

Reducing and Reversing the Diphosphene–Diphosphinylidene Energy Separation

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S Supporting Information

ABSTRACT: The dependence of the relative energies of 116 diphosphene and diphosphinylidene compounds on the modification of their structures is studied theoretically. Optimized geometries and relative energies are reported for all structures. With the purpose of investigating the effects of various substituents on the parent PPH_2 and HPPH molecules, isodesmic reaction energies were obtained for single and double substitution. In the case of the substitution of both H atoms by lithoxy (OLi) or ONa groups is the diphosphinylidene type structure found to be lower in energy. For the lithoxy group, the energy difference amounts to 33 kcal/mol at CCSD(T) cc-pVTZ level of theory. This result is explained through the natural population analyses, where a very favorable Coulombic attraction is found in the OLi substituted diphosphinylidene structure. The order of the effectiveness of the substituents in lowering the relative energy of the diphosphinylidene structure is $\text{OLi} > \text{ONa} > \text{OH} > \text{OSiH}_3 > \text{OCH}_3 > \text{OPh} > \text{NH}_2 > \text{N}(\text{CH}_3)_2 > \text{F} > \text{ONH}_2 > \text{OBH}_2 > \text{CH}_3 > \text{OOH} > \text{Ph} > \text{BF}_2 > \text{PH}_2 > \text{SiH}_3 > \text{SH} > \text{HC}=\text{O} > \text{Cl} > \text{CF}_3 > \text{Br} > \text{SiF}_3 > \text{NF}_2 > \text{NO}_2 > \text{C}\equiv\text{CH} > \text{OF} > \text{CN}$. Natural bond orbital (NBO) analysis explains other qualitative bonding features, for example, phosphorus–phosphorus bond orders as large as 2.5 for R_2PP structures and as small as 1.6 for RPPR structures.

1. INTRODUCTION

Phosphorus chemistry has developed rapidly in the last two decades due to a plethora of interesting properties attributed to this family of compounds.¹ In the midst of this renaissance, secondary diphosphenes and diphosphinylidenes have received considerable attention due to their, for phosphorus compounds, unusual double bonds. This unique feature can be utilized in a variety of applications ranging from novel electron-rich organometallic ligands^{2–4} to potential hydrogen storage systems.⁵ The synthesis and isolation of diphosphenes and especially diphosphinylidenes has been challenging because they tend to oligomerization or polymerization due to thermodynamic preferences.⁶ However, stable phosphorus compounds with $\text{P}=\text{P}$ double bonds have been obtained using bulky substituents, which make the compounds kinetically if not thermodynamically stable.^{7–12} Thus, a significant number of diphosphene-like compounds have been synthesized, and their structures and reactivities have been examined. For example, Robinson and co-workers recently synthesized novel diphosphene compounds where the $\text{P}=\text{P}$ fragment was stabilized by N-heterocyclic carbene donors.¹³

One of the characteristic features of the diphosphene compounds is the length of the $\text{P}=\text{P}$ bond. It has been found that in bulky substituted diphosphenes, the length of the $\text{P}=\text{P}$ bond lies in the range 2.001–2.034 Å, with phosphorus–phosphorus vibrational frequencies of about 610 cm^{-1} , confirming the presence of a $\text{P}=\text{P}$ double bond.¹⁴ Furthermore, the recent important study by Partyka et al. showed that it is possible to further strengthen the double bond by reducing the distance between adjacent phosphorus atoms via auration of the $\text{P}=\text{P}$ moiety of $\text{Mes}^*\text{P}=\text{P}(\text{AuCl})\text{Mes}^*$ ($\text{Mes}^* = 2,4,6$ -tritylphenyl) to a bond length of 1.975 Å.¹⁵

Despite the above, no success has been reported to date in the synthesis and isolation of a diphosphinylidene. It has been shown, however, that diphosphinylidene derivatives can coordinate to transition metals, primarily in an η^2 or side-on fashion. The latter synthesis was accomplished using phosphinophosphinidenephosphoranes $[\text{tBu}_2\text{P}=\text{P}(\text{X})\text{tBu}_2]$, $\text{X} = \text{Me}, \text{Br}$ and $\text{R}_2\text{P}=\text{P}(\text{SiMe}_3)\text{Li}$ as precursors.^{2,4}

