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Effects of Substituents on the Stability of Phosphoranyl Radicals

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The effect of substituents on the geometries, apicophilicities, radical stabilization energies, and bond dissociation energies of $^{\bullet}P(CH_3)_3X$ (X = CH_3, SCH_3, OCH_3, OH, CN, CF_3, Ph) were studied via high-level ab initio molecular orbital calculations. Two alternative definitions for the radical stabilization energy (RSE) were considered: the standard RSE, in which radical stability is measured relative to $H{-}P(CH_3)_3X$, and a new definition, the α-RSE, which measures stability relative to $P(CH_3)_2X$. We show that these alternative definitions yield almost diametrically opposed trends; we argue that α-RSE provides a reasonable qualitative measure of relative radical stability, while the standard RSE qualitatively reflects the relative strength of the P−H bonds in the corresponding $H{-}P(CH_3)_3X$ phosphines. The $^{\bullet}P(CH_3)_3X$ radicals assume a trigonal-bipyramidal structure, with the X-group occupying an axial position, and the unpaired electron distributed between a $3p_\sigma$-type orbital (that occupies the position of the "fifth ligand"), and the σ^* orbitals of the axial bonds. Consistent with this picture, the radical is stabilized by resonance (along the axial bonds) with configurations such as $X^-\ P^{\bullet+}(CH_3)_3$ and $X^\bullet\ P(CH_3)_3$. As a result, substituents that are strong σ-acceptors (such as F, OH, or OCH_3) or have weak P−X bonds (such as SCH_3) stabilize these configurations, resulting in the largest apicophilicities and α-RSEs. Unsaturated π-acceptor substituents (such as phenyl or CN) are weakly stabilizing and interact with the $3p_\sigma$-type orbital via a through-space effect. As part of this work, we challenge the notion that phosphorus-centered radicals are more stable than carbon-centered radicals.

1. Introduction

Phosphoranyl radicals are important in a number of synthetic and biological processes. They have been implicated as possible intermediates in radiation-induced DNA strand breakage[1] and in the biodegradation of environmentally toxic organophosphate pesticides.[2] Depending upon their substituents, phosphoranyl radicals appear to be remarkably stable, and persistent silylated phosphoranyl radicals have even been suggested for dynamic nuclear polarization applications.[3] From a synthetic perspective, the addition of phosphoranyl radicals to alkenes is an important P−C bond formation process, utilized in (for example) the production of organophosphate pesticides.[4] Phosphoranyl radicals are also intermediates in free-radical Arzubov-like processes such as (1) and in related reactions such as (2) and (3).[5]

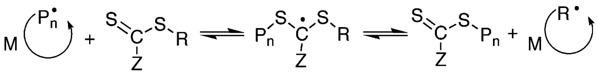
$$R_2N^\bullet + PhCH_2OP(OEt_2)_2 \rightarrow (R_2N)(PhCH_2O)P^\bullet(OEt_2)_2 \rightarrow PhCH_2^\bullet + R_2NP({=}O)(OEt_2)_2 \quad (1)$$

$$RO^\bullet + P(Z)_3 \rightarrow R'OP^\bullet Z_3 \rightarrow R^\bullet + O{=}PZ_3 \quad (2)$$

$$RS^\bullet + P(Z)_3 \rightarrow R'SP^\bullet Z_3 \rightarrow R^\bullet + S{=}PZ_3 \quad (3)$$

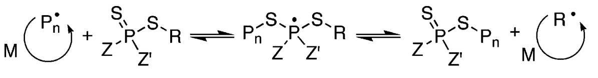
By tailoring the ligands on the phosphine, reactions such as these can be exploited as highly selective alkyl radical sources for use in kinetic studies[6] and in a variety of synthetic procedures.[7]

Our interest in phosphoranyl radicals stems from a recent proposal that dithiophosphinate esters (i.e., S=P(Z)(Z′)SR) might be used as alternatives to dithioesters (i.e., S=C(Z)SR) in the reversible addition fragmentation chain transfer (RAFT) polymerization process.[8] RAFT is an important new method for controlling the molecular weight and architecture in free-radical polymerization.[9] Its basic principle is to protect the majority of the propagating polymeric radicals from bimolecular termination processes through their reversible trapping into a dormant thiocarbonyl compound via the following chain transfer process:



(4)

To achieve control, a delicate balance of the rates of the various competing reactions is required, so as to ensure that the dormant species is orders of magnitude greater in concentration than the active species, the exchange between the two forms is rapid, and side reactions do not occur. When dithiophosphinate esters are used as RAFT agents, the propagating radical adds to the S=P bond of the agent, generating a phosphoranyl radical as the intermediate.[8]



(5)

The introduction of dithiophosphinate esters as RAFT agents may help to broaden the scope of the RAFT process, since one might expect the reactivities of the P=S and C=S bonds of the agents, and the stability of the C-centered and P-centered radical intermediates, to differ substantially. However, to exploit this potential and design optimal agents for controlling free-radical polymerization, an understanding of the effects of substituents on the reactivity of the S=P bond, and on the structure and

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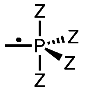
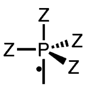
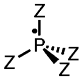
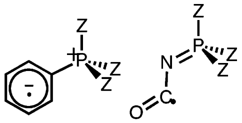
stability of the intermediate phosphoranyl radical, is essential. In the present work we focus on this latter question.

Although key qualitative aspects of the electronic structure and geometry of phosphoranyl radicals are known, there is very little quantitative information on the effects of substituents on their stabilities.[10] Seminal EPR studies[5] in the 1970s and early 1980s established that, depending on the ligands, phosphoranyl radicals can assume a trigonal biypryamidal structure (TBP, I or II), in which the unpaired electron is effectively the fifth ligand; a tetrahedral (σ^*, III) structure, in which the unpaired electron is located in the σ^* orbital of the basal bond; or some intermediate form between these two extremes. In the TBP structures, the unpaired electron is usually located as an equatorial ligand (I), though in rare cases, structures in which the unpaired electron is an axial ligand (II) have also been suggested.[11] It was also found that, in some instances, an additional "ligand π" structure (IV), in which the unpaired electron was carried by one of the ligands (usually a phenyl group), is possible. More recently, ab initio molecular orbital studies have confirmed these electronic structure assignments and provided an insight into the mechanisms for ligand permutation.[12]


I TBP$_e$


II TBP$_a$


III σ^*


IV ligand π

It is known that the electronic structure of the phosphoranyl radicals, and the site selectivity (apicophilicity) of their ligands, is important in determining their preferred fragmentation pathways and even their fragmentation kinetics.[13,14] The apicophilicity of a variety of ligands has been found to depend mainly on their group electronegativities,[5] though other factors (such as the potential for hyperconjugative interactions between the ligands[11]) are also important. Based on qualitative valence bond theory arguments, Roberts and co-workers[13,14] introduced a simple expression for predicting apicophilicity of ligand A in the A(B)P$^\bullet$L$_2$ radical on the basis of the strength of an equatorial P−A bond, D(P−A), the electron affinity (EA) of A$^\bullet$, and the ionization energy (IE) of BPL$_2$. The apicophilicity of A was thought to increase as its value of α_A, as calculated via eq 6, decreases.

$$\alpha_A = \mathrm{IE(BPL_2)} - \mathrm{EA(A^\bullet)} + \mathrm{D(P{-}A)} \qquad (6)$$

Although a qualitative association between the calculated values of α_A and the rates of ligand exchange in phosphoranyl radicals was demonstrated, this expression is yet to be tested quantitatively. More importantly, there do not appear to be any systematic studies of the effects of substituents on the *stabilities* of the phosphoranyl radicals.

