Exploring the Forces That Control the P−C Bond Length in Phosphamides and Their Complexes: The Key Role of Hyperconjugation

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The factors tuning the *R*(P−C) bond length of the labile P−C bond in phosphamides have been explored by means of density functional theory, employing natural bond orbital (NBO) analysis. The second-order perturbation stabilization energy $\Delta E(2)$ due to hyperconjugation accounts well for the unusually long *R*(P−C) bond lengths in a series of phosphamides and related species. Favorable n(O) → σ^*(P−C) interactions primarily affect the *R*(P−C) bond length through electron delocalization. Deleting these interactions from our calculations results in significant shortening of the P−C bond, to a bond length close to that of the P−C(sp^2) bonds. This holds also true if n(O) is "screened" by protonation, while n(P) does not affect the strength of the P−C bond. Moreover, the linear correlations of *R*(P−C) vs $\Delta E(2)$ and of *R*(P−C) vs ΔE_{del} substantiate the validity of the concept that hyperconjugative interactions tune the P−C bond length in phosphamides and provide a novel explanation of P−C bond lability. It was found that the combination of electron-withdrawing substituents on the carbonyl C atom with electron-releasing substituents on the P atom strengthen the P−C bond, thus stabilizing phosphamides. Phosphamides could also be stabilized by coordination with early-transition-metal ions (e.g. $[\mathrm{CpTiCl_2}\{\kappa^1 O\text{-}\mathrm{H_2PC(O)Me}\}]^+$) but are destabilized upon coordination with late-transition-metal ions (e.g. $[\mathrm{Ag}\{\kappa^1 O\text{-}\mathrm{MeC(O)PH_2}\}]^+$ and $[\mathrm{Cu}\{\kappa^2 P,O\text{-}\mathrm{MeC(O)PH_2}\}]^+$). The coordination of phosphamides with Rh(III) in $[\mathrm{CpRhCl_2}\{\kappa^1 P\text{-}\mathrm{H_2PC(OH)CH_3}\}]^+$ only marginally affects the *R*(P−C) bond length. Finally, the interaction of phosphamides with the hard Li$^+$, K$^+$, and Tl$^+$ cations does not affect significantly the n(O) → σ^*(P−C) hyperconjugative interactions, and therefore, the *R*(P−C) bond length is only slightly shortened.

Introduction

The role of phosphorus ligands in coordination chemistry is indisputable, in particular in organometallic chemistry, asymmetric synthesis, and catalysis, due to the possibility of optimizing their chemical function upon selection of the substituents (e.g. alkyl, R, aryl, Ar, alkoxy, OR, ylidene, $\mathrm{R_2C{=}PR_3}$, amine, etc.).[1] However, despite the wide variety of phosphorus ligands used so far, phosphorus ligands that contain the phosphorus donor atom adjacent to a carbonyl group, i.e., acylphosphane (phosphamide) ligands, are rare in organometallic chemistry and catalysis. This could be related with the stability of the P−C bond in phosphamides, which have been shown to easily undergo degradation reactions in the presence of water or oxygen.[2,3] The synthesis and characterization of a number of acylphosphanes and acylarsines with various substituents on the heteroatom and the CO group have been reported by Kostyanovskii et al.[4] three decades ago. More recently, a convenient synthesis of several phosphamide ligands from secondary phosphanes has been reported,[5] while efforts have been made to develop the transition-metal and catalytic chemistry of the new ligands. Along this line, the first stable Rh(III) complexes of phosphamide ligands formulated as $[\mathrm{RhCp^*Cl_2}\{\mathrm{Ph_2PC(O)R}\}]$ (R = Me, $\mathrm{(CF_2)_6CF_3}$, anisoyl) have been isolated and structurally characterized and their catalytic activity in hydroformylation reactions has been explored.[5] It is worth noting the relatively long P−C bond length of 1.917(2) Å of the coordinated phosphamide, $\mathrm{Ph_2PC(O)CH_3}$, which is significantly larger than the other two P−C(sp^2) bonds (the P−C(Ph) bond lengths were found to be 1.833(2) and 1.816(2) Å).[5]

To identify and quantify the determinants of the *R*(P−C) bond lability in phosphamides and their conjugate acids helping further synthetic efforts of stable phosphamide ligands and their complexes with transition metals with application in catalysis, we report on the results of electronic structure calculations by means of density functional theory (DFT) methods at the B3LYP/6-31G(d,p) level of theory employing natural bond orbital (NBO) and atoms in molecules (AIM) analysis methods.

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In particular, the natural bond orbitals (NBOs)[6] provide the atomistic and stereoelectronic detail to analyze the hyperconjugative interactions in detail.

Computational Details

Standard ab initio molecular orbital[7] and density functional theory (DFT)[8] calculations were carried out using the GAUSSIAN 03 program suite.[9] The geometries of the ligands and complexes were fully optimized using density functional theory (DFT). Specifically, DFT was implemented by using the Becke three-parameter hybrid (exchange) functional[10] with gradient corrections provided by the Lee−Yang−Parr[11] correlation functional (B3LYP). The Pople style 6-31G(d,p) basis set was utilized. In all computations no constraints were imposed on the geometry. Full geometry optimization was performed for each structure using Schlegel's analytical gradient method,[12] and the attainment of the energy minimum was verified by calculating the vibrational frequencies that result in the absence of imaginary eigenvalues. All the stationary points have been identified for minimum (number of imaginary frequencies NIMAG = 0) or transition states (NIMAG = 1). The vibrational modes and the corresponding frequencies are based on a harmonic force field. This was achieved with an SCF convergence on the density matrix of at least 10^{-9} and an rms force of less than 10^{-4} au. All bond lengths and bond angles were optimized to better than 0.001 Å and 0.1°, respectively. The computed electronic energies were corrected to constant pressure and 298 K, for zero-point energy (ZPE) differences and for the contributions of the translational, rotational, and vibrational partition functions. The stabilization energy $\Delta E(2)$ associated with the charge transfer (CT) interactions between the relevant donor−acceptor orbitals was computed from the second-order perturbative estimates of the Fock matrix in the natural bond orbital (NBO) analysis.[6,13,14] The electron density topological analysis corresponds to Bader's topological analysis or atoms in molecules (AIM) analysis,[15] as implemented in the GAUSSIAN 03 series of programs.[9]

Results and Discussion

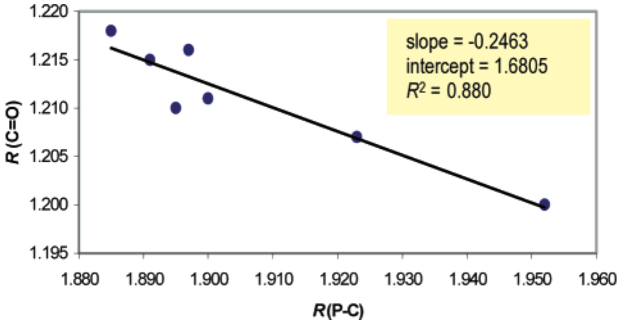
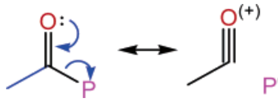


Figure 1. Linear correlation of the R(C=O) bond lengths (bond lengths in Å) of the phosphamide ligands with the R(P−C) bond lengths.