Several theoretical studies have investigated the nature of diphosphene and diphosphinylidene type compounds.^{5,16–20} The electronic ground state of H_2PP was long predicted to be a triplet,^{17,18,21,22} but recent computations using the CCSD(T)/aug-cc-pVQZ level of theory find that the ground state appears to be of singlet nature with a triplet–singlet gap of 2.8 kcal/mol.⁵ In addition, high level *ab initio* computations have shown that the energy gap between the ground state of trans diphosphene (HPPH) and geminal diphosphinylidene (H_2PP) is about 25 kcal/mol.²³ Finally, it has been demonstrated that π -donating and bulky substituents favor the planar singlet state of substituted diphosphinylidenes.¹⁷

In the present research, the effects of a variety of substituents on the relative energies of singly and doubly substituted trans diphosphenes (RPPR) and geminal diphosphinylidene (R_2PP) are studied. Isodesmic reaction schemes are utilized to derive insights concerning substituent effects, and natural bond order (NBO)²⁴ analyses were performed to investigate the nature of the bonding in these molecules.

2. THEORETICAL METHODS

All computations were performed with the Q-CHEM 3.1 Program Suite.²⁵ For geometry optimization, the def2-TZVPP

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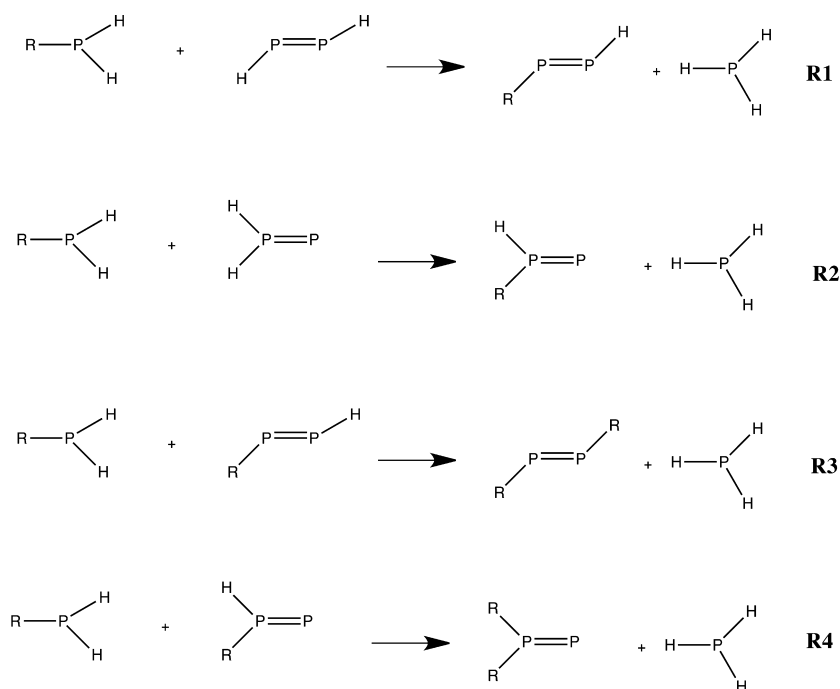


Figure 1. Isodesmic reactions for evaluating energetic effects related to the substitution of one or two hydrogens of diphosphene and diphosphinylidene. Through these equations it is possible to separate the substituent effects on the two isomers, making it easier to study the energetics of single and double substitution.

basis of Weigend and Ahlrichs²⁶ was employed together with the B3LYP functional.²⁷ The stationary points were characterized by evaluating harmonic vibrational frequencies to identify structures as minima on the potential energy surfaces. Furthermore, isodesmic reaction schemes were employed to study substituent effects on the P=P moiety for both geminal (substituted diphosphinylidene) and trans (substituted diphosphene) isomers. Such isodesmic reactions have been extensively used to obtain accurate thermochemical predictions for many organic reactions.²⁸ The isodesmic reactions used in this study are shown in Figure 1. The reaction energies were computed by taking the differences between the energies of reactants and products. Through these isodesmic relationships, it is possible to examine the substituent effects for one (R1 and R2) and two (R3 and R4) substituents and shed light on whether there is a functional group that can substantially reduce the energy gap between the two isomers in question. Furthermore, the natural bond order (NBO)²⁴ method was used to obtain natural atomic charges and Wiberg bond orders²⁹ for the molecules under study.

3. RESULTS AND DISCUSSION

3.1. Energetics. Figure 2 reports the ground-state geometries for six of the 29 doubly substituted *geminal*-R₂PP structures. Similarly, Figure 3 shows the geometries for six of the 29 doubly substituted *trans*-RPPR. The remaining 104 theoretical structures may be found in the Supporting Information.

