

Stretching the P–C Bond. Variations on Carbenes and Phosphanes

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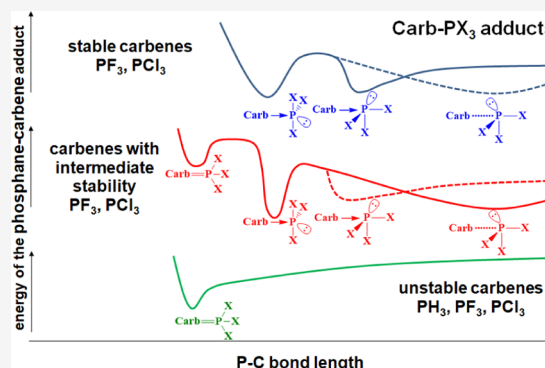
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ABSTRACT: The stability and the structure of adducts formed between four substituted phosphanes (PX_3 , X:H, F, Cl, and NMe_2) and 11 different carbenes have been investigated by DFT calculations. In most cases, the structure of the adducts depends strongly on the stability of the carbene itself, exhibiting a linear correlation with the increasing dissociation energy of the adduct. Carbenes of low stability form phosphorus ylides (F), which can be described as phosphane \rightarrow carbene adducts supported with some back-bonding. The most stable carbenes, which have high energy lone pair, do not form stable F-type structures but carbene \rightarrow phosphane adducts (E-type structure), utilizing the low-lying lowest unoccupied molecular orbital (LUMO) of the phosphane (with electronegative substituents), benefiting also from the carbene–pnictogen interaction. Especially noteworthy is the case of PCl_3 , which has an extremely low energy LUMO in its T-shaped form. Although this PCl_3 structure is a transition state of rather high energy, the large stabilization energy of the complex makes this carbene–phosphane adduct stable. Most interestingly, in case of carbenes with medium stability both F- and E-type structures could be optimized, giving rise to bond-stretch isomerism. Likewise, for phosphorus ylides (F), the stability of the adducts G formed from carbenes with hypovalent phosphorus (PX –phosphinidene) is in a linear relationship with the stabilization of the carbene. Adducts of carbenes with hypervalent phosphorus (PX_3) are the most stable when X is electronegative, and the carbene is highly nucleophilic.



INTRODUCTION

Carbenes (Carb—this notation will be used throughout) are divalent carbon compounds, stabilized mainly by heteroelements like nitrogen or sulfur,^{1–5} yielding N-heterocyclic carbenes (NHCs) or cyclic aminocarbenes (CAACs) just to mention the most widely applied ligands of transition metals.^{6–9} Moreover, as strong nucleophiles,¹⁰ these ligands can stabilize otherwise highly reactive molecules formed from p-block elements.^{11,12} Furthermore, they react with weak Lewis acids as silanes^{13–18} and phosphanes.^{18–40} The NHC–silane adducts could apparently be described by dative bond formation,^{13–18,41,42} being stabilized by (i) electronegative substituents (e.g. halogens) at silicon and (ii) by the increased nucleophilicity of the carbenes.^{41,42} The products from the reactions between different NHCs and phosphanes are more diverse (Figure 1: A–E), depending on the reaction conditions and the nature of the starting materials.^{13–19,22,25–32,34–40} The parent H-phosphanes did not react with imidazol-2-ylidene (1 R:Dipp);²² however, imidazolidine-2-ylidene (2 R:Dipp)²² and CAAC (3)¹⁹ were activating the PH bond, yielding primary phosphanes A (X = alkyl or aryl, Y:H see Figure 1). Imidazol-2-ylidene flanked by iPr groups at the nitrogen atoms reacts with diphenylphosphane in a dehydrocoupling reaction, assumedly via the phosphane intermediate A.⁴³ Various NHCs react with R_2PCl ^{25–27} (R: aryl or alkyl) and often formed cationic species (B)^{28,29} (with chloride counterion).

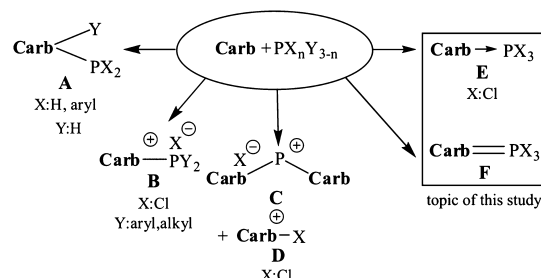


Figure 1. Recently synthesized carbene (Carb)–phosphane systems (A,^{19,22} B,^{28–32,34–37} C,²⁰ D,²⁰ and E^{38–40,44–48}) and the phosphorus ylide (F).

On the other hand, the reaction of PCl_3 with imidazol-2-ylidenes having small substituents (R: Et, iPr, Mes) gave cationic (C) compounds²⁰ (the apparent byproduct Cl_2 being sequestered by a third molecule of NHC). Imidazol-2-ylidene (R:Dipp^{33,34} and R:Me³⁵) formed adducts,^{38–40} which,

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analogous to the silane case, were described with a single dative bond E ($X = Cl$) on the basis of the $P-C$ distance.^{38–40,44–48} These structures exhibit a “see-saw” arrangement at phosphorus.^{38–40} Further interactions between carbenes and phosphanes have also been studied computationally,^{49,50} with specific emphasis on weak pnictogen interactions.^{51–53} According to these calculations, carbene–phosphane distances between ~ 2.0 and 3.3 Å were reported for different stabilized singlet carbenes (including the NHC imidazol-ylidene and its oxygen analogue NOC) and various substituents at phosphorus. In case of the shortest (2.0 – 2.3 Å) distances, the energy of the interaction between carbene and phosphane approaches 15 – 20 kcal/mol,^{49,50} and phosphorus has a distorted trigonal bipyramidal arrangement (E' structure).