The salient structural feature of the MeC(X)PH_2 (X = O, S, Se) and MeC(O)PRR′ (R = R′ = Me, Ph, CN, F; R = H, R′ = CN, F, OH) phosphamide ligands is the relatively long R(P−C) bond distance as compared to the R(P−C) bond lengths of 1.876 and 1.851 Å in MePH_2 and MeC(CH_2)PH_2 (**1**) ligands, respectively. The structural details of the equilibrium structures of all phosphamides computed at the B3LYP/6-31G(d,p) level of theory are given in Figures S1 and S2 in the Supporting Information. It is worth noting the linear correlation of the computed R(C=O) bond lengths of phosphamide ligands with the R(P−C) bond lengths (Figure 1), illustrating that the π-electron density is delocalized over the O=C−P nuclear framework, thus corresponding to a three-center−four-electron (3c-4e) bonding mechanism.

In the language of resonance theory this bonding mode is described by the resonance substructures



To get a deeper insight into the bonding mechanism that is responsible for the unexpected elongation of the P−C bond in MeC(X)PH_2 and MeC(X)PRR′ ligands, we explored the role of specific delocalization (hypeconjugative) interactions in underlying the structural preferences of the ligands, and our findings are presented below.

Effect of Favorable Hyperconjugative Interactions on the *R*(P−C) Bond Length. Let us examine the effect of the hyperconjugation on the R(P−C) bond length. The stabilization energy $\Delta E(2)$ associated with the charge transfer (CT) interactions between the relevant donor−acceptor orbitals computed from the second-order perturbative estimates of the Fock matrix in the NBO analysis according to the equation

$$\Delta E(2) = \frac{q_i {F_{ij}}^2}{\epsilon_i - \epsilon_j}$$

allows specific hyperconjugative (stereoelectronic) interactions to be pinpointed. This equation evaluates the magnitude of the donor−acceptor interaction in terms of the spatial overlap of the NBO, using the off-diagonal Fock-matrix elements F_{ij} and the difference in energy between the NBOs, $\epsilon_i - \epsilon_j$, weighted by the occupancy of the donor NBO, q_i.

Since the identities of the hyperconjugative interactions responsible for the trend in R(P−C) bond lengths are of interest, we focus on interactions with σ^*(P−C) as an acceptor or with σ(P−C) as a donor. It should be noted that the electron density gain in σ^*(P−C) and electron density loss from σ(P−C) both lead to elongation of the P−C bonds. All possible interactions involving σ(P−C) as a donor were found to be marginal, corresponding to stabilization energies less than 5.0 kcal/mol, and therefore will no longer be discussed. The stronger hyperconjugative interactions are those between the antibonding

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Table 1. Stabilization Energies Δ*E*(2) (in kcal/mol) Introduced by the n(O) → *σ(P−C) and n(O) → *σ**(C−C) Hyperconjugative Interactions and Deletion Energies ΔE_{del} for *σ**(P−C) Deletion along with the *R*(P−C) and *R*(C−C) Bond Lengths (in Å) for the Phosphamide Ligands Computed at the B3LYP/6-31G(d,p) Level of Theory**

ligand	n(O) NBO eigenvalue (eV)	*R*(P−C)	Δ*E*(2) n(O) → *σ**(P−C)	ΔE_{del} *σ**(P−C)	*R*(C−C)	Δ*E*(2) n(O) → *σ**(C−C)
MeC(CH$_2$)PH$_2$ (**1**)		1.851			1.510	
MeC(O)PH$_2$ (**2**)	−0.271 72	1.900 (1.808)[a]	29.17	28.94	1.518 (1.484)	20.45
MeC(S)PH$_2$ (**3**)	−0.223 04	1.849 (1.801)	14.50	17.07	1.508 (1.495)	11.17
MeC(Se)PH$_2$ (**4**)	−0.211 41	1.834 (1.791)	11.50	16.45	1.505 (1.495)	9.05
MeC(O)PMe$_2$ (**5**)	−0.260 54	1.885 (1.764)	25.08	27.89	1.520 (1.490)	20.36
MeC(O)PPh$_2$ (**6**)	−0.264 85	1.897 (1.757)	26.02	29.22	1.519 (1.492)	19.80
MeC(O)P(CN)H (**7**)	−0.298 78	1.923 (1.839)	30.54	27.88	1.508 (1.476)	19.45
MeC(O)P(CN)$_2$ (**8**)	−0.318 77	1.952 (1.859)	35.45	33.99	1.506 (1.474)	19.25
MeC(O)P(F)H (**9**)	−0.275 23	1.895 (1.834)	29.39	35.75	1.518 (1.482)	20.81
MeC(O)P(OH)H (**10**)	−0.268 13	1.891 (1.838)	26.25	32.04	1.512 (1.475)	20.18

[a] Values in parentheses are the computed bond lengths for the [MeC(XH)PRR′]$^+$ phosphamide ligands protonated at the carbonyl oxygen atom.