A. Energy Differences for Monosubstituted Systems. The first column in Table 1 shows the values for ΔE_{sing} , which is the energy difference between RHPP and RPPH isomers, that is, $\Delta E = E(\text{RHPP}) - E(\text{RPPH})$. It can be seen that in all cases the monosubstituted RPPH is lower in energy than the RHPP isomer. However, several substituents reduce the ΔE_{sing} energy difference by approximately 4 kcal/mol from the parent H₂PP–

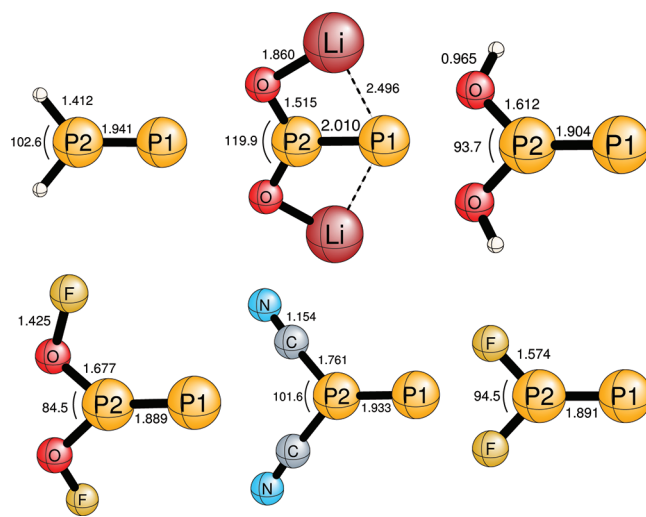


Figure 2. Theoretical geometries for representative diphosphinylidenes R₂PP with R = H, OLi, OH, OF, CN, F. Bond distances are reported in angstroms. As seen in Tables 2 and 3, 23 other structures with different substituents R were also studied.

HPPH energy difference of 24.5 kcal/mol. The most effective functional group in reducing ΔE_{sing} are ONa with a ΔE_{sing} of 8.7 kcal/mol followed by OLi with a ΔE_{sing} of 10.5 kcal/mol. At the CCSD(T)/cc-pVTZ level of theory, this energy difference between the two OLi substituted isomers increases to 13.5 kcal/mol. The least effective substituent, CN, has a ΔE_{sing} value that is 3 kcal/mol higher than that of the parent hydrogen substituted compound. Of the five most effective substituents, four are oxy groups, indicating that this general type of substituent is best for lowering the energy.

B. Energy Differences for Disubstituted Systems. The energy differences ΔE_{doub} between the doubly substituted

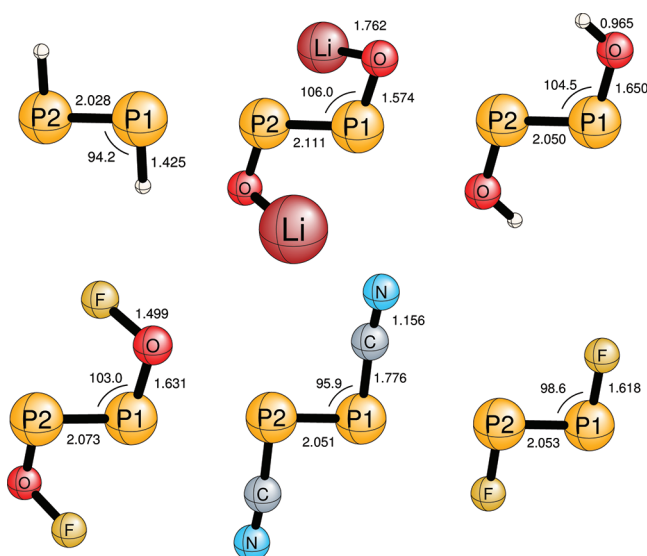


Figure 3. Theoretical geometries for representative diphosphenes RPPR with R = H, OLi, OH, OF, CN, F. Bond distances are reported in angstroms. As seen in Tables 2 and 3, 23 other structures with different substituents R were also studied.