On the contrary, the bonding between a carbene $R_2C:$ and a phosphane $:PR_3$ is traditionally described as an ylidic double bond (λ^5 - $P=C$ bond).^{54–72} While the charge separation ($P^+ - C^-$ character) can clearly be seen in the photoelectron spectrum,⁷³ the bond distance⁷⁴ is matching that of the λ^3 - $P=C$ bond.^{75–79}

Furthermore, Bader analysis provides similar characteristics (density and ellipticity) at the bond critical point for the λ^3 - $P=C$ and λ^5 - $P=C$ bonds.^{80,81} Both the similarities and the differences can be understood, considering the presence of a hyperconjugative pseudo- π center (formed from the orbitals of the P -substituents) in case of the λ^5 -derivative.⁸⁰ In fact, this bonding model is equivalent to the model shown in Figure 2,

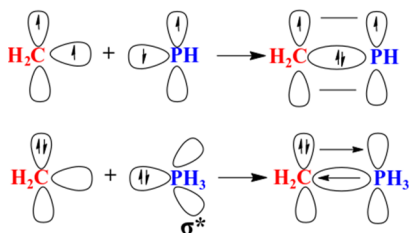


Figure 2. Bonding description of the λ^3 - $P=C$ and λ^5 - $P=C$ double bonds. The nonperpendicular (with respect to the bond) p-orbital lobes symbolize a σ^* phosphorus-substituent orbital, which is involved in π -type back bonding.

considering the donation of the phosphine lone pair to the empty orbital of the (singlet) carbene augmented by a back donation of the carbene lone pair to the σ^* orbitals at phosphorus (negative hyperconjugation).⁸² The highest occupied molecular orbital (HOMO) of $H_2C=PH_3$ (Figure 3 structure a) clearly shows the bond polarization (large

contribution at carbon) but also the back donation toward phosphorus can easily be recognized.

In contrast, the HOMO of the λ^3 - $P=C$ bond ($CH_2=PH$) is nearly equally distributed between phosphorus and carbon (Figure 3 structure b), in accordance with the similarity between the $P=C$ and $C=C$ bonds.^{79,83}

Accordingly, as an adduct between NHC and phosphane, the formation of an F-type structure, which is the λ^5 - $P=C$ counterpart of G, can also be envisaged. Stable singlet carbenes form G-type adducts with phosphinidene (known examples are I–II,^{22,84–87,89,93–98,101–103} III–IV,⁹⁰ V^{91,92,104}), as shown in Figure 4. The resulting inversely polarized^{105,106} phosphalkenes^{107–111} (note the HOMO in Figure 3 structure c),^{91,92,104–106} are of recent interest,^{84,86,87,89,90,94–98} as the phosphorus analogues^{91,92,104–106} of the deoxy-Breslow intermediate (Figure 5),^{112–116} which, as a strong nucleophile, has a key role in umpolung reactions.^{117–119} Moreover, the ^{31}P NMR chemical shifts of these type of compounds were correlated with the π -polarizations of carbene–phosphorus bond as well.¹²⁰

Recently, these kind of adducts were reviewed, and their applications were highlighted as well.^{121–123}

Thus, the formation of any λ^5 - P containing F-type structure, where the NHC and the ylidic structure with opposing polarizing effects on the double bond (Figure 3), is clearly an interesting possibility; however, this type of adduct was not observed in the reactions between NHCs and phosphanes considered so far. This might be in accordance with the known destabilizing effect⁷² of the amino substituents on phosphorus ylides; nevertheless, some C-amino-phosphorus ylides could be synthesized.^{124,125}

In view of the wide variation of the reaction products between phosphanes and different NHCs (Figure 1), the aim of the present computational study is the comprehensive investigation of the systems formed from the PX_3 ($X = H, F, Cl, NMe_2$) moiety and carbenes 1–11, yielding compounds with different electronic structures (in particular A, E, and F in Figure 1). The carbenes selected for our investigation (depicted in Figure 6) include mainly synthesized structures with (i) different σ -donor properties and (ii) with different stabilization (resulting mainly from π -donor interactions, raising the energy of the carbene empty orbital and consequently the singlet–triplet gap). The extent of the stabilizing interaction can be measured by singlet–triplet gap but more conveniently with the energy (ΔE_{ISO}) of the isodesmic reaction 1.¹²⁶

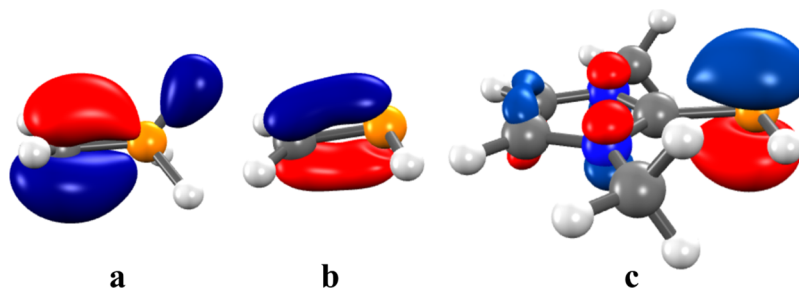
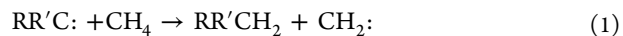


Figure 3. HOMO of $CH_2=PH_3$ (a), $CH_2=PH$ (b), and $NHC=PH$ (c). a has a methylene localized orbital, b exhibits an ethylene-like balanced π -system, while the HOMO of c is localized mainly at phosphorus. Back-bonding can be seen in case of a and also for c.