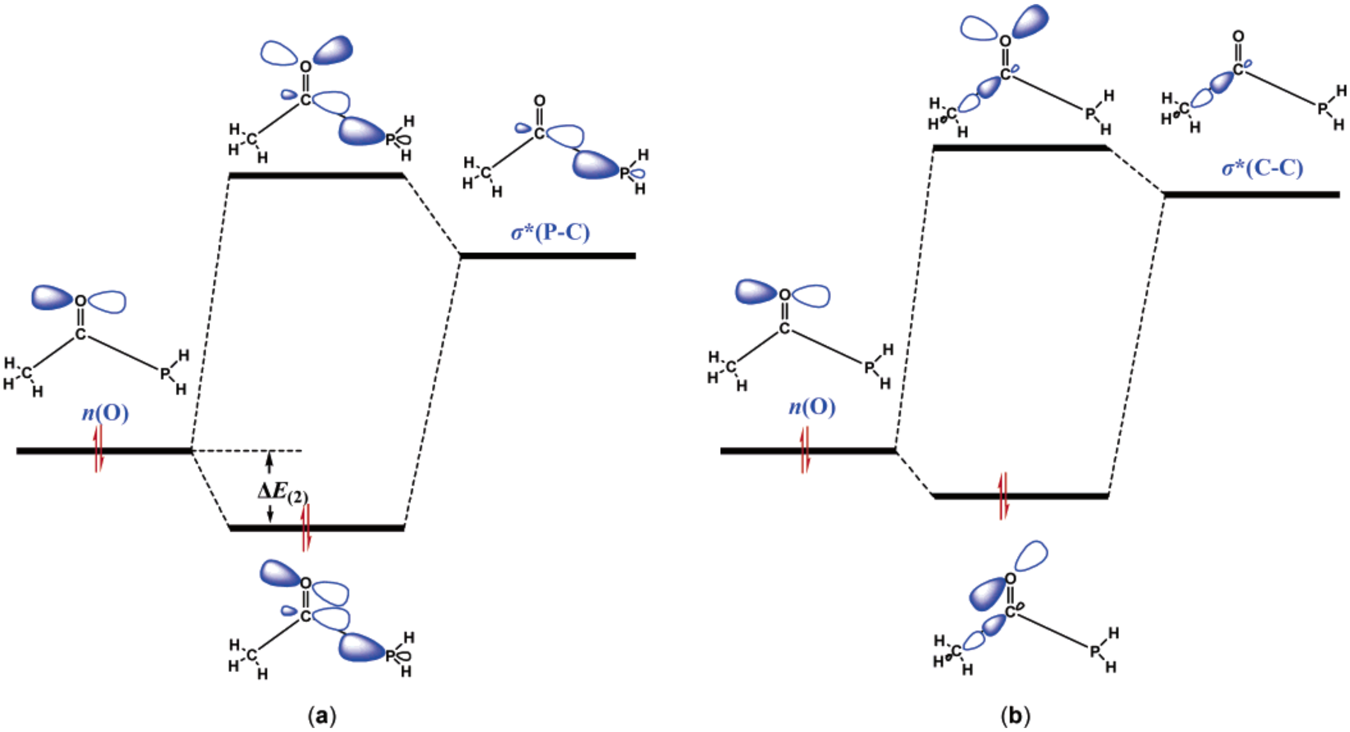
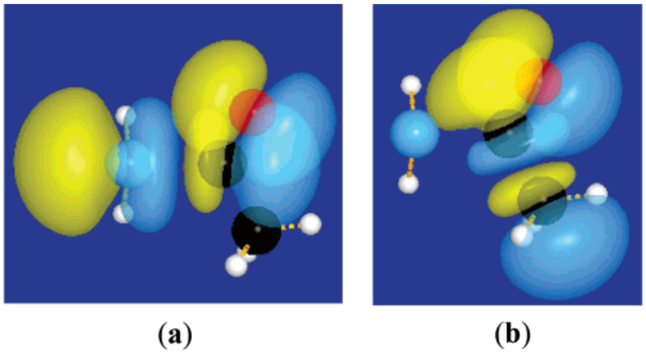


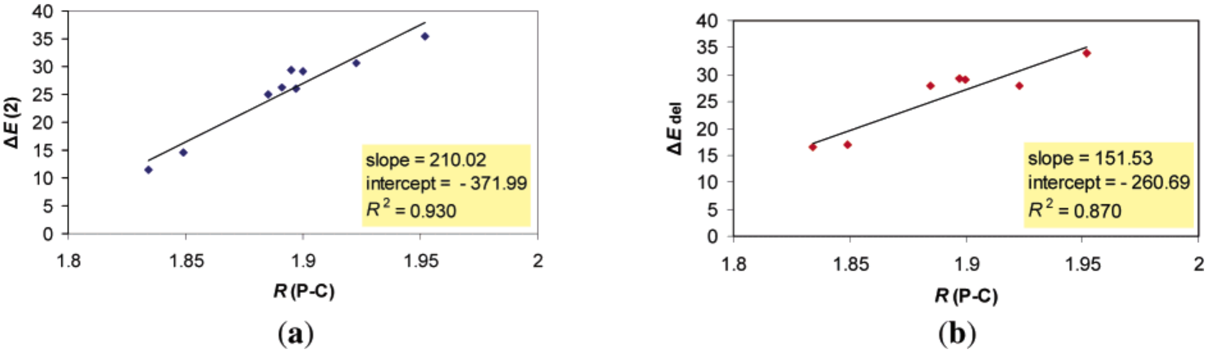
Figure 2. Perturbative donor−acceptor interactions involving a nonbonding n(O) donor orbital of phosphamides with the antibonding *σ**(P−C) (a) and *σ**(C−C) (b) acceptor orbitals (energy on an arbitrary scale).

*σ**(P−C) acceptor orbital and the nonbonding n(O) donor orbitals localized on the carbonyl O atom. The stabilization energy introduced by the favorable interactions of the nonbonding n(O) donor orbitals localized on the carbonyl oxygen atom with the antibonding *σ**(P−C) and *σ**(C−C) acceptor orbitals is summarized in Table 1. For all other hyperconjugative interactions related with the *σ**(P−C) acceptor orbital the stabilization energies were found to be less than 5.0 kcal/mol, except for phosphamides **9** and **10**, where there are also strong reinforcing n(O)P → *σ**(P−C) and n(F) → *σ**(P−C) hyperconjugative interactions with stabilization energies of 7.57 and 7.63 kcal/mol, respectively.

The perturbative donor−acceptor interactions involving the nonbonding n(O) donor orbitals of phosphamides with the antibonding *σ**(P−C) and *σ**(C−C) acceptor orbitals are depicted schematically in the form of qualitative orbital interaction diagrams in Figure 2, while a 3D isosurface plot of the n(O) → *σ**(P−C) and n(O) → *σ**(C−C) interactions for H$_2$PC(O)Me (**2**) is given in Chart 1. These hypeconjugative interactions lead to delocalization of negative charge due to the lone pair of electrons on the O atom into the high-energy unoccupied antibonding *σ**(P−C) and *σ**(C−C) orbitals. This charge transfer is reflected on the occupation of the *σ**(P−C) and *σ**(C−C) orbitals, which for **2** is equal to 0.098 and 0.056 |e|, respectively. Therefore, the occupation of the n(O) orbital in **2** is lower than 2.000 (1.860 |e|). Obviously, the lone pair donor → antibonding acceptor orbital interactions will have as a result the weakening of both the P−C and C−C bonds.

Chart 1. 3D Isosurface Plot of the n(O) → *σ(P−C) (a) and n(O) → *σ**(C−C) (b) Hyperconjugative Interactions for H$_2$PC(O)Me (2)**





(a) (b)

Figure 3. Linear correlation between the energy values (in kcal/mol) of the n(O) → σ*(P−C) hyperconjugative interactions with the R(P−C) bond length (in Å) of phosphamide ligands using the stabilization energy $\Delta E(2)$ (a) and the deletion energy ΔE_{del} (b).