With the growing interest in exploiting phosphoranyl radicals as intermediates in synthesis, an understanding of the effects of substituents on radical stability would be invaluable in designing optimal reagents, and a high-level theoretical investigation is timely. In the present work we explore the effect of a variety of substituents (X = CH$_3$, CN, OH, CF$_3$, Ph, OCH$_3$, SCH$_3$, F) on the structure, stabilities, and apicophilicities of the phosphoranyl radicals, $^\bullet$P(CH$_3$)$_3$X. We also compare the stabilities of phosphoranyl radicals with their carbon-centered radical counterparts and uncover the surprising result that, although more persistent in many situations, phosphorus-centered radicals may actually be less intrinsically stable than carbon-centered radicals.

2. Definitions of Radical Stability

The term "radical stability" is loosely defined, and it is important to clarify how it will be used in the present work. Griller and Ingold[15] suggested that a distinction be made between the "persistence" of a radical, which relates to its kinetic lifetime in a particular chemical environment, and its thermodynamic "stabilization energy" (now referred to as the radical stabilization energy, RSE) which they suggested was an "intrinsic property" of the radical. It is the thermodynamic stability of the radicals that we are concerned with in the present work. For a carbon-centered radical (R$^\bullet$), the RSE is defined as the energy change of the following isodesmic reaction:[16]

$$\mathrm{R^\bullet + H{-}CH_3 \rightarrow R{-}H + {}^\bullet CH_3} \qquad (7)$$

This compares the energies of the radical (R$^\bullet$) with a reference radical ($^\bullet$CH$_3$) and uses the corresponding alkanes to balance the reaction. The radical R$^\bullet$ is said to be "stabilized" (relative to $^\bullet$CH$_3$) if the RSE is positive and "destabilized" if it is negative.[15]

In reality, the RSE depends of course on both the relative stabilities of the radicals ($^\bullet$CH$_3$ and $^\bullet$R) and those of the corresponding closed-shell compounds (H−CH$_3$ and H−R).[17,18] In other words, a positive RSE could result from R$^\bullet$ being more intrinsically stable than $^\bullet$CH$_3$, or from the C−H bond in R−H being less intrinsically stable than the C−H bond in H−CH$_3$, or from both simultaneously. If the RSE is to measure the relative stabilities of the radicals only, it is necessary that the differences in the C−H bond energies of the closed shell compounds are negligible and therefore cancel from the reaction energy. It is only under those circumstances that it makes sense to rationalize the trends in a series of RSEs in terms of orbital interactions involving the unpaired electron and to use the resulting insights to predict the behavior of the radicals in a wider chemical context. In the case of the carbon-centered radicals, it does seem reasonable to suppose that the differences in C−H bond energies of the closed shell compounds largely cancel from the RSEs because the steric and polar effects on C−H bond energies are likely to be small.[15,17] In support of this, we note that the relative RSEs of a series of carbon-centered radicals can be rationalized in terms of orbital interactions involving the unpaired electron,[19−21] have useful predictive value in other chemical reactions such as addition to C=C[22] and C=S double bonds,[21] and have even been exploited in the successful design of new reagents.[23,24]

The assumption that the stabilities of the closed-shell species largely cancel from the calculated RSEs thus appears to hold (at least qualitatively) for carbon-centered radicals. However, this will not necessarily be generally the case, as it depends heavily on the nature of the bond that it is used to balance the isodesmic reaction. For example, even for carbon-centered radicals, if eq 7 is balanced using the corresponding fluorides (instead of alkanes), the resulting stabilization energies for alkyl radicals have diametrically opposed trends to those of their standard RSEs, indicating the significant contribution of the stabilities of the closed-shell species.[17,18] It is therefore important to choose the isodesmic reaction carefully.

In the present work we aim to study the effects of substituents on the thermodynamic stability of phosphoranyl radicals and choose an isodesmic reaction for this purpose that minimizes the contribution of the closed-shell species to the calculated stabilization energy. To this end, two alternative definitions of the radical stabilization energy are considered. First, we calculate the standard RSE, which for the case of a phosphoranyl radical $^{\bullet}P(CH_3)_3X$ could be defined as the energy change of the following reaction.

$$^{\bullet}P(CH_3)_3X + H{-}P(CH_3)_4 \rightarrow H{-}P(CH_3)_3X + {}^{\bullet}P(CH_3)_4 \tag{8}$$

This differs from the standard RSE for a carbon-centered radical only in that the relative values have been systematically shifted so that the reference species is $^{\bullet}P(CH_3)_4$ rather than $^{\bullet}CH_3$. Second, we introduce an alternative isodesmic reaction:

$$^{\bullet}P(CH_3)_3X + P(CH_3)_3 \rightarrow P(CH_3)_2X + {}^{\bullet}P(CH_3)_4 \tag{9}$$

This equation also compares the energies of the $^{\bullet}P(CH_3)_2X$ and $^{\bullet}P(CH_3)_4$ radicals but balances the equation using the corresponding P(III) phosphines rather than P(V) phosphines. In other words, the stability of the radical is assessed on the basis of its susceptibility to α-scission of the (common) $^{\bullet}CH_3$ radical (rather than its susceptibility to hydrogen abstraction):

$$^{\bullet}P(CH_3)_3X \rightarrow P(CH_3)_2X + {}^{\bullet}CH_3 \tag{10}$$

In the present work we refer to the energy change of eq 9 as the α-RSE, so as to distinguish it from the standard RSE, as defined by eq 8.

As noted above, as part of this work we hope to identify a suitable isodesmic reaction that will measure (at least qualitatively) the relative stabilities of phosphoranyl radicals. The RSE will measure radical stability if X does not significantly affect the stability of the P−H bond in the corresponding P^V phosphines ($H{-}P(CH_3)_3X$); the α-RSE will measure radical stability if X does not significantly affect the stability of the lone pair in the P^{III} phosphines ($P(CH_3)_2X$). In reality neither assumption will hold exactly, but it is possible that one or both definitions may provide an approximate measure of radical stability that has some practical value, in the same way that the standard RSE has been successfully used to study the stabilities of carbon-centered radicals. Since intrinsic radical stabilities are essentially unmeasurable, our analysis will necessarily be qualitative in nature. Our criteria for evaluating whether the RSE or α-RSE can measure relative radical stabilities are on the basis of whether either measure yields trends that are chemically intuitive and whether the arguments used to rationalize the trends are consistent with other observables, such as the apicophilicities.