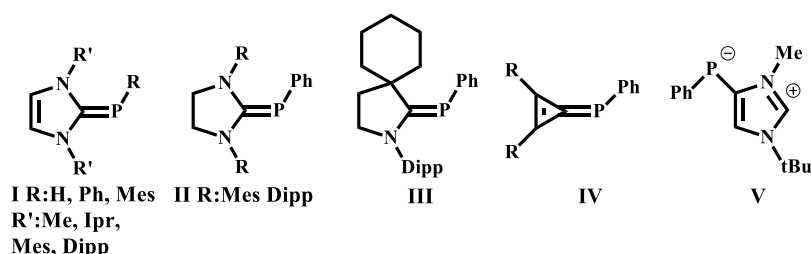


Figure 4. Selected carbene–phosphinidene (G-type) adducts which were synthesized recently.^{30,83–100}

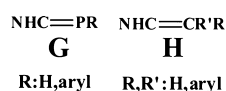


Figure 5. Double bonded adduct of the NHC and phosphinidene (G) and its analogue, the deoxy-Breslow intermediate (H).

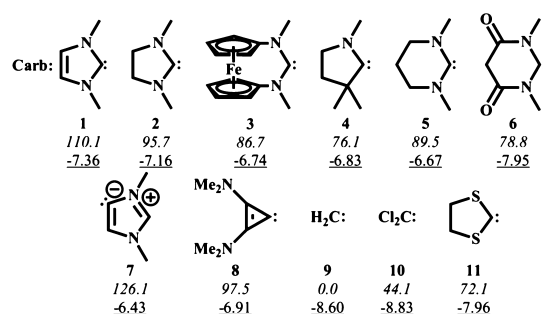


Figure 6. “Reactant” carbenes considered in the present study, together with stabilization energies in the isodesmic reaction 1 (ΔE_{ISO} italics and in kcal/mol) and their HOMO energies (ϵ underlined and in eV).

The stabilization energies (ΔE_{ISO}) from reaction 1 for the targeted carbenes are given in Figure 6 and Table S1. In the present work, we investigate the relative stability of the possible isomers, in case of the different carbenes, and discuss comprehensively the effect of the formal increase of the phosphorus valency on the P–NHC bond of the G-type compounds.

COMPUTATIONAL DETAILS

All calculations have been carried out with the Gaussian 09 program package.¹²⁷ Full geometry optimization was performed for all molecules at the ω -B97XD/cc-pVTZ¹²⁸ and M06-2X/cc-pVTZ¹²⁹ levels and also at the B3LYP-D3/cc-pVTZ level for calculations on isodesmic reaction 1 and on G-type adducts,^{130,131} followed by calculation of harmonic vibrational frequencies at the same levels to establish the nature of the stationary points obtained, as characterized by only positive eigenvalues of the Hessian for minima. Gibbs free energies were obtained from the calculated harmonic frequencies at 298 K and atmospheric pressure. During the discussion, we use M06-2X/cc-pVTZ results, the slightly different data obtained at the other levels of the theory are given in the Supporting Information. The Multiwfn program¹³² was used for the determination of the bond critical points with the corresponding electron densities and ellipticities. For the visualization of the molecules and molecular orbitals, MOLDEN¹³³ and IQmol¹³⁴ programs were used.

RESULTS AND DISCUSSION

First, we discuss briefly the G-type carbene–phosphinidene adducts with carbenes 1–11. The P–C bond distance in these compounds (1.638–1.762 Å—see Table S2 of the Supporting Information) varies significantly, but it is in each case shorter than the P–C single bond (1.87 Å),¹³⁵ allowing to conclude that G is a (polarized) double bonded structure. As it can be expected, the molecules with longer P–C distances generally exhibit smaller dissociation energies (see Table S2 in the Supporting Information). The strongest bond (high adduct stability) belongs to those carbenes which exhibit the smallest stabilization energies (ΔE_{ISO}) in reaction 1,¹²⁶ as is evidenced by the linear correlation shown in Figure 7. It should be noted

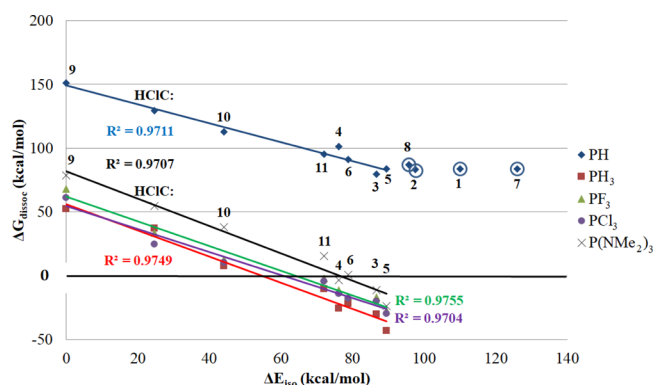


Figure 7. Correlation between ΔE_{ISO} carbene stabilization energy and the dissociation Gibbs free energy of the Carb=PH systems into carbene and (singlet) PH, and the F-type Carb=PX₃ systems into carbene and PX₃ (X: H, F, Cl, NMe₂). The numbers of the “complexed” carbenes are given in the figure. Also the points for HCIC: are added to provide additional points in the 0–40 kcal/mol ΔE_{ISO} range. In case of the G-type compounds, the dissociation energy remains unchanged above $\Delta E_{\text{ISO}} > 90$ kcal/mol. These points (encircled) were excluded from the correlation.

that for the most stabilized carbenes ($\Delta E_{\text{ISO}} > 90$ kcal/mol), the dissociation energy remains nearly unchanged showing a saturation effect, and accordingly, we have excluded these points from the correlation. The decrease of the double bond character results here in the polarization of the π -type HOMO, which then has a significant lone pair character as demonstrated in Figure 3c by the case of the most stabilized carbene 1. The polarization of this orbital decreases in case of the G-type compounds derived from less stabilized carbenes (see Figure S1 in the Supporting Information). Furthermore, these compounds also possess the “usual” in-plane lone pair orbital (shown also in Figure S1 of the Supporting Information) characteristic for the P=C bond. Utilizing these two orbitals, the most polarized G-type compounds