The linear correlation of $\Delta E(2)$ with the R(P−C) bond length (Figure 3) illustrates that the hyperconjugative interactions indeed play a key role in tuning the R(P−C) bond length in phosphamides. This is further corroborated by the shorter R(P−C) bond length in **1,** where analogous hyperconjugative interactions are not possible. There are no lone pairs of electrons on the CH_2 moiety to interact with the σ*(P−C) orbital.

To quantitatively assess further the role of electronic delocalization, the specific n(O) → σ*(P−C) hyperconjugative interactions have been deleted (via the NBO$DEL orbital deletion keyword[14]) from our calculations. In that case the net energy difference ΔE_{del} (Table 1) gives the stabilizing effect of the delocalizing contributions. The deletion method in NBO analysis is important to evaluate the possibility of anticooperative energy interactions and as a check of the computed $\Delta E(2)$ energy values. Generally, the ΔE_{del} values were found to be close to the $\Delta E(2)$ values. The small deviations observed are due to the deletion of some other weak hyperconjugative interactions involving the deleted σ*(P−C) acceptor orbital. The higher deviations observed for **9** and **10**, amounting to 6.36 and 5.79 kcal/mol, respectively, account well for the reinforcing n(O)P → σ*(P−C) and n(F) → σ*(P−C) hyperconjugative interactions involving the deleted σ*(P−C) acceptor orbital as well. The geometry optimization allowed us to determine what the R(P−C) bond length would be in the *absence* of the n(O) → σ*(P−C) hyperconjugative interactions. In all cases, deleting the n(O) → σ*(P−C) hyperconjugative interactions results in significant shortening of the P−C bond; for all phosphamides, after deletion of the n(O) → σ*(P−C) hyperconjugative interactions the P−C bond acquires a bond length of 1.807−1.816 Å. Notice that a good linear correlation also holds between ΔE_{del} and R(P−C) bond length when phosphamides **9** and **10** are excluded from the correlation (Figure 3b).

To come to a decisive conclusion concerning the role of hyperconjugation in tuning the R(P−C) bond length in phosphamides, the lone pair electrons of the carbonyl oxygen atom were screened by means of protonation, thus prohibiting their involvement in any favorable hyperconjugative interaction related with the P−C bond. The computed R(P−C) and R(C−C) bond lengths of the protonated $[\text{MeC(XH)PH}_2]^+$ (X = O (**11**), S (**12**), Se (**13**)) and $[\text{MeC(OH)PRR}']^+$ (R = R′ = Me (**14**), Ph (**15**), CN (**16**); R = H, R′ = CN (**17**), F (**18**), OH (**19**)) ligands are also given in Table 1 (figures in parentheses). It can be seen that protonation at the X (O, S, Se) donor atoms strengthens the P−C bond; the P−C bond shortening found in the range of 0.043−0.140 Å follows the trend **6** > **5** > **2** > **8** > **7** > **9** > **10** > **3** > **4**. On the other hand, the C−X bonds are lengthened upon protonation at the X donor atoms, thus exhibiting a lower bond order than the unprotonated species. This observation is consistent with the bond order conservation principle for a 3c-4e O−C−P framework and is further substantiated by the excellent linear correlation of the R(P−C) with the R(C═O) bond lengths of the protonated phosphamides shown in Figure 4. More structural details of the equilibrium structures of the $[\text{MeC(XH)PRR}']^+$ species are given in Figure S3 in the Supporting Information.

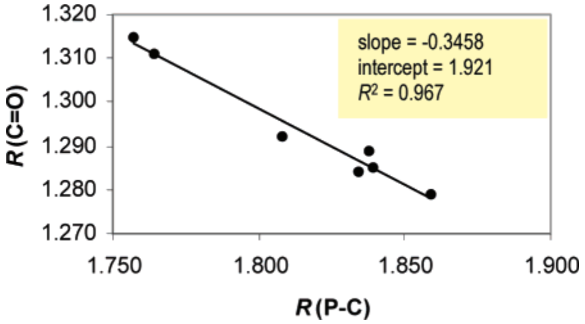
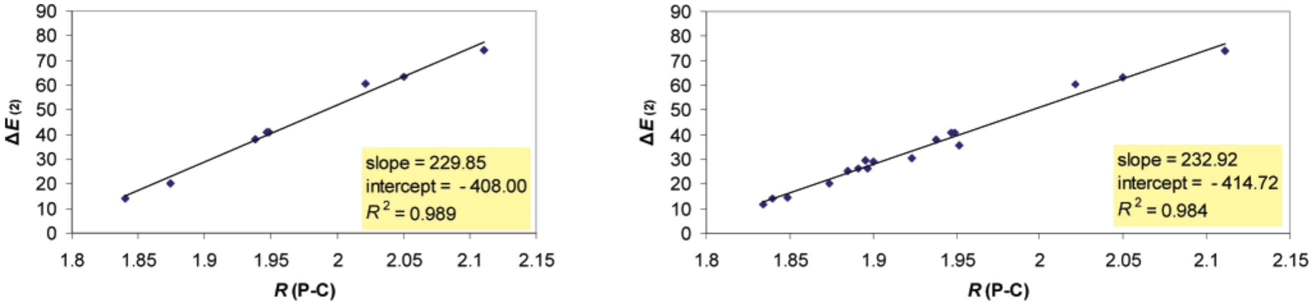


Figure 4. Linear correlation of $R(\text{C═OH}^+)$ with R(P−C) bond lengths of the phosphamide ligands protonated at the O donor atom (bond lengths in Å).

Effect of the Phosphorus Lone Pair on the *R*(P−C) Bond Length. Surprisingly, the lone pair of electrons on the P atom does not affect the strength of the P−C bond, since it is not involved in favorable hyperconjugative interactions with P−C bond orbitals in either the phosphamides or their X-protonated species. The role (if any) of the P lone pair on the P−C−O bonding in phosphamides was explored by means of protonation of the phosphamides at the P atom. Structural details of the equilibrium structures of the $[\text{MeC(X)PRR}'\text{H}]^+$ species are given in Figure S4 in the Supporting Information. Protonation at the phosphorus atom lengthens the P−C bond; the P−C bond lengthening found in the range of 0.007−0.188 Å follows the trend **7** > **2** ≫ **9** > **5** > **10** > **6** > **3** > **4**. Interestingly, the acetyldicyanophosphane ligand upon protonation dissociates to dicyanophosphane, $\text{P(CN)}_2\text{H}$, and acetyl cation, $[\text{MeC(O)}]^+$. The very weak P−C bond in the protonated cyano-substituted species is reflected by the computed bond dissociation energy of only 5.4 kcal/mol for **27**. Similarly, the bond dissociation energies of the P−C bond in the ligands $[\text{MeC(O)PH}_3]^+$ (**21**) and $[\text{MeC(O)PMe}_2\text{H}]^+$ (**24**) were found to be 17.6 and 44.3 kcal/mol, respectively.