It will be clear from the above discussion that the use of isodesmic reactions to study the stability of a species has inherent limitations. Although stabilization energies can be precisely defined, they will only have predictive value in a wider chemical context if they can be attributed primarily to the "intrinsic" stabilities of one or other of the components. A means of measuring the intrinsic stabilities themselves would therefore be of major practical value. Although intrinsic stability is difficult to define unambiguously, there is an interesting body of work toward this goal. In particular, it has been suggested that the bond dissociation energy (BDE) of a compound can be decomposed into a "bond energy" (which could be associated with the intrinsic stability of the bond itself) and a total (electronic and geometric) "reorganization energy" of the components.[25] If the intrinsic bond energies of the species in reactions 7−9 were known, they could then be subtracted from the calculated reaction energies. The remaining quantity would then provide a relative measure of the inherent stabilities of the radicals. Of course, decomposing the BDE into two nonobservable[26] components introduces assumptions and limitations of its own; however, chemically intuitive approaches have been developed using Atoms-In-Molecules (AIM) theory.[25,27,28] Although appealing, these schemes are not adopted in the present work as they need further development before they can be applicable to phosphoranyl radicals. In particular, the present methods are based on an assumption that there is minimal charge transfer between the bonded atoms, an assumption that is not justifiable for the present systems. However, with further development these schemes offer a possible means of quantitatively evaluating the extent to which RSEs measure relative radical stabilities, both for phosphoranyl radicals of the present work and more generally.

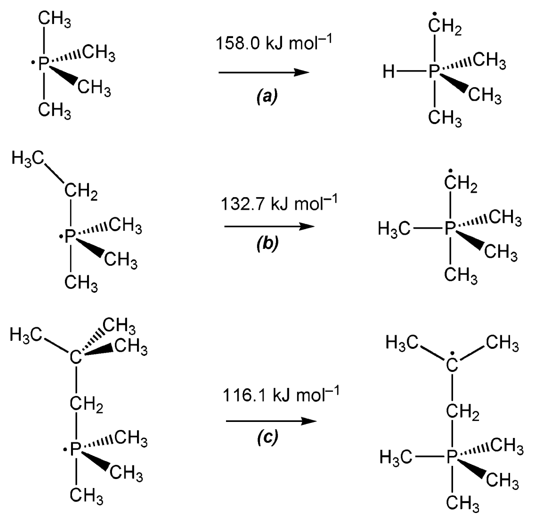
3. Theoretical Procedures

The RSEs and α-RSEs of the phosphoranyl radicals $^{\bullet}P(CH_3)_3X$ (X = CH_3, CN, OH, CF_3, Ph, OCH_3, SCH_3, F) were calculated at 0 K, using standard ab initio molecular orbital theory[29] and density functional theory[30] calculations, carried out using GAUSSIAN 03[31] and MOLPRO 2000.6.[32] The geometries of the radicals and closed-shell species were optimized at the B3-LYP/6-31G(d) level of theory, and the nature of the stationary points was confirmed via frequency calculations at this level. The scaled[33] B3-LYP/6-31G(d) frequencies were also used to calculate the zero-point vibrational energy corrections. Improved energies were calculated at the G3(MP2)-RAD[34] level of theory. This is a high-level composite procedure that attempts to approximate coupled-cluster [URCCSD(T)] energies with a large triple-ζ basis set via additivity approximations. To assist in the qualitative rationalization of the results, the charge and spin density distributions within the phosphoranyl radicals were calculated via NBO population analyses, carried out at the B3-LYP/6-311+G(3df,2p) level of theory.

Although the performance of these theoretical procedures has not as yet been explicitly tested for the case of phosphoranyl radicals, the G3(MP2)-RAD//B3-LYP/6-31G(d) method has previously been shown to provide accurate results (within 5 kJ mol^{-1}) for the thermochemistry of open-shell species when compared with a large test set of experimental data.[34] Moreover, it has previously been shown that G3(MP2)-RAD provides accurate values for the RSEs of carbon-centered radicals[20,21] and nitrogen-centered radicals[35] and the kinetics and thermodynamics of a variety of radical reactions.[36−40]

As in our recent study of carbon-centered radicals,[21] the RSEs were calculated using the minimum energy conformation of the radical (as identified via extensive conformational searches at the B3-LYP/6-31G(d) level). However, the minimum energy conformation of the radical was used as a basis for selecting the conformation of the corresponding P(V) phosphine. The geometry of the phosphine was then of course fully optimized to a (local) minimum energy structure within that conformation. In this way, the RSE is calculated for the most stable conformation of the radical, but any possible contribution to the RSE arising from conformational changes between the radical and phosphine is minimized. In the case of the α-RSEs, the P(III) phosphines were conformationally simpler than the phosphoranyl radicals and P(V) phosphines, and the conformation that most closely matched that of the phosphoranyl radical was also the lowest energy conformation. It should be noted that all radicals and all closed-shell phosphines considered in this study were true (local) minimum energy structures (i.e. having no imaginary frequencies).

SCHEME 1



As part of the present work we also explored the effects of substituents on the apicophilicity of the ligands. This was calculated as the energy difference between the minimum energy conformation of the $^{\bullet}P(CH_3)_3X$ radical in which the X-ligand was located axially and the minimum energy conformation in which the X-ligand was located equatorially. This provided a measure of the apicophilicity of the X-ligand, relative to the methyl group. The observed apicophilicities were then compared with those calculated on the basis of eq 6.[13,14] Applying this expression to the present systems, the apicophilicities of the X-group (α_X) in the $^{\bullet}P(CH_3)_3X$ radical were calculated via eq 11

$$\alpha_X = IE(P(CH_3)_3) - EA(X^{\bullet}) + D(P{-}X) \qquad (11)$$

where D(P−X) is the energy of the P−X bond in the phosphoranyl radicals, and IE and EA refer to the vertical ionization energy and electron affinity of the separated $P(CH_3)_3$ and $X^{\bullet}$ groups. In the original expression, Roberts and coworkers[13,14] specified that the D(P−X) should refer to the energy of the equatorial P−X bond in the phosphoranyl radicals, presumably as this provided a better approximation of the covalent bond energy (i.e. in the absence of the stabilization from the ionic configuration, which is significant when the X group is in the axial position). However, since these energies were difficult to extract experimentally, they were approximated using the corresponding P−X bond dissociation energies in the PX_3 phosphines. In the present work we were able to calculate the P−X bond dissociation energies in the phosphoranyl radicals themselves, as follows:

$$^{\bullet}P(CH_3)_3X \rightarrow P(CH_3)_3 + {}^{\bullet}X \qquad (12)$$

So that the BDEs represented the energies of an equatorial bond, we calculated the energy of eq 12 for the equatorial conformations of the phosphoranyl radicals. As in the case of the RSEs, all calculations were performed at the G3(MP2)-RAD//B3-LYP/6-31G(d) level of theory and include scaled B3-LYP/6-31G(d) zero-point vibrational energy.