Table 1. M06-2X/cc-pVTZ Dissociation Gibbs Free Energy (ΔG_{diss} in kcal/mol) and Distance between the P Moiety and the Carbene Unit (A) of the Investigated Compounds with Different Substituents (X) at Phosphorus^a

X	H			F			Cl			NMe ₂		
	A	E	E'	A	E	E'	A	E	E'	A	E	E'
1	ΔG_{diss}	-8.4	-27.7	-9.1	-2.6	-2.6	-16.6	-41.2	-2.4	-16.6	-41.2	-39.0
	$d_{\text{p-C}}$	1.973	1.876	1.897	2.633	2.633	1.941	1.919	2.285	1.941	1.919	1.713
2	ΔG_{diss}	7.8	-15.6	-9.7	-2.5	-2.5	-12.6	-28.0	-2.3	-12.6	-28.0	-28.0
	$d_{\text{p-C}}$	1.907	1.892	1.910	2.619	2.619	1.943	1.947	2.335	1.943	1.947	1.707
3	ΔG_{diss}	12.9	-20.8	-15.3	-5.9	-16.8	-15.2	-11.3	-6.0	-15.2	-11.3	-11.3
	$d_{\text{p-C}}$	1.891	1.937	1.956	2.904	1.634	2.002	1.685	2.884	2.002	1.685	1.695
4	ΔG_{diss}	27.9 ^d	1.7 ^d	-3.0 ^d	-2.3 ^d	-11.0	17.8 ^d	-42.5 ^d	-1.5 ^d	-2.4 ^d	-42.5 ^d	-3.5
	$d_{\text{p-C}}$	1.875	1.877	1.885	2.485	1.627	1.939	1.867	2.243	1.939	1.867	1.673
5	ΔG_{diss}	3.1	-15.4	-9.9	-2.7	-27.0	-19.8	-23.5	-2.6	-19.8	-23.5	-23.5
	$d_{\text{p-C}}$	1.892	1.909	1.936	2.784	1.651	1.912	1.906	2.855	1.912	1.906	1.685
6	ΔG_{diss}	23.7	-10.2	-20.0	-3.7	-16.1	7.0	1.1	-4.2	7.0	1.1	1.1
	$d_{\text{p-C}}$	1.908	1.912	1.951	2.891	1.665	1.976	1.897	3.025	1.976	1.897	1.697
7	ΔG_{diss}	-15.6	-33.9	0.0	0.0	0.0	-24.0	-34.6	4.8	-24.0	-34.6	-34.6
	$d_{\text{p-C}}$	1.983	1.852	1.884	2.352	1.863	1.958	1.863	2.041	1.958	1.863	1.933
8	ΔG_{diss}	7.2	-17.7	-8.0	-3.3	-3.3	-2.1	-31.5	-3.2	-2.1	-36.4	-31.5
	$d_{\text{p-C}}$	1.861	1.825	1.878	2.700	1.831	1.859	1.865	2.104	1.859	1.865	1.717
9	ΔG_{diss}	100.5	57.3	68.2	68.2	68.2	86.5	79.0	61.4	86.5	79.0	79.0
	$d_{\text{p-C}}$	1.859	1.850	1.608	1.608	1.608	1.877	1.629	1.629	1.877	1.629	1.656
10	ΔG_{diss}	57.7	20.5	12.8	12.8	12.8	50.2	38.3	10.6	50.2	38.3	38.3
	$d_{\text{p-C}}$	1.870	1.889	1.628	1.628	1.628	1.947	1.664	1.664	1.947	1.664	1.689
11	ΔG_{diss}	31.9	-3.3	-24.3	-5.7	2.0	17.7	15.4	-5.4	17.7	15.4	15.4
	$d_{\text{p-C}}$	1.867	1.874	1.924	3.035	1.645	1.938	1.689	3.012	1.938	1.689	1.702

^aEndoergic dissociation energies (stable compounds) are given in bold letters. B3LYP/cc-pvDZ and ω -B97XD/cc-pvTZ data are compiled in Table S4 in the Supporting Information—all giving similar results. ^bThe optimized structure (-10.8 kcal/mol) has a 2.41 Å C-Cl distance, indicating the easy formation of a C-type structure (see also Figure S2 in the Supporting Information). ^cThe optimized structure has a 3.67 Å C-Cl distance, indicating the easy formation of a C-type structure (see also Figure S2 in the Supporting Information). ^dIt should be noted that the prochiral carbene 4 can form two stereoisomers with phosphanes; however, the stability of the two structures does not differ significantly.

can even complex two Lewis acids.⁹⁶ Bader analysis¹³⁶ on the P–C bond shows that at the bond critical point, electron densities are between 0.150 and 0.190 (single bond 0.148, double bond 0.187).⁷⁶ The ellipticity values (0.407–0.550) indicate an asymmetric electron distribution characteristic for π -systems (see Table S3 in the Supporting Information).

In a noteworthy contrast with the above discussed carbene–phosphinidene adducts, the optimized structures of the adducts between carbenes (1–11) and phosphanes PX_3 ($X = H, F, Cl, NMe_2$) exhibit high diversity, and the optimized structures can be classified as A, E, and F types on the basis of the atomic connectivity and the P–C distance. C-type structures from apparent reasons cannot be obtained in the gas phase optimization. However, in some cases, cationic like structures could be optimized, see footnotes a and b in Table 1. To characterize the different structures and their stability, we collected the P–C distances and the dissociation Gibbs free energies in Table 1 for the different carbene–phosphane adducts. Compounds with endoergic dissociation energies (stability against dissociation) are given in bold letters. Clearly, the least stabilized carbenes 9 and 10 (see Figure 6) form the most stable adducts throughout.

