carbenes, transition-metal complexes with phosphinidene ligands are accessible and widely used in coordinative and organophosphorus chemistry. Recent reviews: a) K. Lammertsma, Phosphinidenes, *Top. Curr. Chem.* **2003**, *229*, 95–119; b) F. Mathey, *Dalton Trans.* **2007**, *19*, 1861–1868.

[8] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1981**, *103*, 4587–4589.

[9] a) S. Shah, M. C. Simpson, R. C. Smith, J. D. Protasiewicz, *J. Am. Chem. Soc.* **2001**, *123*, 6925–6926; b) I. Kovács, E. Matern, E. Sattler, G. Fritz, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1819–1822; c) H. Krautscheid, E. Matern, I. Kovács, G. Fritz, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1917–1924; $R'-P=PR_3$: note that these compounds can be considered as phosphinidene complexes of a phosphane.

[10] a) A. Marinetti, F. Mathey, F. Fischer, A. Mitschler, *J. Chem. Soc. Chem. Commun.* **1982**, *12*, 667–668; b) A. Marinetti, F. Mathey, F. Fischer, A. Mitschler, *J. Am. Chem. Soc.* **1982**, *104*, 4484–4485.

[11] Recent papers: a) N. H. T. Huy, S. Hao, L. Ricard, F. Mathey, *Organometallics* **2006**, *25*, 3152–3155; b) I. Kalinina, F. Mathey, *Organometallics* **2006**, *25*, 5031–5034.

[12] M. L. G. Borst, R. E. Bulo, C. W. Winkel, D. J. Gibney, A. W. Ehlers, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2005**, *127*, 5800–5801.

[13] S. B. Clendenning, P. B. Hitchcock, M. F. Lappert, P. G. Merle, J. F. Nixon, L. Nyulászi, *Chem. Eur. J.* **2007**, *13*, 7121–7128.

[14] A. Sundermann, M. Reiher, W. W. Schoeller, *Eur. J. Inorg. Chem.* **1998**, *3*, 305–310.

[15] a) T. Gans-Eichler, D. Gudat, M. Nieger, *Angew. Chem.* **2002**, *114*, 1966–1969; *Angew. Chem. Int. Ed.* **2002**, *41*, 1888–1891; b) T. Gans-Eichler, D. Gudat, K. Nättinen, M. Nieger, *Chem. Eur. J.* **2006**, *12*, 1162–1173.

[16] First example: a) M. K. Denk, S. Gupta, R. Ramachandran, *Tetrahedron Lett.* **1996**, *37*, 9025–9028; b) A. H. Cowley, C. J. Carmalt, V. Lomeli, *Chem. Commun.* **1997**, *21*, 2095–2096; c) M. K. Denk, S. Gupta, A. J. Lough, *Eur. J. Inorg. Chem.* **1999**, *1*, 41–49.

[17] S. Bonnet, J.-P. Collin, M. Koizumi, P. Mobian, J.-P. Sauvage, *Adv. Mater.* **2006**, *18*, 1239–1250.

[18] a) B.-H. Ye, M.-L. Tong, X.-M. Chen, *Coord. Chem. Rev.* **2005**, *249*, 545–565; b) C. Kaes, A. Katz, M. W. Hosseini, *Chem. Rev.* **2000**, *100*, 3553–3590.

[19] Gaussian 03 (Revision C.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian Inc., Wallingford CT, **2004**.

[20] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[21] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

[22] G. Schaftenaar, J. H. Nordik, *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123–134.

[23] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553–566.

[24] a) D. Gudat, A. Haghverdi, M. Nieger, *Angew. Chem.* **2000**, *112*, 3211–3214; *Angew. Chem. Int. Ed.* **2000**, *39*, 3084–3086; b) S. Burck, D. Gudat, F. Lissner, K. Nättinen, M. Nieger, T. Schleid, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2738–2745.

[25] H. H. Karsch, P. A. Schlüter, F. Bienlein, M. Herker, E. Witt, A. Sladek, M. Heckel, *Z. Anorg. Allg. Chem.* **1998**, *624*, 295–309.

[26] D. Gudat, A. Haghverdi, H. Hupfer, M. Nieger, *Chem. Eur. J.* **2000**, *6*, 3414–3425.

[27] a) Experimental value: 20 kcal mol^{-1}: P. F. Zittel, W. C. Lineberger, *J. Chem. Phys.* **1976**, *65*, 1236–1243; b) Calculated value at QCISD(T)/6-311++G(3df,2p) 28 kcal mol^{-1}: M. T. Nguyen, A. V. Keer, L. G. Vanquickenborne, *J. Org. Chem.* **1996**, *61*, 7077–7084.

[28] At QCISD(T)/6-311++G(3df,2p), the reported value is 1.2 kcal mol^{-1} (see reference [27b]).

[29] P. v. R. Schleyer, F. Puhlhoffer, *Org. Lett.* **2002**, *4*, 2873–2876.

[30] For a recent review see Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842–3888. Nevertheless, it should be noted that the usefulness of NICS values to assess the extent of aromaticity in polycyclic arenes has recently been questioned (P. Bultink, S. Fias and R. Ponec, *Chem. Eur. J.* **2006**, *12*, 8813).

[31] S. Grigoleit, A. Alijah, A. Rozhenko, R. Streubel, W. W. Schoeller, *J. Organomet. Chem.* **2002**, *643–644*, 223–230.

Received: July 13, 2007
Published online: October 22, 2007