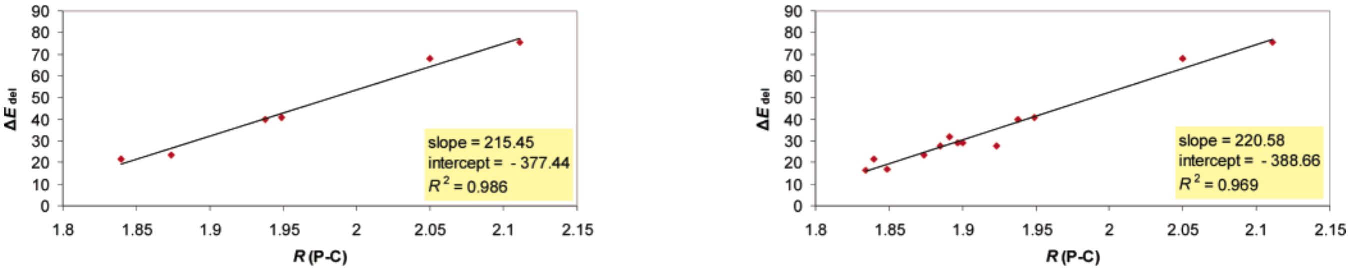
The effect of hyperconjugation on the R(P−C) bond length is manifested in the case of the protonated $[\text{MeC(X)PRR}'\text{H}]^+$ species. The stabilization energy introduced by the favorable interactions of the nonbonding n(O) donor orbitals with the antibonding σ*(P−C) and σ*(C−C) acceptor orbitals are summarized in Table 2.

It can be seen that these interactions lead to much higher stabilization energies in the protonated species, which exhibit



(a) **(b)**

Figure 5. Linear correlation of the stabilization energy Δ*E*(2) (in kcal/mol) with the *R*(P−C) bond length (in Å) of the conjugate acids of the phosphamide ligands protonated at the P donor atom (a) and the whole series of the phosphamide ligands and their conjugate acids protonated at the P donor (b).



(a) **(b)**

Figure 6. Linear correlation of the deletion energy ΔE_{del} (in kcal/mol) with the *R*(P−C) bond length (in Å) of the conjugate acids of the phosphamide ligands protonated at the P donor atom (a) and the whole series of the phosphamide ligands and their conjugate acids protonated at the P donor (b).

Table 2. Stabilization Energies Δ*E*(2) (in kcal/mol) Introduced by the n(O) → σ*(P−C) and n(O) → σ*(C−C) Hyperconjugative Interactions and Deletion Energies ΔE_{del} for σ*(P−C) Deletion along with the *R*(P−C) and *R*(C−C) Bond Lengths (in Å) for the Conjugate Acids of the Phosphamide Ligands Protonated at the P Donor Atom Computed at the B3LYP/6-31G(d,p) Level of Theory

ligand	n(O) NBO eigenvalue (eV)	*R*(P−C)	Δ*E*(2) n(O) → σ*(P−C)	ΔE_{del} σ*(P−C)	*R*(C−C)	Δ*E*(2) n(O) → σ*(C−C)
$[MeC(CH_2)PH_3]^+$ (**20**)		1.802			1.510	
$[MeC(O)PH_3]^+$ (**21**)	−0.502 28	2.050	63.39	68.11	1.487	16.29
$[MeC(S)PH_3]^+$ (**22**)	−0.417 11	1.874	20.36	23.66	1.495	12.27
$[MeC(Se)PH_3]^+$ (**23**)	−0.418 81	1.840	14.29	21.57	1.494	10.47
$[MeC(O)PMe_2H]^+$ (**24**)	−0.464 41	1.949	40.71	40.69	1.497	18.26
$[MeC(O)PPh_2H]^+$ (**25**)	−0.436 00	1.938	37.98	40.00	1.500	18.86
$[MeC(O)P(CN)H_2]^+$ (**26**)	−0.521 91	2.111	73.94	75.46	1.483	15.07
$[MeC(O)P(CN)_2H]^+$ (**27**)			dissociates to $[MeC(O)]^+$ and $P(CN)_2H$			
$[MeC(O)P(F)H_2]^+$ (**28**)	−0.504 26	2.021	60.29	52.76	1.487	16.42
$[MeC(O)P(OH)H_2]^+$ (**29**)	−0.492 51	1.947	40.59	51.69	1.487	16.79

much longer P−C bonds. There is an excellent linear correlation of the *R*(P−C) bond length with the Δ*E*(2) values (Figure 5a) conforming to the linear equation ($R^2 = 0.989$)

$$\Delta E(2) = 229.85[R(\mathrm{P-C})] - 408.00$$

This equation, being analogous to that of the unprotonated species (Figure 3), suggests that all species could be considered as a set in exploring the Δ*E*(2)/*R*(P−C) correlation (Figure 5b) given by the general linear equation ($R^2 = 0.984$)

$$\Delta E(2) = 232.92[R(\mathrm{P-C})] - 414.72$$

Accordingly, hyperconjugation is shown to be of key importance in tuning the *R*(P−C) bond length in phosphamides. It is worth noting that in the absence of the hyperconjugative interactions (Δ*E*(2) = 0) the *R*(P−C) bond length becomes equal to 1.781 Å.

Analogous excellent linear correlations also hold between the ΔE_{del} values and the *R*(P−C) bond lengths of the $[MeC(X)PRR'H]^+$ species (Figure 6a) and the whole series including the phosphamides as well (Figure 6b). In the $[MeC(X)PRR'H]^+$ species, deleting the n(O) → σ*(P−C) hyperconjugative interactions results in significant shortening of the P−C bond; for all $[MeC(X)PRR'H]^+$ species, after deletion of the n(O) → σ*(P−C) hyperconjugative interactions the P−C bond acquires a bond length of 1.762−1.784 Å.

Notice that the protonated species **28** and **29** have been omitted from the correlations, since in these species deletion of the σ*(P−C) acceptor orbital deletes also the strong reinforcing n(O)P → σ*(P−C) and n(F) → σ*(P−C) hyperconjugative interactions, respectively, thus resulting in a mismatch between the computed ΔE_{del} and Δ*E*(2) values.