In case of the PH_3 adducts, only A- and F-type structures were obtained, the A-type structure being always the more stable one. This is in accordance with the general understanding¹³⁷ that in the condensed phase H-ylides of phosphorus (F) rearrange to their phosphane (A) counterparts via 1,2-H-shift¹³⁸ with the exception of some notable kinetically hindered cases.^{139,140} In case of 1, 2, 7, and 8, no F-type structure could be optimized (neither at ω -B97XD/cc-pVTZ nor at M06-2X/cc-pVTZ see Tables 1 and S4), only very weakly bonded complexes with P–C distance over 3.2 Å could be obtained. Furthermore, among the F-type PH_3 adducts, only the least stabilized carbenes ($\Delta E_{ISO} < \text{ca. } 50$ kcal/mol) are stable against dissociation (Figure 7). It is noteworthy that in case of 1 and 7, also the A-type phosphanes tend to dissociate; in accordance, no reaction product was obtained in the reaction of PH_3 with an unsaturated imidazol-2-ylidene (flanked by bulky Dipp substituents).²² In contrast, the saturated analogue (the Dipp substituted analogue of 2) gave the insertion product,²² in agreement with its calculated stability against dissociation to $PH_3 + 2$. Altogether, these results provide an indirect evidence on the reliability of our calculations.

For the PX_3 ($X: F, Cl, NMe_2$) series in case of the least stabilized methylene (9) and dichlorocarbene (10), once more only the A- and F-type structures could be optimized, and all of them turned out to be stable against dissociation. Similar to the PH_3 adducts, A-type structures are more stable than F-type structures with the sole exception of $F_3P=CH_2$. For the most stabilized carbenes (ΔE_{ISO} larger than ca. 90 kcal/mol—Figure 6), no F-type structures could be optimized, while for carbenes with ΔE_{ISO} between 70 and 90 kcal/mol, the F-type structures obtained are unstable against dissociation (Table 1). The decreasing stability of the carbenes (ΔE_{ISO}) correlates with the increasing stability (in terms of Gibbs free energy) of the F-type adducts, as shown in Figure 7, exhibiting similar slope for all phosphorus compounds, including the above discussed G-type phosphinidene adducts. Depending on the phosphane substituent, the dissociation Gibbs free energy of the F-type adducts is by about 70–100 kcal/mol smaller than that in the G series. Amongst the F-type systems, Carb + $P(NMe_2)_3$ (black points in Figure 7) exhibits the highest, while Carb +

PH_3 (red points in Figure 7) exhibits the lowest stability. Similar linear correlation was also observed between ΔE_{ISO} of a series of carbenes and the stability of the corresponding Breslow intermediates, which can be described as a hydroxycarbene adduct of the given carbene.¹⁴¹ Also the dimerization Gibbs free energy of the carbene itself correlates with ΔE_{ISO} .¹²⁶ Clearly, the raising energy of the carbene empty orbital (due to the stabilizing π -interactions) makes the donation from the lone pair of the attacking phosphane less effective. From this point of view, it is noteworthy that the above mentioned “saturation effect” in the stabilization of the G-type adducts for the carbenes with $\Delta E_{ISO} > 90$ kcal/mol is in line with the fact that we were not able to optimize F-type structures for the same carbenes. This fact further corroborates the importance of the donation from the phosphorus lone pair in the F-type structures.

Contrary to the PH_3 adducts in case of the PF_3 , PCl_3 , and $P(NMe_2)_3$ series, most carbenes (with the exception of the least stabilized 9 and 10) form single P–C bonded E-type structures. It is especially noteworthy that the PCl_3 series, where most of the E-type adducts were reported experimentally, is the most stable against dissociation. The P–C distance (1.831–1.948 Å in Table 1) in these compounds falls basically in the single bond regime. The most stable adduct is formed with 7, but even in this case, the ~ 20 kcal/mol interaction Gibbs free energy (without BSSE correction) is far less than a usual P–C bond energy (ca. 63 kcal/mol).¹⁴² These structures exhibit a see-saw arrangement, in accordance with the reported X-ray structures,^{33–35} the chlorophosphane part having a T-shaped form. In this structure, the lone pair on the phosphorus is the HOMO, as shown on the example of the adduct formed between 4 and PCl_3 in Figure 8a. It is

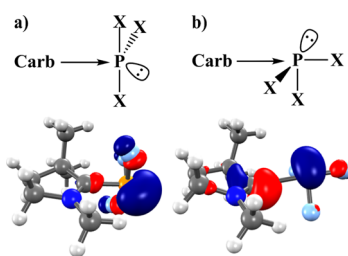


Figure 8. (a) HOMO of the E-type adduct of carbene 4 and PF_3 and (b) HOMO of the E'-type adduct of carbene 4 and PF_3 .

noteworthy that the HOMO of the T-shaped PCl_3 unit (Figure S3 in the Supporting Information) is similar to that of adduct 4, indicating that this feature is unperturbed upon complexation. The T-shaped PCl_3 structure is known as a transition state for the inversion of the phosphorus pyramid,^{143,144} and the barrier of this inversion is 52.0 kcal/mol (55.8 kcal/mol in case of PF_3). This type of molecular geometry was also observed in case of tetrafluorophosphite anion.¹⁴⁵