Finally, to compare the relative stabilities of the phosphoranyl and carbon-centered radicals, a number of additional calculations were undertaken. The enthalpies of selected isomerization reactions (converting phosphoranyl radicals into carbon-centered radicals, see Scheme 1) were calculated at the RMP2/6-311+G(3df,2p) level of theory, and the P−P bond dissociation energy of the $(CH_3)_4P{-}P(CH_3)_4$ dimer and the corresponding C−C bond dissociation energies of $CH_3{-}CH_3$ and $(CH_3)_3C{-}C(CH_3)_3$ were calculated at the G3(MP2)-RAD level of theory.

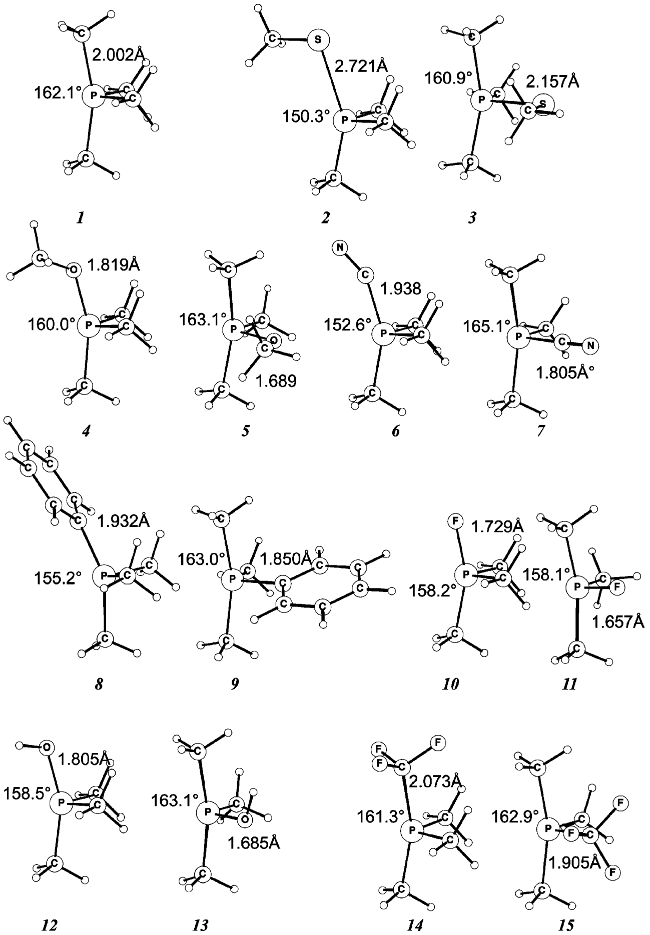


Figure 1. B3-LYP/6-31G(d) optimized geometries for $P^{\bullet}(CH_3)_3X$ (X = CH_3, SCH_3, OCH_3, CN, Ph, F, OH, CF_3), showing the angles between the axial ligands, and P−X bond lengths. The minimum energy axial and equatorial conformations are shown; in all cases the axial conformation is the global minimum, and all are true minimum energy structures (i.e. having zero imaginary frequencies).

4. Results and Discussion

The B3-LYP/6-31G(d) optimized geometries of the phosphoranyl radicals $^{\bullet}P(CH_3)_3X$ are displayed in Figure 1; complete geometries in the form of Gaussian archive entries are provided in the Supporting Information. The energy differences between the lowest energy axial and equatorial conformations of the radicals are shown in Table 1, together with the corresponding calculated apicophilicites of the X substituents, as obtained via eq 11. Also included in this table are the P−X bond dissociation energies of the equatorial conformations of the radicals and the vertical electron affinities of the $X^{\bullet}$ ligands, as used in evaluating eq 11, and also the charges and spin densities on phosphorus and X in the axial conformations of the radicals. Using the lowest energy (axial) conformations, the RSEs and α-RSEs of the phosphoranyl radicals were calculated and are displayed in Table 2, together with the corresponding RSEs of the carbon-centered analogues $^{\bullet}CH_2X$ and $^{\bullet}C(CH_3)_2X$.[17,20,21,41] So as to allow comparisons between the carbon- and phosphorus-centered radicals, the RSEs of the phosphoranyl radicals were evaluated via both eqs 7 and 8; that is, with respect to a $^{\bullet}CH_3$ reference species, as well as the $^{\bullet}P(CH_3)_4$ reference. In what follows, we first examine the geometries and apicophilicities of the substit-

TABLE 1: Axial−Equatorial Energy Differences (A−E) and P−X Bond Dissociation Energies (BDE) for $^\bullet P(CH_3)_3X$ (kJ mol^{-1}), Electron Affinities (EA) and Apicophilicities (α_X) of X (eV), and Charges (Q) and Spin Densities (Spin) on Phosphorus[a]

X	A−E	BDE(P−X)	EA(X$^\bullet$)	α_X	Q(P)	spin(P)	spin(X)
CH_3	0.0	−5.3	−0.12	8.8	1.056	0.459	0.276
Ph	−8.5	52.6	0.75	8.5	1.164	0.431	0.324
OH	−22.6	102.8	1.79	8.0	1.279	0.601	0.208
CN	−23.6	130.4	3.91	6.2	1.171	0.471	0.338
CF_3	−26.2	12.9	0.55	8.3	1.034	0.457	0.338
F	−29.2	210.4	3.41	7.5	1.383	0.674	0.137
OCH_3	−32.3	51.2	1.42	7.8	1.314	0.584	0.229
SCH_3	−70.7	−40.0	1.87	6.4	0.968	0.281	0.646

[a] Axial−equatorial energy differences, bond dissociation energies, and vertical electron affinities were calculated at the G3(MP2)-RAD level of theory using B3-LYP/6-31G(d) optimized geometries and include scaled B3-LYP/6-31G(d) zero-point energy corrections. The P−X BDE for $^\bullet P(CH_3)_3X$ was calculated for the lowest energy equatorial conformation of the radical. Apicophilicities (α_X) of X were calculated via eq 11 using the calculated D(P−X) and vertical EAs values above, together with the vertical ionization energy of $P(CH_3)_3$ of 8.72 eV. Charges and spin densities on phosphorus were calculated via NBO analysis at the B3-LYP/6-311+G(3df,2p)//B3-LYP/6-31G(d) level of theory on the lowest energy axial conformations of the $^\bullet P(CH_3)_3X$ radicals.