Equilibrium Geometry, Stability, and Electronic Properties of “Real” Acylphosphane and Related Ligands. Next we will examine the equilibrium geometry, stability, and electronic properties of the following “real” acylphosphane ligands that have been isolated and characterized experimentally:[5,16] (trifluoroacetyl)diphenylphosphane, $CF_3C(O)PPh_2$ (**30**), (anisoyl)-

Table 3. Stabilization Energies ΔE(2) (in kcal/mol) Introduced by the n(O) → σ*(P−C) and n(O) → σ*(C−C) Hyperconjugative Interactions and Deletion Energies ΔE_{del} for σ*(P−C) Deletion, along with the R(P−C) and R(C−C) Bond Lengths (in Å) for the "Real" Phosphamide Ligands 30−39 Computed at the B3LYP/6-31G(d,p) Level of Theory

ligand	n(O) NBO eigenvalue (eV)	n(O) NBO occ	R(P−C)	Δ$E_{(2)}$ n(O) → σ*(P−C)	ΔE_{del}	R(C−C)	ΔE(2) n(O) → σ*(C−C)
30	−0.288 82	1.853	1.881 (1.860)[a]	23.72	32.07	1.557	26.18
31	−0.263 48	1.858	1.904 (1.860)	26.87	33.25	1.500	19.73
32	−0.288 77	1.867	1.892 (1.837)	25.63	27.37	1.495	19.42
33	−0.259 01	1.871	1.881 (1.819)	24.01	26.91	1.504	19.73
34	−0.273 66	1.866	1.866 (1.812)	22.27	25.46	1.522	22.44
35	−0.294 75	1.854	1.885 (1.880)	23.99	31.59	1.557	25.07
36	−0.261 73	1.824	1.936 (1.841)	34.08	32.43	1.487	21.73
37	−0.269 74	1.813	1.972 (1.863)	36.88	34.24	1.488	22.39
38	−0.283 76	1.859	1.957 (1.877)	28.87	26.51	1.492	20.34
39	−0.024 50	1.823	1.950 (1.808)	36.31	31.79	1.313[b]	122.79[c]

[a] Values in parentheses are the R(P−C) bond lengths that result after deletion of the σ*(P−C) acceptor orbital. [b] R(C−N). [c] ΔE(2) of the n(O) → σ*(C−N) interaction.

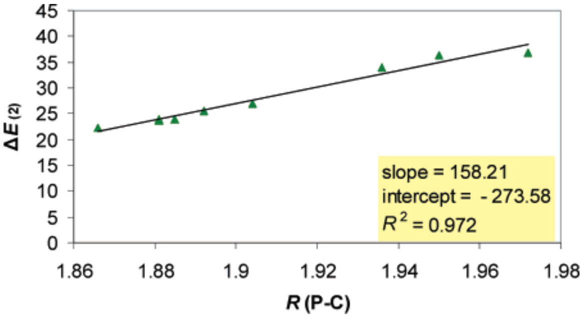


Figure 7. Linear correlation of the stabilization energy ΔE(2) (in kcal/mol) with the R(P−C) bond length (in Å) of the "real" phosphamide ligands.

diphenylphosphane, (o-MeOC$_6$H$_4$)C(O)PPh$_2$ (**31**), (anisoyl)bis(ethylcyano)phosphane, (o-MeOC$_6$H$_4$)C(O)P(NCCH$_2$CH$_2$)$_2$ (**32**), (anisoyl)dicyclohexylphosphane, (o-MeOC$_6$H$_4$)C(O)PCy$_2$ (**33**), (pentafluorophenyl)dicyclohexylphosphane, (C$_6$F$_5$)C(O)PCy$_2$ (**34**), (perfluorooctanoyl)diphenylphosphane, [CF$_3$(CF$_2$)$_6$]C(O)PPh$_2$ (**35**), 1,3,4-triphenylphosphet-2(1H)-one (**36**), and the parent 1-phenylphosphet-2(1H)-one (**37**), the phosphorus analogues of unsaturated β-lactams,[16] the 2H-phosphol-2-one (**38**), and the anionic heteroallene [HNC(O)PH$_2$]$^-$ (**39**). The equilibrium geometries of phosphamides **30**−**39** computed at the B3LYP/6-31G(d,p) level of theory are given in Figure S5 in the Supporting Information. The stabilization and deletion energies introduced by the favorable interactions of the nonbonding n(O) donor orbitals with the antibonding σ*(P−C) and σ*(C−C) acceptor orbitals in phosphamides **30**−**39** along with the R(P−C) bond lengths (figures in parentheses) that result after deletion of the σ*(P−C) acceptor orbital are summarized in Table 3.

Interestingly, the phosphorus analogues of the unsaturated β-lactams **36** and **37** showed longer intracyclic R(P−C) bond lengths of 1.936 and 1.972 Å, respectively. This is consistent with the higher values of the stabilization energies ΔE(2), thus illustrating further the key role of the hyperconjugative interactions on the R(P−C) bond lengths of phosphamides. Notice also that the other P−C bond has a normal R(P−C) bond length of 1.869 Å, while the C═C double bond remains well localized.

As expected, there is an excellent linear correlation of the R(P−C) bond length with the ΔE(2) values for the "real" phosphamide ligands shown in Figure 7. However, there is no correlation between the deletion energy ΔE_{del} and the R(P−C) bond length, because the deleted σ*(P−C) acceptor orbital of the "real" phosphamide ligands participates in a number of various weaker hyperconjugative interactions with donor orbitals localized on the substituents of both the carbonyl C and the P atoms. The nature and magnitude of such interactions depend on the nature of the subsituents and contribute to a different extent to the stabilization energy. This is also reflected on the different magnitude of the P−C bond shortening upon deleting the n(O) → σ*(P−C) hyperconjugative interactions (Table 3); for the "real" phosphamide ligands, after deletion of the n(O) → σ*(P−C) hyperconjugative interactions, the P−C bond acquires a bond length in the range of 1.808−1.880 Å.

It is worth noting the strong contribution of the hyperconjugative n(O) → σ*(P−C) interactions on the R(P−C) bond lengths of the cyclic 2H-phosphol-2-one **36** and the anionic heteroallene ligand [HNC(O)PH$_2$]$^-$ (**37**). The computed ΔE(2) values of 27.15 and 34.45 kcal/mol for **36** and **37**, respectively, are consistent with the relatively long R(P−C) bond lengths (Table 3). However, the computed R(P−C) bond length in the cyclic phosphamides **36** and **37** is higher than that predicted from the magnitude of the ΔE(2) values, indicating that in the cyclic phosphamides the ring strain contributes further to the lengthening of the labile P−C bond.

In summary, it can be concluded that the R(P−C) bond length in acylphosphanes can be tuned upon careful selection of the substituents on both the carbonyl C and the P atoms. *Generally, it is the combination of electron-withdrawing substituents on the carbonyl C atom with electron-releasing substituents on the P atom that strengthens the P−C bond in phosphamides.*

It should be noted that the R(P−C) bond length of the phosphamide CF$_3$C(O)PMe$_2$, involving the strongly electron-withdrawing F substituents on the carbonyl C atom and the strongly electron-releasing methyl substituents on the P atom, was found to be 1.869 Å. In the phosphamide CF$_3$C(O)PMe$_2$ the ΔE(2) values for the n(O) → σ*(P−C) and n(O) → σ*(C−C) hyperconjugative interactions are 22.64 and 26.56 kcal/mol, respectively. It can be seen that the combination of the electron-withdrawing substituents on the carbonyl C with the electron-releasing substituents on the P atoms disfavors the n(O) → σ*(P−C) and favors the n(O) → σ*(C−C) hyperconjugative interactions. The high n(O) → σ*(C−C) hyperconjugative interactions are reflected in the long R(C−C) bond length of 1.554 Å.