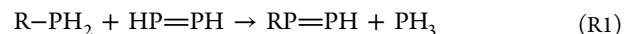
diphosphinylidene and diphosphene isomers $\Delta E = E(R_2PP) - E(HPPR)$ are given in the second column of Table 1. The only substituents capable of inverting the energy gap are OLi and

Table 1. Energy Differences (kcal/mol) between the Monosubstituted RHPP and RPPH Isomers (ΔE_{sing}) and between Disubstituted R_2PP and RPPR (ΔE_{doub})

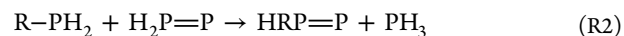
-R	ΔE_{sing}	ΔE_{doub}
-H	24.5	24.5
-CN	27.5	32.0
-OF	23.9	27.1
-C≡CH	25.3	27.1
-NO ₂	22.4	26.7
-NF ₂	24.3	26.0
-SiF ₃	25.7	25.9
-Br	22.9	25.8
-CF ₃	24.3	25.3
-Cl	23.3	24.3
-CH=O	23.5	24.3
-SH	24.1	22.0
-SiH ₃	23.0	21.6
-PH ₂	22.7	21.3
-BF ₂	22.0	20.4
-Ph	18.9	18.0
-OOH	22.4	19.1
-CH ₃	20.1	15.9
-N(CH ₃) ₂	22.6	14.0
-OBH ₂	21.0	13.1
-ONH ₂	20.5	12.6
-F	20.6	12.1
-NH ₂	23.0	8.8
-OPh	20.5	8.0
-OCH ₃	17.9	6.6
-OSiH ₃	18.4	5.4
-OH	18.2	4.5
-ONa	8.7	-27.0
-OLi	10.5	-27.6

ONa, where the C_{2v} (OLi)₂PP isomer lies 27.6 kcal/mol below the C_i (OLi)PP(OLi) isomer. The best of the other substituents in reducing the energy gap are OH and OSiH₃ with R_2PP -RPPR energy gaps of 4.5 and 5.4 kcal/mol, respectively, such that the isomer is still moderately lower in energy. OCH₃ and NH₂ also perform well, as they reduce the energy difference by more than 15 kcal/mol. Because of the unusually large difference of over 30 kcal/mol between OLi and ONa and the next best substituent OH, both lithoxy substituted and diphosphinylidene and diphosphene isomers were reoptimized at the CCSD(T)/cc-pVTZ level of theory. The energy difference between (OLi)₂PP and (OLi)PP(OLi) is predicted to be 33.0 kcal/mol, which is 6 kcal/mol higher than the energy separation found at the B3LYP/def2-TZVPP level of theory, thus confirming the large energy difference favoring the diphosphinylidene isomer. A low lying triplet state for the (OLi)PP(OLi) isomer was also not found since the lowest triplet state lies 41.7 kcal/mol higher in energy than the singlet ground state. Another noteworthy substituent is the borane substituent BH₂. The geminal and trans isomers are second-order saddle points; however, a minimum structure corresponding to a dibridged diphosphene is found on the potential energy surface. The good performance of OLi, ONa, OH, OSiH₃, and OCH₃ indicates that functional groups that have electropositive atoms bonding to oxygen seem to be the best substituents for reducing the energy gap ΔE_{doub} . Among the less effective substituents, CN is the worst with a ΔE_{doub} of 32.0 kcal/mol, meaning that the energy difference between R_2PP and RPPR is increased by 7.5 kcal/mol with respect to the parent P_2H_2 isomers. NO₂ and the higher row halogens Cl and Br also increase the energy difference, thus further favoring the isomer. In general, all π -donating and σ -withdrawing groups significantly decrease the energy gap, with the exception of substituents containing a second row atom bonding to the phosphorus, where steric repulsion between the adjacent functional groups seems to disfavor the diphosphinylidene isomer. On the other hand, σ - and π -withdrawing functional groups like CN and NO₂ are among the least effective substituents for reducing ΔE_{doub} .

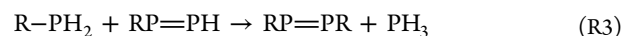
3.2. Analysis from Isodesmic Reactions. To study in more detail the substituent effects on the P=P moiety for both diphosphinylidene and diphosphene isomers, the reaction energies of the following isodesmic reactions were obtained.



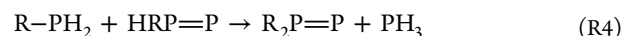
$$\Delta E(R1) = [E(R-PH_2) + E(HP=PH)] - [E(RP=PH) + E(PH_3)]$$



$$\Delta E(R2) = [E(R-PH_2) + E(H_2P=P)] - [E(HRP=P) + E(PH_3)]$$



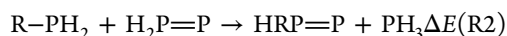
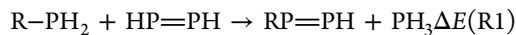
$$\Delta E(R3) = [E(R-PH_2) + E(RP=PH)] - [E(RP=PR) + E(PH_3)]$$



$$\Delta E(R4) = [E(R-PH_2) + E(HRP=P)] \\ - [E(R_2P=P) + E(PH_3)]$$

The reaction energies for monosubstitution [$\Delta E(R1)$ and $\Delta E(R2)$] and disubstitution [$\Delta E(R3)$ and $\Delta E(R4)$] are reported in Tables 2 and 3, respectively. In the monosub-