TABLE 2: Radical Stabilization Energies (RSEs) of $^\bullet P(CH_3)_3X$, $^\bullet CH_2X$, and $^\bullet C(CH_3)_2X$ and P−Me Bond Dissociation Energies (BDEs) and α-RSEs of $^\bullet P(CH_3)_3X$ (0 K, kJ mol^{-1})[a]

	$^\bullet P(CH_3)_3X$					
X	vs $^\bullet CH_3$	vs $^\bullet P(CH_3)_4$	BDE(P−Me)	α-RSE	$^\bullet CH_2X$[b] vs $^\bullet CH_3$	$^\bullet C(CH_3)_2X$ vs $^\bullet CH_3$
CH_3	162.3	0.0	−5.3	0.0	14.1	29.7[d]
Ph	162.4	0.1	5.1	10.4	58.9	70.3
OH	130.2	−32.1	28.7	34.0	31.6	40.8
CN	138.7	−23.6	16.0	21.3	31.9	59.0[e]
CF_3	139.6	−22.6	14.3	19.6	−7.7	18.4
F	105.3	−56.9	45.0	50.3	12.4	23.8
OCH_3	121.1	−41.1	29.5	34.8	31.0	36.4
SCH_3	174.0	11.7	51.8	57.2	40.7[c]	45.8

[a] RSEs and BDEs calculated at the G3(MP2)-RAD level of theory using B3-LYP/6-31G(d) optimized geometries of the minimum energy conformations and include scaled B3-LYP/6-31G(d) zero-point energy corrections. RSEs vs $^\bullet CH_3$ for $R^\bullet$ (R = $P(CH_3)_3X$ CH_2X, $C(CH_3)_2X$) were calculated as the energy change of reaction 7: $R^\bullet + CH_4 \rightarrow R{-}H + {}^\bullet CH_3$. RSEs vs $^\bullet P(CH_3)_4$ for $R^\bullet$ (R = $P(CH_3)_3X$) were calculated as the energy change of the reaction 8: $R^\bullet + HP(CH_3)_4 \rightarrow R{-}H + {}^\bullet P(CH_3)_4$. α-RSEs for $^\bullet P(CH_3)_3X$ were calculated as the energy change of the reaction 9: $^\bullet P(CH_3)_3X + P(CH_3)_3 \rightarrow {}^\bullet P(CH_3)_4 + P(CH_3)_2X$. [b] Taken from ref 20 unless otherwise specified. [c] Taken from ref 41. [d] Calculated from the R−H BDEs for CH_4 and $HC(CH_3)_3$ reported in ref 17. [e] Taken from ref 21.

uents, then discuss the effects of substituent on the relative stabilities of the phosphoranyl radicals, and conclude with an examination of the relative stabilities of phosphorus-centered and carbon-centered radicals.

Geometries and Apicophilicities. From Figure 1, it is seen that the phosphoranyl radicals $^\bullet P(CH_3)_3X$ (X = CH_3, CN, CF_3, OH, OCH_3, SCH_3, Ph) all assume a largely trigonal bipyramidal structure. The axial X−P$^\bullet$−Me bond angles range from 150.3 to 162.1° and are thus closer to the 180° expected for an ideal TBP_e structure than the 109.4° for the ideal σ^* structure. Figure 2 shows the singly occupied molecular orbital (SOMO) of the $^\bullet P(CH_3)_4$ radical, as calculated at the B3-LYP/6-311+G(3df,2p) level of theory. Consistent with the assignments based on the earlier EPR studies,[5] it is clear that the unpaired electron mainly occupies a $3p_\sigma$-type orbital in the position of the fifth equatorial ligand; however, there is also considerable unpaired electron density in the σ^* orbitals of the axial bonds. The phosphorus center bears a considerable positive charge (1.056) and a relatively low spin density (0.459), with the remainder of the unpaired electron density distributed mainly between the axial ligands.

The SOMOs of most of the other radicals are similar to that of $^\bullet P(CH_3)_4$, though there are some minor variations in the distribution of the unpaired electron density (see Table 2). The SOMO of $^\bullet P(CH_3)_3F$ is shown in Figure 2 as a typical example. However, the axial $^\bullet P(CH_3)_3SCH_3$ radical is somewhat exceptional; in this case the P−S axial bond lengthens considerably (2.721 Å, compared with 2.157 Å in the equatorial conformation), and there is considerable unpaired electron density on the sulfur (0.638). Though the charge on phosphorus is similar (0.968) to that in the $^\bullet P(CH_3)_4$ radical, the spin density on phosphorus in this case is just 0.281. Hence, it would appear that this radical has a large contribution from the $CH_3S^\bullet$ $P(CH_3)_3$ configuration. The other notable species are the axial conformations of the radicals bearing the unsaturated π-acceptor ligands, CN and phenyl. In the corresponding carbon-centered radicals (e.g. $^\bullet CH_2X$), the π system is collinear with the C$^\bullet$−X bond, so as to maximize overlap between the 2p(C$^\bullet$) orbital and the π^* orbitals of X. However, in the phosphoranyl radicals, the P$^\bullet$−X bond angle is quite bent, with the π^* orbital aligning with unpaired electron density in $3p_\sigma$ on phosphorus in a “face-on”, rather than “end-on” manner. It seems that π-acceptor ligands may interact with phosphorus-centered radicals via a through-space rather than through-bond effect.

In all cases the X-group prefers an axial location; however, the energy difference between the lowest energy axial and equatorial conformations varies considerably (see Table 1). The SCH_3 group is the most strongly apicophilic (−70.7 kJ mol^{-1}), followed by OCH_3, fluorine, CF_3, CN, and OH (with values ranging from −32.6 to −22.6 kJ mol^{-1}). The phenyl group (−8.5 kJ mol^{-1}) is only weakly apicophilic, despite the fact that the equatorial conformation is considerably more crowded. Consistent with the arguments of Roberts and co-workers,[13,14] the apicophilicities appear qualitatively to increase as the sigma withdrawing capacity of the X-group increases and the X−P bond dissociation energy decreases. There is a reasonable correlation between the calculated α_X values ($R^2 = 0.927$) and the axial−equatorial energy differences, provided the CN group is excluded from the analysis. This group is a clear outlier from the other substituents (see Figure 3), being much less apicophilic than might be predicted in the basis of its large electron affinity.