Thus, it is reasonable to consider that a T-shaped chlorophosphane (fluorophosphane) is able to be complexed by the carbene. Although, the planarization energy is quite large, the lowest unoccupied molecular orbital (LUMO) of the T shaped PCl_3 , which is basically of “p” type (Figure 9), is at -4.27 eV(!), which is much lower than the LUMO energy of the pyramidal phosphane (-0.46 eV). The presence of this easily accessible empty orbital facilitates the complex formation between the strongly nucleophilic carbenes and the T-shaped PCl_3 , by formation of a dative bond. In case of PF_3 , the

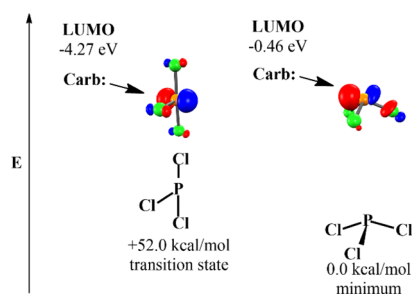


Figure 9. Relative energies of the pyramidal ground state and the T-shaped transition state of PCl_3 (in kcal/mol), together with their LUMO (energies in eV). The direction of the attacking carbene nucleophile (Carb:) is shown by arrows pointing to the LUMO.

corresponding orbital appears at somewhat higher energy (-2.87 eV in Table S5 of the Supporting Information), and accordingly, the dative bond is weaker, explaining the lower dissociation Gibbs free energies in the fluorophosphine complexes. Altogether, the energy gain upon formation of the new P–C (dative) bond of the E structure should cover the energy demand for the formation of the T-shaped PX_3 structure. Because in the most strongly bound E-type structures (Table 1), the P–C distance falls in the usual single bond range, the usual bond strength (about 63 kcal/mol²⁵) can be surmised. Because the energy requirement of the formation of the T-shaped structure is ca. 50 kcal/mol (see above), the calculated 10 – 20 kcal/mol binding Gibbs free energy of the E-type adducts (Table 1) is in reasonable accordance with the aforementioned considerations. The most stable adducts (Table 1) are indeed obtained with the most nucleophilic carbenes (4, 7, 8—their HOMO energies are listed in Figure 6). On the contrary, 6 and 9–11 exhibit the most negative HOMO energies, and accordingly, their complexes are unstable against dissociation. Clearly, the plot of $\Delta\varepsilon$ —the energy difference of the carbene lone pair and the LUMO of the T-shaped PX_3 (X: F, Cl) fragment—against the adduct stabilization energy shows a common correlation (Figure 10), for the PF_3 and PCl_3 adducts. It is noteworthy that 3, 5, and 11 (all large bond angle carbenes—see Table S6 of the Supporting Information) are outliers, exhibiting smaller stability than expected on the basis of the HOMO–LUMO interaction energy of the fragments. Apparently, the steric requirement of these rings is larger than that of the smaller rings, reducing the stability of the adduct. Each PF_3 compound has reduced stability with respect to the corresponding PCl_3 counterpart, in accordance with the difference between the LUMO energies of the T-shaped PF_3 and PCl_3 structures (see Table S5 of the Supporting Information). It is also worthy to mention that the LUMOs of the T-shaped PH_3 and $\text{P}(\text{NMe}_2)_3$ are at significantly higher energies (see Table S5 in the Supporting Information); thus it is understandable that these phosphanes do not form stable “see-saw” adducts with the carbenes. Altogether, in contrast with the F-type structures, where the decisive stabilizing contribution comes from the donation of the phosphorus lone pair to the empty carbene orbital, which is available (having a low energy) only for the less stabilized carbenes, in case of the E-type structure, the donation from the carbene lone pair has the largest stabilizing contribution, in particular with those phosphanes, where the T-shaped structure has a low energy LUMO. It is worth mentioning that the formation of the E-type structure can alternatively be explained starting from the highly stable G-

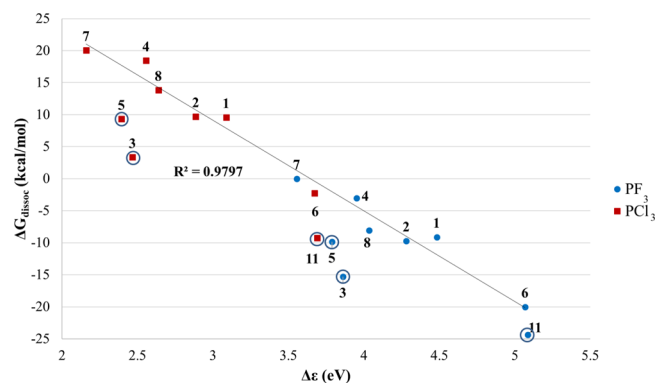


Figure 10. Stability of the E-type complex with the T-shaped PX_3 , ΔG (in kcal/mol), against $\Delta\varepsilon$ the energy difference of the carbene lone pair HOMO and the LUMO of the T-shaped PX_3 fragment (in eV). X: Cl and F. Carbenes 3, 5, and 11 are outliers due to the expanded bond angle around the carbene (as shown in Table S5 of the Supporting Information) and are not considered in the correlation. 9 and 10 do not form E-type adducts. It should also be mentioned that 6 also belongs to the large bond angle carbenes; however, due to its stable HOMO, it forms a weak complex with a long P–C distance, and thus the effect of the steric encumbrance is less important.

type carbene–phosphinidene adduct. By forming a $3c-4e$ hypercoordinate, X–P–X bond with the involvement of the HOMO of G (Figure 3c) and two halogens, the see-saw structure with the T-shaped PX_3 unit, and the residual HOMO – 1 in-plane phosphorus lone pair of G, which becomes then the HOMO (Figure 8a), can clearly be understood.