Table 2. Isodesmic Reaction Energies (kcal/mol) for the Singly Substituted Diphosphenes and Diphosphinyldenes

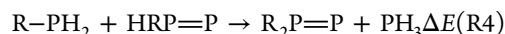
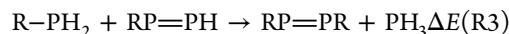


-R	$\Delta E(R1)$	$\Delta E(R2)$
-H	0.0	0.0
-CN	-2.3	0.7
-OF	-7.9	-8.5
-C \equiv CH	-4.2	-3.4
-NO ₂	-2.5	-4.5
-NF ₂	-2.4	-2.5
-SiF ₃	1.4	2.7
-Br	-5.9	-7.4
-CF ₃	0.5	0.3
-Cl	-6.6	-7.8
-CH=O	-1.0	-2.0
-SH	-6.4	-6.8
-SiH ₃	-0.2	-1.6
-PH ₂	-2.3	-4.1
-BF ₂	2.3	-0.2
-Ph	-3.9	-9.5
-OOH	-8.7	-10.8
-CH ₃	-2.0	-6.4
-N(CH ₃) ₂	-12.7	-14.6
-OBH ₂	-7.4	-11.0
-ONH ₂	-9.7	-13.7
-F	-7.9	-11.8
-NH ₂	-10.8	-12.3
-OPh	-8.6	-12.6
-OCH ₃	-9.8	-16.7
-OSiH ₃	-9.2	-15.2
-OH	-9.1	-15.3
-ONa	-26.8	-42.6
-OLi	-22.5	-36.5

stituted cases (R1 and R2), a positive reaction energy indicates that the H₂PP and HPPH reactants are preferred, such that replacement of one hydrogen by a substituent increases the energy of the products. On the other hand, a negative reaction energy accounts for an energetically favorable effect upon the inclusion of a substituent to the P=P moiety, in the sense that the sum of the product energies is lower than the sum of the reactant energies. For the reactions leading to the disubstituted molecules (R3 and R4), a positive reaction energy favors the monosubstituted compound, which now is on the reactant side of the reaction, whereas a negative reaction energy signals a preference for the disubstituted product side of the reaction. Thus, it is possible to analyze independently the energetics of the substituent effect of a functional group on H₂PP, HPPH and RHPP, RPPH.

Upon the replacement of one hydrogen by a functional group in (R1) and (R2), most substituents yield negative isodesmic reaction energies for both isomers, meaning that both monosubstituted isomers are preferred relative to the

Table 3. Isodesmic Reaction Energies (kcal/mol) for the Doubly Substituted Diphosphenes and Diphosphinyldenes



-R	$\Delta E(R3)$	$\Delta E(R4)$
-H	0.0	0.0
-CN	0.3	4.9
-OF	-2.4	0.8
-C \equiv CH	-3.8	-2.0
-NO ₂	3.1	7.4
-NF ₂	3.6	5.3
-SiF ₃	3.1	3.3
-Br	-3.9	-1.1
-CF ₃	3.1	4.1
-Cl	-2.6	-1.5
-CH=O	1.2	0.5
-SH	-0.8	-2.8
-SiH ₃	-1.1	-1.5
-PH ₂	-2.3	-3.7
-BF ₂	2.9	1.26
-Ph	-2.2	-3.3
-OOH	-2.8	-4.7
-CH ₃	-2.0	-5.3
-N(CH ₃) ₂	2.2	-6.4
-OBH ₂	0.8	-6.9
-ONH ₂	-0.4	-8.3
-F	2.5	-6.1
-NH ₂	2.7	-11.6
-OPh	2.9	-9.6
-OCH ₃	-1.8	-13.1
-OSiH ₃	0.4	-12.6
-OH	1.1	-12.6
-ONa	-7.4	-43.1
-OLi	-3.3	-41.4

parent H₂PP and HPPH compound. However, one can see that replacement of the hydrogen atom by substituent R is, in most cases, energetically more favorable for the RHPP [$\Delta E(R2)$] than the RPPH [$\Delta E(R1)$] conformation, because the latter yields a greater negative energy. The only exception to this trend is CN, where the monosubstituted RPPH conformation is favored upon substitution, whereas the substituted RHPP isomer gives a positive reactions energy, indicating an energetically less favorable configuration with respect to the parent diphosphinyldene. This result is reflected in the value of ΔE_{sing} which is the energy difference between RHPP and RPPH. No particular diphosphinyldene conformation is sufficiently lowered that ΔE_{sing} remains close to the 24.5 kcal/mol of the parent molecules. Nonetheless, CH₃, OH, and especially OLi reduce the energy difference by 5.6, 6.3, and 14.0 kcal/mol, respectively, which represents some improvement.