The apicophilicity equation of Roberts et al.[13,14] was derived on the basis of the assumption that the phosphoranyl radical is stabilized by resonance between the following configurations and that this resonance is best accommodated through the σ^* orbitals of the axial bonds.

$$X{-}P\bullet(CH_3)_3 \leftrightarrow X^-\ P^{\bullet+}(CH_3)_3 \leftrightarrow X\bullet\ P(CH_3)_3 \qquad (13)$$

Thus, for example, substituents such as SCH_3 are strongly apicophilic because $X^\bullet$ $P(CH_3)_3$ configuration is relatively low in energy; substituents such as F are strongly apicophilic because they are strong sigma acceptors and this stabilizes the X^- $P^{\bullet+}(CH_3)_3$ configuration. The CN substituent has a high electron affinity and is thus predicted, on the basis of eq 11, to be strongly apicophilic. However, unlike the other substituents, the CN substituent owes much of its electron-withdrawing capacity to its π-accepting properties, which are not relevant to stabilizing the X^- $P^{\bullet+}(CH_3)_3$ configuration in the present cases. As a result its σ-withdrawing capacity (and hence its apicophilicity) is

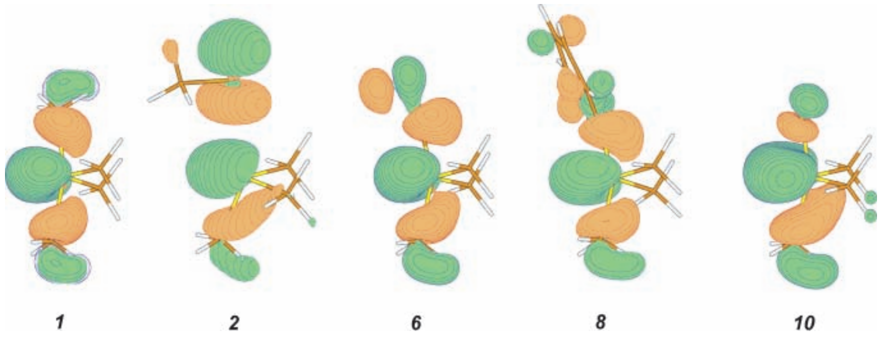


Figure 2. The singly occupied molecular orbitals of $^{\bullet}P(CH_3)_4$, (**1**), $^{\bullet}P(CH_3)_3SCH_3$ (**2**), $^{\bullet}P(CH_3)_3CN$ (**6**), and $^{\bullet}P(CH_3)_3Ph$ (**8**), and $^{\bullet}P(CH_3)_3F$ (**10**) as calculated at the B3-LYP/6-311+G(3df,2p) level of theory.

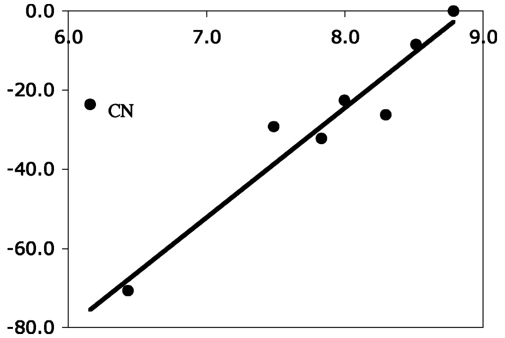


Figure 3. Axial−equatorial energy differences in $^{\bullet}P(CH_3)_3X$ (X = CH_3, SCH_3, OCH_3, OH, CN, phenyl, CF_3,F) versus calculated apicophilicities α_X. The line of best fit ($R^2 = 0.927$) was calculated with the X = CN data point omitted.

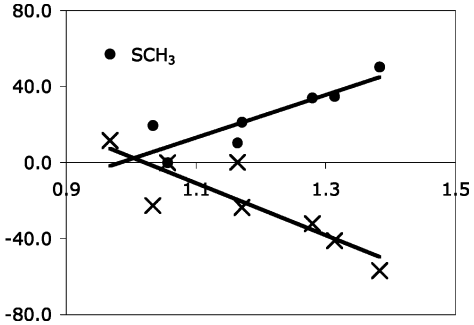


Figure 4. RSEs (×) and α-RSEs (•) versus charge on phosphorus for $^{\bullet}P(CH_3)_3X$ (X = CH_3, SCH_3, OCH_3, OH, CN, phenyl, CF_3,F). The line of best fit for the RSEs ($R^2 = 0.751$) was calculated using all data points in this series; the line of best fit for the α-RSEs ($R^2 = 0.768$) was calculated with the X = SCH_3 data point omitted.

overestimated by its electron affinity and hence by eq 11. This is further evident when we examine the charges on phosphorus (see Table 1) in the axial $^{\bullet}P(CH_3)_3X$ radicals. When X = CN, the charge (1.171) is lower than that in the radicals substituted with the sigma withdrawing X = OH (1.279) or OCH_3 (1.314) groups, despite that fact that the electron affinities of these groups are considerably lower than that of CN.

Radical Stabilities. If we examine next the radical stabilization energies (RSEs) in Table 2, we first note that, when calculated against a common reference species (i.e., $^{\bullet}CH_3$), the phosphoranyl radicals have considerably greater RSEs (by over 100 kJ mol^{-1} in many cases) than their carbon-centered analogues. Although this might seem to suggest that phosphoranyl radicals are more stable than carbon-centered radicals, weaker P−H versus C−H bonds may instead cause these results. The question of whether phosphoranyl radicals are more intrinsically stable than carbon-centered radicals will be explored in the next section; for the remainder of this section we consider the effects of substituents on the *relative* stabilities of the phosphoranyl radicals.

In the present work we consider two alternative methods for measuring the relative stabilities of the phosphoranyl radicals, the standard RSE (defined in this case as the energy change of $^{\bullet}P(CH_3)_3X + H{-}P(CH_3)_4 \rightarrow H{-}P(CH_3)_3X + {}^{\bullet}P(CH_3)_4$) and the α-RSE (which we define as the energy change of $^{\bullet}P(CH_3)_3X + P(CH_3)_3 \rightarrow P(CH_3)_2X + {}^{\bullet}P(CH_3)_4$). As explained in the Definitions of Radical Stability section, the former value measures radical stability if X does not significantly affect the stability of the P−H bond in the corresponding P^V phosphines ($H{-}P(CH_3)_3X$), and the latter measures radical stability if X does not significantly affect the stability of the lone pair in the P^{III} phosphines ($P(CH_3)_2X$). A priori, it is not clear whether either assumption would be reasonable for phosphoranyl radicals, and indeed, from Table 2, it is seen that these two alternative definitions lead to almost diametrically opposed trends. For example, on the basis of the RSEs, the F-substituent appears to be the most destabilizing substituent, while on the basis of the α-RSEs, it is one of the most stabilizing. This is further evident in Figure 4, in which it is seen that, while the RSEs decrease as the charge on phosphorus decreases, the α-RSEs generally increase.

To determine which (if either) definition of the RSE actually reflects the "intrinsic" stability of the phosphoranyl radicals, we need to consider whether either definition yields trends that are chemically intuitive and consistent with the other observable properties of the radicals, such as their apicophilicities. As we saw above, the apicophilicity formula of Roberts and coworkers[13,14] shows excellent predictive value in determining the apicophilicities of most of the substituents in the present phosphoranyl radicals, except for the strong π accepting CN-group. More generally this supports the notion that the $X{-}P^{\bullet}(CH_3)_3$ phosphoranyl radicals are stabilized through resonance with $X^-\ P^{\bullet+}(CH_3)_3$ and/or $X^{\bullet}\ P(CH_3)_3$ configurations along the axial σ* bonds. In what follows we show that the α-RSEs but not the RSEs yield trends that are consistent with these ideas.