Effect of Coordination with a Metal Center on the R(P−C) Bond Length of Acylphosphane Ligands. Finally, we explored the effect of coordination of the phosphamide ligands with a metal center on the R(P−C) bond length. Both main-group and transition-metal complexes of the MeC(O)PH$_2$ ligand have been considered. Thus, we studied the complexes [Li{MeC(O)PH$_2$}]$^+$ (**40**), [K{MeC(O)PH$_2$}]$^+$ (**41**), [Tl{MeC(O)PH$_2$}]$^+$ (**42**), [CpRhCl$_2${κ^1P-H$_2$PC(O)Me}] (**43**), [CpRhCl$_2${κ^1P-H$_2$PC(OH)Me}]$^+$ (**44**), *trans*-[RhCl(CO){κ^1P-H$_2$PC(O)Me}$_2$]

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Table 4. Stabilization Energies Δ*E*(2) (in kcal/mol) Introduced by the n(O) → σ*(P−C) and n(O) → σ*(C−C) Hyperconjugative Interactions for the Phosphamide Complexes 40−50 along with the Metal−Ligand (M−L) Dissociation Energies (in kcal/mol) and Natural Atomic Charges Computed at the B3LYP/lanl2dz(heavy element) ∪ 6-31G(d,p) Level of Theory

complex	n(O) NBO eigenvalue (eV)	n(O) NBO occ	*R*(P−C)	Δ*E*(2) n(O) → σ*(P−C)	*R*(C−C)	Δ*E*(2) n(O) → σ*(C−C)	M−L dissociation energy
40	−0.486 20	1.909	1.853	16.40	1.499	14.06	46.9
41	−0.434 64	1.904	1.872	18.91	1.507	16.75	21.3
42	−0.460 06	1.894	1.862	19.50	1.505	17.79	25.6
43	−0.307 99	1.862	1.900	28.99	1.505	21.02	23.3
45	−0.299 75	1.851	1.911	31.91	1.505	20.95	26.7
	−0.302 77	1.861	1.900	30.38	1.505	22.10	
46	−0.314 56	1.846	1.916	33.34	1.504	20.64	
47	−0.733 91	1.822	1.835	10.28	1.494	10.16	53.4
48	−0.289 09	1.850	1.943	32.70	1.512	21.93	15.9
49	−0.453 61	1.815	1.951	40.65	1.499	19.77	43.8
50	−0.560 84	1.864	1.920	15.04	1.482	14.80	94.5

(**45**), [RhCl(CO){κ^1*P*-$H_2PC(O)Me$}] (**46**), [CpTiCl$_2${κ^1*O*-$H_2PC(O)Me$}]$^+$ (**47**), [Pd{κ^1*P*-$H_2PC(O)Me$}$_2$] (**48**), [Ag{κ^1*O*-$MeC(O)PH_2$}]$^+$ (**49**), and [Cu{κ^2*P*,*O*-$MeC(O)PH_2$}]$^+$ (**50**).

The equilibrium geometries of complexes **40**−**50** are presented in Figure S6 in the Supporting Information, while selected structural, energetic, and stereoelectronic properties are given in Table 4. The hard Li^+, K^+, and Tl^+ cations interact with $MeC(O)PH_2$ from the site of the carbonyl O atom, with the interactions being primarily electrostatic (ion−dipole interactions). Therefore, the effect of the cation on the favorable n(O) → σ*(P−C) and n(O) → σ*(C−C) hyperconjugative interactions would be expected to be relatively small. Actually, the stabilization energies for the n(O) → σ*(P−C) and n(O) → σ*(C−C) interactions were found to be 16.40 and 14.06 kcal/mol for **40**, 18.91 and 16.75 kcal/mol for **41**, and 19.50 and 17.79 kcal/mol for **42**, respectively, consistent with the relatively small shortening of the *R*(P−C) bond length upon interaction of the phosphamide with the Li^+, K^+, and Tl^+ cations. The computed M−L interaction energies were found to be 46.9, 21.3, and 25.6 kcal/mol for **40**−**42**, respectively.

On the other hand, phosphamide ligands could be coordinated to a transition-metal atom through either the soft P (κ^1P bonding mode) or the hard O (κ^1O bonding mode) donor atoms or through both of them (κ^2P,O bonding mode), forming a four-membered chelate ring. The first coordination mode occurs in the Rh(III) complexes **43** and **45**, the Rh(I) complex **46**, the Pd(0) complex **48**, and the Ag(I) complex **49** and the second one in the Ti(IV) complex **47**, while the third one occurs in the Cu(I) complex **50**.

It should be noted that the Rh−P bond strength in [CpRhCl$_2${κ^1*P*-$H_2P(CO)CH_3$}] (**43**) is comparable to that of the complex *trans*-[RhCl(CO){κ^1*P*-$H_2P(CO)CH_3$}$_2$] (**45**), used as a model of the recently isolated and characterized *trans*-[RhCl(CO){$Ph_2P(CO)CH_3$}$_2$] complex,[5] with the bond dissociation energies found to be 23.3 and 26.7 kcal/mol, respectively. It is also interesting to note that upon coordination of the $H_2P(CO)CH_3$ ligands with the Rh(I) atom in **45**, the P−C bond of one of the ligands is elongated by 0.011 Å, while the length of the second bond remains unchanged. Such an elongation of the P−C bond is reflected in the computed Δ*E*(2) values (Table 4). Dissociation of one of the coordinated $H_2P(CO)CH_3$ ligands from complex **45** yields the three-coordinated complex **46**, which adopts a T-shaped structure. In **46** the P−C bond of the coordinated $H_2P(CO)CH_3$ ligand is elongated by 0.016 Å with respect to the "free" ligand. This elongation is possibly due to the enhancement of the hyperconjugative interactions by the electron density transfer from the coordinated P donor atom of the ligand to the metal center. To assess the role of hyperconjugation on the P−C bond lability of the coordinated phosphamide ligand in **43**, we explored the effect of protonation at the carbonyl O atom. In effect, in the protonated complex [CpRhCl$_2${κ^1*P*-$H_2PC(OH)CH_3$}]$^+$ (**44**), the protonation shields the n(O) lone pair which could not participate in the favorable n(O) → σ*(P−C) and n(O) → σ*(C−C) hyperconjugative interactions, and therefore, both the P−C and C−C bonds are strengthened; the *R*(P−C) and *R*(C−C) bonds are shortened by 0.050 and 0.038 Å, respectively.