Table 3 shows the reaction energies for the isodesmic reactions R3 and R4. In these reactions, the remaining hydrogen is replaced by the second substituent, resulting in the disubstituted compound. For the substitution in the diphosphinyldene isomer R4, a trend similar to the replacement of the first hydrogen can be recognized. Most of the functional groups have a negative reaction energy $\Delta E(R4)$ upon the inclusion of the second substituent. The isomers with the greatest substituent effects are OH (-12.6 kcal/mol), NH₂ (-11.6 kcal/mol), OCH₃ (-13.1 kcal/mol), and especially

lithoxy OLi (−41.4 kcal/mol) and ONa (−43.1 kcal/mol). These reaction energies are only slightly lower than $\Delta E(R2)$, suggesting an additive substituent effect. The only substituent that presents a larger $\Delta E(R4)$ than $\Delta E(R2)$ is OLi where the reaction energy for the replacement of the second hydrogen increases by almost 5 kcal/mol. The picture is somehow different for the reaction energies of the diphosphene isomer ($\Delta E(R3)$). The addition of a second substituent is only favorable for a few functional groups, whereas others even have a slightly positive reaction energy, meaning that they are energetically less favorable with respect to the monosubstituted compound. This suggests that the substitution by a second functional group does not contribute in lowering the energy of the disubstituted RPPR isomer, thus contrasting to the result found in the replacement of the first hydrogen. Figure 4 plots

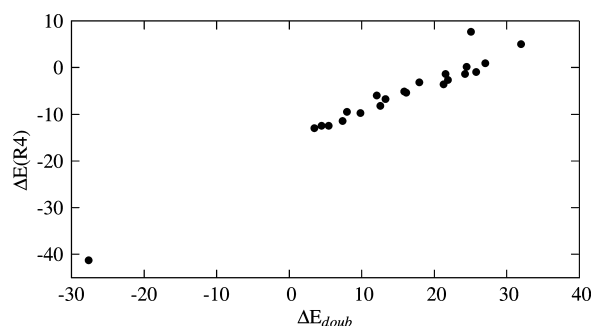


Figure 4. Plot of the doubly (doub) substituted diphosphinyldene–diphosphene energy gap $\Delta E_{\text{doub}} = E(R_2P=P) - E(RP=PR)$ against the reaction energies for isodesmic reaction R4 $R-PH_2 + HRP=P \rightarrow R_2P=P + PH_3$. The good correlation between $\Delta E(R4)$ and ΔE_{doub} indicates that the reduction of the energy difference between diphosphene and diphosphinyldene isomers is mainly due to a favorable substituent effect after the incorporation of the second substituent into the parent diphosphinyldene compound.

the relation between ΔE_{doub} and $\Delta E(R4)$. A good correlation between these two energies can be appreciated, showing that an energetically more favorable substituent effect for the diphosphinyldene than for the diphosphene isomer, upon the inclusion of the second substituent, seems to be responsible for the reduction of the energy gap. To explain the origin of the reduction of the energy difference between the R_2PP and RPPR isomer, the nature of the effect of adding a second substituent to the diphosphinyldene isomer must be investigated.

3.3. Analysis of the Bonding. To get more insight into the electronic effects responsible for reducing the energy gap between RPPR and R_2PP isomers, NBO analysis was performed. Wiberg bond orders were obtained for all disubstituted diphosphenyldene and diphosphene isomers and are shown in Table 4. For the R_2PP conformation, the substituent yielding the highest $P=P$ bond order is fluorine with a bond order of 2.50. Jin et al. attributed this to negative hyperconjugation of the in-plane lone pair on the terminal phosphorus atom with low lying $P-F \sigma^*$ orbitals.¹⁹ The NBO analysis confirms this assumption, because it renders a third partial phosphorus–phosphorus bond, which is polarized toward the terminal phosphorus atom with a natural orbital occupation of 1.87. Such a partial triple bond is found for several other substituents, which have an electronegative atom attached to the $P=P$ moiety. Moreover, the relatively short $P-P$ bond length in these isomers also suggests the presence of a partial $P-P$ triple bond. However, this does not seem to be the