Further type of complexes with somewhat extended P–C interatomic distance can also be optimized in case of X: Cl and F. These E' structures (Figure 8b) not only exhibit extended P–C bond distances (2.041 – 3.025 Å with the stabilized carbenes: 1–8) compared to the E “see-saw” adduct, but they form a typical trigonal bipyramidal arrangement, with the carbene and one P–X bond aligned axially. The assembly is held together by the recently intensively discussed pnictogen interaction,^{51,146,147} which is interpreted as (i) the electrostatic attraction between the positively charged region (σ -hole) next to the phosphorus lone pair and negative charge at the carbene lone pair and (ii) the donation of the carbene lone pair to the σ^* orbital of the axially aligned P–X bond (see on Figure 8b).^{48–51} The resulting structures were discussed in detail in case of the adducts between highly stabilized carbenes (as imidazol-2-ylidene) and PH_2X (X: halogen).^{48,49} This interaction is weaker than in case of the T-shaped PX_3 because the LUMO is at higher energy (in case of PCl_3 as much as by 3.81 eV—see Figure 9). However, because the T-shaped transition state itself is by about 50 kcal/mol higher energy as was mentioned above, the E and E' structures have comparable stability. While for the PCl_3 series, E structures are more stable than E' (Table 1) due to the highly stabilized LUMO of the T-shaped structure, the stability order is reversed for the PF_3 series, where the LUMO of the T-shaped PF_3 structure has higher energy (see Table S5 in the Supporting Information). Altogether, most of the E' structures are unstable against dissociation. The P–C distances are varied over a wide range (2.041 – 3.025 Å in case of PCl_3 adducts, as seen in Table 1) for the different carbenes. Similarly, a large variation was found in the P–C distances in the case of the adducts of a single carbene (e.g. imidazol-2-ylidene) and a series of phosphanes (H_2PX (X: F, Cl, Br, OH, NH_2 , CN, NC)).^{48,49} In that papers,

two types of adducts (nonplanar and coplanar) were distinguished based on the alignment of the phosphane to the carbene. In case of **1**, **2**, **5**, **7**, and **8** with PCl_3 , both nonplanar and coplanar structures could be optimized; however, the Gibbs free energy differences are within 2 kcal/mol (more details in Supporting Information, Table S7). In fact, it was shown that while dominantly the carbene is the donor in these structures,⁴⁹ also the phosphorus lone pair contributes with some reverse donation effect. Accordingly, we were not able to find correlation between the P–C distance of the adducts and neither the HOMO nor the LUMO energy of the carbenes (see Table S8 in the Supporting Information). Nevertheless, the P–C distances of the PCl_3 adducts are in an inverse correlation with the PCl distances, and accordingly, the formation of the strongest complexes facilitates the cleavage of the PCl bond, in accordance with the formation of the B- and D-type ion pair structures.

In case of carbenes, which are not “too much” stabilized ($\Delta E_{\text{ISO}} = 70\text{--}90$ kcal/mol) and are also rather nucleophilic, two or three different types of adducts could be optimized with X: Cl and F. In case of **3**, **5–6**, and **11**, these three structures are F, E, and E', and in case of **4** and PF_3 , all the structures F, E, and E' could be optimized. This is an interesting example of the rare and somewhat debated bond-stretch isomerism.^{148–155} To our best knowledge, this is the first case where three distinct minima could be located from two reactants, without breaking the other bonds of the interacting units. We were also able to locate the transition states between the minima for the PF_3 adduct with carbene **4** (Figure 11). Because the reaction barriers are not too high, it seems unlikely that all three structures could be detected at room temperature.

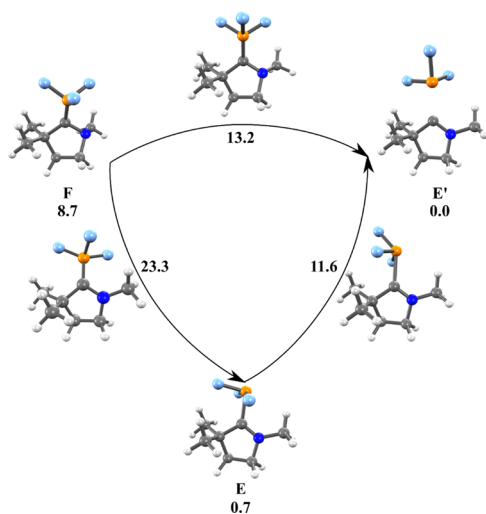


Figure 11. Bond-stretch isomers (E, E', and F) and their connecting transition structures for the adducts between PF_3 and **4**.

Table 2. Dissociation Gibbs Free Energy (ΔG_{diss}) of **I** in kcal/mol

X		carbene										
		1	2	3	4	5	6	7	8	9	10	11
F	ΔG_{diss}	31.4	30.2	14.4	33	24	10.2	41.1	31.5	^a	6.1	14.4
	$d_{\text{P-C}}$	1.909	1.929	2.006	1.921	1.967	2.018	1.884	1.873		2.019	1.955
Cl	ΔG_{diss}	17.6	15.5	−8.1	18.7	5.8	−12.5	35.1	32.4		2.1	11.0
	$d_{\text{P-C}}$	1.961	1.990	2.094	1.978	2.021	2.142	1.907	1.856		2.006	1.955

^aAdducts with carbene **9** are transition states of the $\text{S}_{\text{N}}^{\text{i}}$ -type inversion of $\text{PX}_4\text{-CH}_2\text{X}$ (X: F, Cl) molecules.