If the phosphoranyl radicals are stabilized by resonance with the $X^-\ P^{\bullet+}(CH_3)_3$ and/or $X^{\bullet}\ P(CH_3)_3$ configurations, we would predict that the "stability" of the radical should increase as the relative contribution of the $X^-\ P^{\bullet+}(CH_3)_3$ and/or $X^{\bullet}\ P(CH_3)_3$ configurations increases. From Figure 4, we see that for the α-RSEs this is indeed the case. There is a reasonable correlation between radical stability and the charge on phosphorus, with the stability increasing as the charge (and hence contribution of the $X^-\ P^{\bullet+}(CH_3)_3$ configuration) increases. The SCH_3 group is the only substituent that does not fit this trend, having the smallest charge but the highest α-RSE. However, this is also easily explicable. In this case, it is the $X^{\bullet}\ P(CH_3)_3$ configuration that is more relevant to stabilizing the radical, the $X-P^{\bullet}(CH_3)_3$ BDE and the spin density on phosphorus being considerably lower than in all of the other radicals and the spin density on X being considerably higher (see Table 1).

In contrast to the α-RSEs, the trends in the RSEs seem counterintuitive. The RSEs decrease as the charge on phosphorus increases, which might suggest that resonance with the $X^- P^{\bullet+}(CH_3)_3$ configuration is actually a destabilizing influence. However, if that were really the case, one might have expected that electronegative substituents such as F would have preferred to occupy the equatorial (rather than the axial) position of the radical, so that this resonance could be minimized. Instead, it seems more reasonable to suppose that both the radical and the reference P^V phosphine are stabilized by resonance with the ionic configuration, but the effect on stability of the P^V phosphine dominates. As a result, the RSEs decrease as the "intrinsic" radical stabilities increase. Similar behavior has previously been reported for carbon-centered radicals when radical stability is measured via isodesmic reactions involving polar reference compounds such as fluorides (i.e., X = F) rather than the nonpolar alkanes (i.e., X = H):[17,18]

$$R^{\bullet} + X\text{-}CH_3 \rightarrow R-X + {}^{\bullet}CH_3 \qquad (14)$$

Whereas using the standard definition of the RSE (i.e. X = H), the RSEs of the alkyl radicals $R^{\bullet}$ increase in the order Me < Et < *i*-Pr < *t*-Bu, when X = F the reverse trend is obtained. It was shown that this was because the increasing alkylation of R stabilizes both the radical $R^{\bullet}$ (via increasing hyperconjugation) and the R−F bond (through its increasing resonance with $R^+ F^-$), and the effect on the bond dominates.[17] In the highly polar $H-P(CH_3)_3X$ phosphines, it seems reasonable to suppose that similar increases to the stability of the $H-P(CH_3)_3X$ bond should occur as the phosphorus becomes more positively charged.

Using the α-RSEs we can now compare the differing effects of the X-groups on the stabilities of the phosphoranyl ${}^{\bullet}P(CH_3)_3X$ radicals and their carbon-centered analogues, ${}^{\bullet}C(CH_3)_2X$ and ${}^{\bullet}CH_2X$. From Table 2 we see that the main differences are that, in the carbon-centered radicals, the π-accepting substituents (such as phenyl) are more stabilizing and the sigma-withdrawing substituents (such as CF_3 and F) are much less stabilizing. This is a result of the differing electronic structures of the radicals. As is well-known, in the carbon-centered radicals the unpaired electron occupies a 2p-type orbital and can be delocalized into the π^* (or pseudo-π^*) orbitals of neighboring π (or pseudo-π) acceptor substituents.[20] In contrast, σ-withdrawing substituents cannot delocalize the radical and merely remove electron density from the electron deficient center.[20] As is clear from the SOMOs shown in Figure 2, in the phosphoranyl radicals there is considerable unpaired electron density in the σ^* orbitals of the axial bonds. As a result, the σ-withdrawing substituents can stabilize the phosphoranyl radicals through resonance with $X^- P^+(CH_3)_3$, and this is evident in the increased apicophilicity of the σ-withdrawing substituents. The reduced role of the π-acceptor ligands in the phosphoranyl radicals is also easily explicable in terms of its electronic structure. As was clear from Figures 1 and 2, in the phosphoranyl radicals the interaction between the unpaired electron and π^* orbitals of the ligand is a through-space (rather than a through-bond) effect, and the unpaired electron only partially occupies the $3p_\sigma$ orbital on phosphorus. As a result the stabilizing effect of the π acceptor ligands is much weaker than in the carbon-centered radicals.

In summary, it appears as if the standard RSEs do not reflect the intrinsic stability of the phosphoranyl radicals. In contrast, the α-RSEs provide trends that are reasonably chemically intuitive and consistent with the observed apicophilicities. On the basis of these trends, it appears as if the phosphoranyl radicals are stabilized by resonance between with the $X^{\bullet}\ P(CH_3)_3$ and/or $X^-\ P^{\bullet+}(CH_3)_3$ configurations. The former is most important for X = SCH_3, and this is also the most stable of the radicals considered in the present work. The latter is most important for the strong σ-accepting substituents (such as F, OH, or OCH_3), and these are also strong radical stabilizers. In contrast to carbon-centered radicals, π-accepting groups (such as phenyl) play only a minor role in stabilizing the phosphoranyl radicals.

Relative Stabilities of Phosphoranyl and Carbon-Centered Radicals. Finally, we compare the overall stabilities of the phosphoranyl radicals with their carbon-centered counterparts. It is generally held that phosphorus-centered radicals are more stable than carbon-centered radicals, because P−H bond dissociation energies (BDEs) are typically smaller than C−H BDEs.[10] Indeed, as we saw in Table 2, if the RSEs of the phosphoranyl radicals of the present work are calculated relative to the ${}^{\bullet}CH_3$ radical, the calculated RSEs fall into the range 105−174 kJ mol^{-1}, and thus one might conclude that phosphoranyl radicals are at least 100 kJ mol^{-1} more stable than ${}^{\bullet}CH_3$. Of course, it is impossible to determine if the greater RSEs for the phosphoranyl radicals are the result of the greater stability of the $P^{\bullet}$ (versus $C^{\bullet}$) radicals or merely a weaker P−H versus C−H bond. This is also the case if the stabilities of the P-centered and C-centered radicals are compared more directly via isomerization reactions such as those in Scheme 1. In each case, the reactions converting phosphoranyl radicals into carbon-centered radicals are strongly endothermic, but it is impossible to determine if this is a result of the differing radical stabilities and/or the differing energies of the P−H versus C−H or P−C versus C−C bonds. We also compared the formation of the ${}^{\bullet}P(CH_3)_4$ phosphoranyl radical, via the dissociation of the $(CH_3)_4P-P(CH_3)_4$ dimer, with the formation of the ${}^{\bullet}CH_3$ and ${}^{\bullet}C(CH_3)_3$ radicals, via dissociation of CH_3-CH_3 and $(CH_3)_3C-C(CH_3)_3$, respectively. The calculated P−P BDE is 80.4 kJ mol^{-1}, the corresponding C−C BDEs are 361.0 kJ mol^{-1} and 332.3 kJ mol^{-1} for formation of ${}^{\bullet}CH_3$ and ${}^{\bullet}C(CH_3)_3$, respectively. Again it appears as if the phosphoranyl radicals are more stable than the carbon-centered radicals, but it is impossible to determine whether this is due to their greater intrinsic stability or merely a weaker P−P versus C−C bond.