In bis(acetylphosphane)palladium(0) (**48**), the phosphamide ligand is loosely associated with the soft P donor atom of the phosphamide ligand; the computed Pd−P bond dissociation energy is found to be only 15.9 kcal/mol. In contrast to the case for the Rh(III) phosphamide complex **43**, in the Pd(0) complex **48** the coordination further weakens the P−C bond, which is elongated by 0.043 Å. Such an elongation is consistent with the strong n(O) → σ*(P−C) hyperconjugative interactions in **48** with a Δ*E*(2) value of 32.70 kcal/mol.

The $MeCOPH_2$ ligand is much more strongly bonded via the hard O donor atom with an early first-row transition metal, such as Ti(IV) in [CpTiCl$_2${κ^1*O*-$H_2P(CO)CH_3$}]$^+$ (**47**). The computed Ti−O bond dissociation energy was found to be 53.4 kcal/mol at the B3LYP/6-31G(d,p) level of theory. This coordination mode of the phosphamide ligand protects the n(O) lone pair, which then could not participate in the n(O) → σ*(P−C) hyperconjugative interactions, and therefore, the P−C bond is strengthened, acquiring a very short *R*(P−C) bond length of 1.835 Å. It is evident that *an alternative way for a phosphamide ligand to be stabilized is its coordination via the carbonyl O donor atom with an early-transition-metal ion.*

On the other hand, coordination of phosphamides to a late-transition-metal ion, such as Cu(I) and Ag(I), lengthens remarkably the P−C bond and therefore the ligands are destabilized. In [Ag{$MeC(O)PH_2$}]$^+$ (**49**) the $MeC(O)PH_2$ ligand is coordinated to the soft Ag^+ cation via the soft P donor atom. The computed Ag−P bond dissociation energy of 43.8 kcal/mol illustrates that the Ag−P bond is stronger than the Rh−P and Pd−P bonds in **43** and **48**, respectively. Moreover, the long Ag···O distance of 3.740 Å excludes any interaction of the Ag^+ cation with the carbonyl O donor atom of the phosphamide ligand. The coordination of the $MeC(O)PH_2$ ligand to the Ag^+ cation via the soft P donor atom leaves "free" the n(O) lone pair to participate in the n(O) → σ*(P−C) hyperconjugative interactions. Therefore, the computed high Δ*E*(2) value of 40.65 kcal/mol accounts well for the long *R*(P−C) bond length of 1.951 Å. For the [Ag{κ^1*P*-$MeC(O)PH_2$}]$^+$ complex one would expect a facile decarbonylation of the phosphamide ligand analogous to the decarbonylation of the acetyl- and (trifluoroacetyl)diphenylphosphane ligands with the [RhCl{$P(C_6H_5)_3$}$_3$] complex observed several years ago.[17]

Finally, in $[Cu\{\kappa^2P,O\text{-}MeC(O)PH_2\}]^+$ (**50**), the $MeC(O)PH_2$ ligand is coordinated to Cu(I) central atom in a bidentate fashion, forming a four-membered chelate ring. The participation of the n(O) lone pair in a "loose" association with the Cu(I) central atom diminishes the n(O) → σ^*(P−C) hyperconjugative interactions, thus decreasing $\Delta E(2)$ from 29.17 in the "free" ligand to 15.04 kcal/mol in the complex. The n(O) → σ^*(P−C) hyperconjugative interactions combined with the covalent interactions of Cu(I) with the P donor atom and the ring strain of the four-membered chelate ring account well for the observed elongation of the P−C bond in **50**.

Concluding Remarks

In this paper we report on the results of a comprehensive study of the forces that control the labile P−C bond strength in phosphamides and their conjugate acids and related species. The results can be summarized as follows.

Three principal forces, due to electrostatic, covalent, and hyperconjugative interactions, control the structural preferences of the phosphamide ligands and their conjugate acids.

The P−C bond in phosphamides exhibits both an ionic and covalent character, with the two components having almost the same contribution. Thus, for the parent $MeCOPH_2$ ligand the contributions of the two components amount roughly to 41% and 38%, respectively.

The linear correlation of the R(P−C) with the R(C═O) bond lengths is indicative of a three-center−four-electron (3c-4e) bonding in the P−C═O nuclear framework.

Hyperconjugative (anomeric) n(O) → σ^*(P−C) interactions were found to play a key role in tuning the R(P−C) bond length in phosphamides and their conjugate acids. The n(O) → σ^*(P−C) interactions contribute significantly to the elongation of the R(P−C) bond length. It is worth noting the linear correlation of the stabilization energy due to the n(O) → σ^*(P−C) hyperconjugative interactions with the R(P−C) bond length.

The lone pair of electrons on the P atom does not make any contribution to the strength of the P−C bond, since the directionality of the lone pair orbital is in the opposite direction to the bond; thereby its involvement in favorable hyperconjugative interactions with orbitals localized on the P−C bond in both the phosphamides and their protonated species at the O atom is not allowed.

It was found that the combination of electron-withdrawing substituents on the carbonyl C atom with electron-releasing substituents on the P atom strengthen the labile P−C bond in phosphamides and stabilize the ligands. Moreover, phosphamides were found to be stabilized by coordination with early-transition-metal ions, such as Ti(IV), but are strongly destabilized by coordination with late-transition-metal ions, such as Ag(I) and Cu(I). In the former case the phosphamides are coordinated with the central metal ion in a unidentate fashion through the carbonyl O donor atom, while in the latter case they are coordinated to the central metal ion either in a unidentate fashion through the P donor atom or in a bidentate fashion through both the O and P donor atoms, forming a four-membered chelate ring. Coordination of phosphamides with Rh(III) via the P donor atom only marginally affects the R(P−C) bond length.

Finally, the interaction of phosphamides with the hard cations Li^+, K^+, and Tl^+ from the site of the hard carbonyl O atom being primarily electrostatic (ion−dipole interactions) does not affect significantly the favorable n(O) → σ^*(P−C) hyperconjugative interactions and, therefore, the R(P−C) bond length is only sligthly shortened with respect to that of the "free" ligands.

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Supporting Information Available: Text giving the complete reference 9, Cartesian coordinates and energies of all stationary points (Tables S1 and S2, respectively), NBO data, including the more significant donor−acceptor NBO interactions and their second-order perturbation stabilization energies (Table S3), equilibrium structures of the phosphamides and their conjugate acids (Figures S1−S4), and equilibrium structures of "real" phosphamide ligands and metal complexes of phosphamides (Figures S5 and S6, respectively). This information is available free of charge via the Internet at http://pubs.acs.org.

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