As we mentioned above, the E-type structure can be derived from **G**, by the formation of a 3c–4e bond with the phosphorus localized HOMO (Figure 3c). Accordingly, it is reasonable to consider that the remaining phosphorus lone pair at E (see Figure 8a) is able to form a further 3c–4e bond with two halogens, yielding Carb → PX_5 adducts. Indeed, we could optimize stable adducts (**I**) between most carbenes (see footnote in Table 2) and PF_5 or PCl_5 (as an example, the PF_5 adduct of **7** is shown in Figure 12). A few adducts of this type

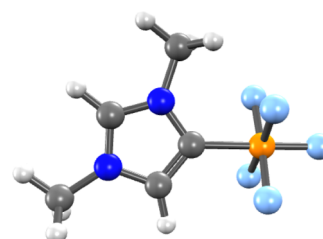


Figure 12. The most stable I-type structure formed between carbene **7** and PF_5 .

have already been reported before in case of carbenes **1** and **2** with PF_5 .^{156–161} The ΔG_{diss} values of **I** for different carbenes cover a wide range (−12.5–41.1 kcal/mol in Table 2). The dissociation Gibbs free energies of the PF_5 adducts are higher than for the PCl_5 adducts for most carbenes. Likewise, carbene SiF_4 adducts were more stable than the analogous carbene SiCl_4 adducts.⁴⁰ The optimized P–C lengths (in the 1.85–2.15 Å range) correspond to somewhat extended P–C single bonds, again the (less stable) PCl_5 adducts exhibiting larger distances than their PF_5 counterparts. While the stability of the I-type compounds is related to the nucleophilicity of the carbene (similarly to the E-type adducts), no joint correlation line could be obtained for the chloro and the fluoro compounds (see Figures S4–S5 of the Supporting Information). Nevertheless, the trends are similar for the two series, although it is difficult to discuss correlation in statistical terms, due to the small number of data points. However, it is noteworthy that the outliers correspond to the same carbenes as in the case of the PX_3 series, assumedly in accordance with the steric effect.

It is noteworthy that the aNHC (**7**) adducts exhibit larger stability against dissociation than the isomeric NHC (**1**) adducts. This suggests that the aNHC (**7**) adducts of both the PF_5 and PCl_5 remain stable once synthesized, as was reported for CO_2 ^{162,163} and SiCl_2 ¹⁶ adducts before.

CONCLUSIONS

The structure and the properties of the carbene–phosphane adducts depend strongly on the interacting carbenes and phosphanes, yielding in principle three different types of structures. The stability of these adducts against dissociation is

rarely exceeding 50 kcal/mol (Table 2), and—especially in case of H-phosphanes—they can be stabilized by shifting one substituent from phosphorus to carbon, resulting in A-type structures. For the least stabilized carbenes, the double bonded/ylydic (F type) structure with some double bond character/back bonding is preferred. In case of these structures, the stability of the adduct is determined by the strength of the donation from the phosphorus lone pair to the empty orbital of the carbene augmented by back-bonding from the carbene lone pair to the proper σ^* orbital of the P–X bonds. The stability of this type of adducts is in strong correlation with the (de)stabilization of the carbene, similarly to other double-bonded carbene adducts (e.g. the Breslow intermediates or the G-type carbene–phosphinidene adducts).

In case of the most stabilized carbenes, the stability of the adduct is determined by the nucleophilicity of the carbene (the energy of the HOMO, which is basically a carbon centered lone pair) and that of the phosphane LUMO. It is noteworthy that in case of PCl_3 , the energy of the LUMO in case of the T-shaped transition structure is extremely low. This facilitates the adduct formation even with the high energy T-shaped phosphane, yielding a “see-saw” structure (E), while for other P-substituents (F, NMe_2), the formation of the usual trigonal bipyramidal adduct (E') is more preferred. These structures are mainly stabilized by pnictogen interactions; nevertheless, these E' structures are rather unstable against dissociation, even with the most nucleophilic carbenes.

In case of medium stabilized and rather nucleophilic carbenes (with high HOMO energy) more structures can be optimized, giving rise to the formation of bond-stretch isomers. In case of some phosphanes and carbenes (e.g. PF_3 with CAAC 4) even three different types of bond-stretch isomers could be optimized.

The electronic structure of the adducts can also be understood from the phosphinidene carbene adducts (G structure), utilizing the lone pair for the formation of 3c–4e bond as was discussed before for simple phosphorus ylides.⁸⁰ The formation of a further 3c–4e bond with the remaining phosphorus lone pair of the resulting E-type structure yields I-type structures, which are neutral hexacoordinate phosphorus compounds.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.0c00641>.

Various DFT levels of theory stabilization energies for the investigated carbenes in the isodesmic reaction; various DFT levels of theory dissociation energies and P–C bond lengths of the carbene–phosphinidene adducts; the electron densities, the ellipticity values, and the Mayer covalent bond indices of the P–C bond in the optimized carbene–phosphinidene type of structures; $\omega\text{B97X-D/cc-pVTZ}$ dissociation Gibbs free energy and distance between the P moiety and the carbene unit of the investigated compounds; LUMO energy of the T-shaped transition structure of PX_3 , and its relative energy with respect to the pyramidal minimum; M06-2X/cc-pVTZ bond angle around the carbene center for the investigated carbenes; the lone pair orbitals of the G type phosphinidene adducts; the HOMO of the C type structures; the M06-2X/cc-pVTZ

HOMO of the PCl_3 structure; relative stability and P–C distance of the coplanar and nonplanar aligned E' type adducts with PCl_3 ; orbital and electronegativity parameters of the investigated carbenes 1–8; The correlation of the dissociation Gibbs free energy of the $\text{Carb}=\text{PX}_3/\text{Carb}=\text{PX}_5$ (X: F, Cl) systems into carbene and (singlet) PX_3/PX_5 and the difference between T-shaped PX_3 LUMO energy/tetragonal pyramidal PX_5 LUMO energy and the singlet carbene HOMO energy; and energies and XYZ coordinates of the investigated adducts and structures for the isodesmic reaction calculations (PDF)

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Notes

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