Table 4. Wiberg Bond Orders for R_2PP and RPPR Structures

–R	R_2PP	RPPR
–H	2.14	2.03
–CN	2.05	1.78
–OF	2.33	1.78
–C≡CH	2.03	1.72
–NO ₂	2.39	1.90
–NF ₂	2.35	1.83
–SiF ₃	2.45	1.98
–Br	2.29	1.88
–CF ₃	2.22	1.96
–Cl	2.32	1.86
–CH=O	1.98	1.83
–SH	2.22	1.81
–SiH ₃	1.95	1.96
–PH ₂	2.13	1.90
–BF ₂	1.82	1.92
–Ph	2.11	1.81
–OOH	2.38	1.79
–CH ₃	2.20	1.93
–OBH ₂	2.42	1.86
–ONH ₂	2.37	1.81
–F	2.51	1.89
–N(CH ₃) ₂	2.24	1.68
–OPh	2.41	1.82
–NH ₂	2.37	1.81
–OCH ₃	2.36	1.80
–OSiH ₃	2.36	1.84
–OH	2.40	1.83
–ONa	1.68	1.62
–OLi	1.77	1.62

energetic effect responsible for the decrease of the RPPR– R_2PP energy gap, because the substituents NO₂ (2.39) and OH (2.40) yield almost the same bond order and almost identical bond distances, while having very different R_2PP –RPPR energy gaps (25.1 kcal/mol for NO₂ vs 4.5 kcal/mol for OH). Also, ONa and OLi, have the lowest phosphorus–phosphorus bond orders (1.68 and 1.77) and the longest $P-P$ bond lengths (2.035 and 2.010 Å) of all, suggesting that there is another energetically more significant effect than negative hyperconjugation of the in-plane phosphorus lone pair.

For the *trans*-RPPR isomers, the picture is somewhat different. The parent diphosphene has a well localized $P=P$ bond with a bond order of 2.03, while all other substituted compounds have lower bond orders. This is especially the case for substituents with an out-of-plane lone pair, due to delocalization of that lone pair into $P-P \pi^*$. Because in the RPPR isomer there is no possible negative hyperconjugation of an in-plane lone pair to form a third bond, as in the R_2PP case, the resulting bond order is lowered. It is noteworthy that this is the inverse effect to that found for the R_2PP isomers, where most substituents increase the bond order of the $P-P$ bond. Electrostatic effects also seem to be important in weakening the $P-P$ bond, because the adjacent phosphorus atoms have the same charge upon substitution, resulting in repulsion and an increase in the $P-P$ bond distance and hence a weaker π -bond.

Table 5 shows the atomic charges for the doubly and singly (in parentheses) substituted R_2PP , RHPP and RPPR, RPPH isomers. In the parent isomer, the terminal phosphorus possesses a negative charge, while the phosphorus atom bonded to the substituents has a positive charge. When

Table 5. Natural Atomic Charges from NPA for the Doubly Substituted Isomers^a

-R	diphosphinylidene				diphosphene			
	P1	P2	H		P1	P2	H	
-H	-0.12	0.16	-0.02		0.04	0.04	-0.04	
-F	P1	P2	F		P1	P2	F	
	-0.25 (-0.16)	1.32 (0.74)	-0.54 (-0.56)		0.56 (-0.097)	0.56 (0.68)	0.56 (-0.56)	
-NH ₂	P1	P2	N		P1	P2	N	
	-0.39 (-0.28)	1.11 (0.67)	-1.16 (-1.14)		0.35 (-0.21)	0.35 (0.55)	-1.13 (-1.12)	H(N)
-CN	P1	P2	C		P1	P2	C	
	0.06 (-0.03)	0.55 (0.36)	-0.11 (-0.11)		0.37 (0.11)	0.37 (0.29)	-0.14 (-0.11)	0.39 (0.39)
-CH ₃	P1	P2	C		P1	P2	C	N
	-0.22 (-0.18)	0.71 (0.44)	-0.95 (-0.94)		0.25 (-0.03)	0.25 (0.31)	-0.92 (-0.94)	-0.24 (-0.27)
-SiH ₃	P1	P2	Si		P1	P2	Si	H(C)
	-0.09 (-0.05)	-0.27 (-0.11)	0.61 (0.61)		-0.12 (0.05)	-0.12 (-0.13)	0.57 (0.55)	0.22 (0.23)
-OF	P1	P2	O		P1	P2	O	H(Si)
	-0.13 (-0.13)	1.19 (0.63)	-0.45 (-0.37)		0.52 (-0.01)	0.54 (-0.07)	-0.38 (0.62)	-0.14 (-0.14)
-OSiH ₃	P1	P2	O		P1	P2	O	F
	-0.37 (-0.23)	1.33 (0.76)	-1.12 (-1.12)		0.51 (-0.10)	0.51 (0.64)	-1.12 (-1.13)	-1.16 (-0.38)
-OH	P1	P2	O		P1	P2	O	Si
	-0.39 (-0.24)	1.27 (0.73)	-0.94 (-0.95)		0.46 (-0.11)	0.46 (0.60)	-0.94 (-0.95)	1.21 (1.23)
-OCH ₃	P1	P2	O		P1	P2	O	H(O)
	-0.41 (-0.27)	1.30 (0.75)	-0.76 (-0.76)		0.47 (-0.12)	0.47 (0.61)	-0.75 (-0.76)	0.48 (0.49)
-OLi	P1	P2	O		P1	P2	O	C
	-1.11 (-0.58)	1.60 (0.91)	-1.17 (-1.17)		0.33 (-0.53)	0.33 (0.80)	-1.12 (-1.92)	-0.25 (-0.24)
								Li
								0.88 (0.90)