Thus far, we have shown that phosphoranyl radicals appear to be more stable than carbon-centered radicals. However, in these comparisons, the reactions are balanced using closed shell molecules, and it is impossible to determine if this apparent stability is due to the greater inherent stability of the radical or merely the lower stability of the P−H versus C−H, P−C versus C−C, or P−P versus C−C bonds. One might wonder whether this is merely a matter of semantics. After all, regardless of what is really being measured, the relative P−H and C−H BDEs reflect the greater (thermodynamic) stability of phosphoranyl radicals toward the common addition, transfer, and coupling reactions that normally consume carbon-centered radicals. Indeed, as noted in the Introduction, phosphoranyl radicals are well-known to be remarkably persistent.[10] However, the question does become relevant if one wishes to compare their stability in other types of chemical reactions, such as α- and β-scission, that do not involve the simultaneous formation of these P−H, P−C, or P−P bonds. For example, in the RAFT process, are the phosphoranyl radicals generated by radical addition to dithiophosphinate esters (see reaction 5) more or less stable than the carbon-centered radicals generated via addition to dithioesters (see reaction 4)?

To determine whether phosphoranyl radicals are more intrinsically stable than carbon-centered radicals, we considered the following α-scission reaction:

$$^{\bullet}P(CH_3)_4 \rightarrow P(CH_3)_3 + {}^{\bullet}CH_3 \qquad (15)$$

As would have been evident from Table 2, this reaction is weakly exothermic ($\Delta H = -5.3$ kJ mol^{-1}). This is despite the fact that a P$-$C bond is broken and no new bonds are formed. It would appear that the energy cost of breaking the P$-$C bond has been met by the conversion of a phosphoranyl radical into the *more stable* $^{\bullet}CH_3$ radical. It should also be noted that there is experimental evidence for the rapid decomposition of certain phosphoranyl radicals via α-scission into a carbon-centered radical and the corresponding phosphine. For example, Saveant and Binh[42] showed that the *t*-BuP$^{\bullet}$Ph$_3$ radical generated by 1-electron oxidation of *t*-BuP$^+$Ph$_3$ rapidly decomposed to PPh$_3$ and the *t*-Bu$-$*t*-Bu coupled product. On this basis one could argue that the *t*-BuP$^{\bullet}$Ph$_3$ radical is less stable than the *t*-Bu radical.

It therefore seems likely that phosphoranyl radicals are less intrinsically stable than carbon-centered radicals, though in most chemical reactions this instability is normally counteracted by the weakness of P$-$H, P$-$C, or P$-$P bonds that are formed when these radicals react. In other words, for most practical purposes, phosphoranyl radicals are much more stable to coupling, addition, or transfer reactions than their carbon-centered radical counterparts and hence are remarkably persistent. However, due to their lower intrinsic stability, it seems likely that they may be less stable to reactions (such as α- and β-scission) that do not involve the simultaneous creation of P$-$H, P$-$C, or P$-$P bonds. This combination of persistence with low intrinsic stability makes phosphoranyl radicals particularly interesting prospects as highly selective chain carriers in organic synthesis and as possible radical sinks in the RAFT polymerization process.

5. Conclusions

Phosphoranyl radicals are intriguing species that differ substantially from their carbon-centered counterparts. The $^{\bullet}P(CH_3)_3X$ (X = CH$_3$, SCH$_3$, OCH$_3$, OH, CN, CF$_3$, Ph) radicals of the present work assume a largely trigonal-bipyramidal structure, with the X-group occupying an axial position, and the unpaired electron distributed between a 3p$_\sigma$-type orbital (that occupies the position of the "fifth ligand") and the σ* orbitals of the axial bonds. The radical is stabilized by resonance (along the axial bonds) with configurations such as $X^-\ P^{\bullet +}(CH_3)_3$ and $X^{\bullet}\ P(CH_3)_3$. As a result, substituents that are strong σ-acceptors (such as F, OH, or OCH$_3$) or have weak P$-$X bonds (such as SCH$_3$) stabilize these configurations, resulting in the largest apicophilicities and radical stabilities. This is in contrast to carbon-centered radicals, which, since the unpaired electron is located primarily in the 2p-type orbital, are destabilized by σ-withdrawal. Another interesting difference between phosphoranyl radicals and their carbon-centered counterparts is that, in the former, the unsaturated π-acceptor substituents (such as phenyl or CN) are less stabilizing and appear to interact with the 3p$_\sigma$-type orbital via a through-space (rather than through-bond) effect.

The present work also suggests that the relative stabilities of phosphoranyl radicals should not be measured using the standard radical stabilization energy (RSE) but instead using a new measure, the α-RSE, which we define as the energy change of the reaction: $^{\bullet}P(CH_3)_3X + P(CH_3)_3 \rightarrow P(CH_3)_2X + {}^{\bullet}P(CH_3)_4$. This measures stability relative to the corresponding P^{III} phosphines (P(CH$_3$)$_2$X) rather than the P^V phosphines (H$-$P(CH$_3$)$_3$X). Although neither quantity can be said to measure intrinsic radical stability, we show that the α-RSEs yield trends in radical stabilities that are chemically intuitive and consistent with other observable data, while the RSEs yield diametrically opposed trends and probably reflect the differing stabilities of the P$-$H bonds in the H$-$P(CH$_3$)$_3$X reference compounds.

Finally, the present work challenges the notion that phosphoranyl radicals are more stable than carbon-centered radicals. Phosphoranyl radicals are more (thermodynamically) stable than their carbon-centered analogues to a wide variety of chain transfer, coupling, and radical addition reactions. However, this persistence appears to be the result of the lower stability of the P$-$H versus C$-$H or P$-$C versus C$-$C, or P$-$P versus C$-$C bonds, rather than the greater intrinsic stability of the P-centered versus C-centered radicals. We show that the α-scission reaction, $^{\bullet}P(CH_3)_4 \rightarrow P(CH_3)_3 + {}^{\bullet}CH_3$, is weakly exothermic, and hence the energy required to break the P$-$C bond is provided by the conversion of a less stable phosphoranyl radical into a *more* stable methyl radical. This combination of stability to many of the numerous reactions that normally consume radical chain carriers, with sufficiently low intrinsic stability (so that reactions such as α- or β-scission may still occur), is what makes phosphoranyl radicals particularly interesting as highly selective chain carriers in organic synthesis and as possible radical sinks in the RAFT polymerization process.

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Supporting Information Available: B3-LYP/6-31G(d) optimized geometries in the form of GAUSSIAN archive entries (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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