^aIn parentheses are the charges for the singly substituted isomer.

comparing the singly substituted RHPP with the singly substituted RPPH isomers, good agreement between the atomic charges can be found. Substitution by a more electronegative functional group increases, in both isomers, the positive charge on phosphorus P2, which is bonded to that functional group, while the substitution of a more electropositive compound yields a negative charge on P2, as expected. The remaining hydrogen does not seem to play a preponderant role, because the charges on both isomers are fairly similar.

When comparing the singly with the doubly substituted diphosphinylidene isomers, some noticeable changes can be appreciated. The charge on both substituents in the disubstituted isomer is of the same magnitude as that for the monosubstituted compound, indicating the absence of a saturation effect on the ability to withdraw electron density from the phosphorus. Furthermore, the charge on P2 nearly doubles as compared to the singly substituted case, thus gaining a significant positive charge. This generates a very favorable electrostatic interaction in the diphosphinylidene case, which is accentuated by electronegative substituents like NH_2 , OH, and F. This finding is in good agreement with the isodesmic reaction energies, because these substituents have significant negative reaction energies for the second substitution. For the electropositive SiH_3 , the phosphorus atom forming bonds to the substituents has a negative charge, whereas the charge on silicon is positive, showing the same trend with opposing polarity as with the electronegative substituents.

In the case of the two substituents that energetically favor the diphosphinylidene structure (OLi, ONa), a significant charge separation can be appreciated where atom P1 almost doubles its negative charge (−1.11), whereas P2 acquires a significant positive charge (1.60) after replacing the second hydrogen on P2. Furthermore, the negative charge on the atom bonded to phosphorus is the same as in the singly substituted case for both atoms. This charge separation, induced by geminal substitution, creates a strong and favorable diphosphinylidene isomer Coulombic interaction that is not present in the diphosphene isomer. The destabilization of the diphosphene isomer with the substitution of the second hydrogen can also be rationalized, as mentioned before, in terms of unfavorable charge distribution that puts positive charge on adjacent phosphorus atoms. These interactions seem to be responsible for the reduction and inversion of the energy gap between both. This becomes especially evident when looking at the hydroxyl derived substituents OF, OH, and OLi, where the energy gap decreases as the electropositive character of the atom bonded to the oxygen increases. Additionally, the positively charged Li can further interact with the negatively charged terminal phosphorus, providing additional energetic stabilization to this isomer and thus successfully inverting the energy gap between diphosphinylidene and diphosphene isomers.

4. CONCLUSIONS

Theoretical methods have been employed to obtain the energy separation between substituted singlet diphosphenes (R_2PP) and diphosphinylidenes (RPPR). Among R groups considered here, the only substituents capable of inverting the energetic ordering between both isomers are lithoxy (OLi) and ONa, while several others (e.g., OCH_3) reduce the gap quite substantially.

Natural charge analysis helps to elucidate how the second substituent on the R_2PP isomer lowers its energy with respect to the RPPR isomer. It is found that a very favorable

Coulombic interaction is present in the diphosphinylidene structure $(\text{OLi})_2\text{PP}$ but not in the $(\text{OLi})\text{PP}(\text{OLi})$ diphosphene isomer.

■ ASSOCIATED CONTENT

Supporting Information

Figures with the theoretical structures and xyz-coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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