

Electronic Structure of Aryl- and Alkylphosphines

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The electronic structure of tertiary arylphosphines and methylphosphines are explored, using *ab initio* calculations and a detailed analysis of properties based on the electron distribution $\rho(\mathbf{r})$. The comparison concentrates on the topology of ρ and $\nabla^2\rho$ in the vicinity of the phosphorus atom, and the integrated atomic properties (energies, multipole moments) of this atom. Some trends are revealed which are consistent with the known relative basicities of these compounds, whereas others are unexpected. In particular (i) neither methyl nor aryl substituents substantially alter the charge on phosphorus, (ii) and the phosphorus–phenyl P–C bond of triarylphosphines, phenylphosphabicyclo[3.3.1]nonane and its [4.2.1] analogue indicate a significant conjugative effect, unlike in phenyl or pyridylphosphine.

Introduction

The application of tertiary arylphosphines as ligands in homogeneous transition metal catalysis is well-known. Functionalized arylphosphines have been investigated for a variety of reasons including the modification of solubilities (*e.g.* in water) and the immobilization (*e.g.* upon a silica support) of the complexes that exhibit catalytic activity. Modification of the functions attached to phosphorus may influence both the steric properties of the ligand as a whole, as well as the electronic nature of the metal–phosphine interaction. The variation in steric and electronic properties is probably more evident for tertiary alkylphosphines where there is greater freedom to vary the nature of the function directly bonded to phosphorus. As the influences of both steric and electronic properties are both known to influence rates and stereochemical control of reactions, it is of interest to evaluate the relative importance of these two factors in specific cases.

Triphenylphosphine is probably the most commonly-used tertiary phosphine in homogeneous catalysis due to its ready availability, air-stability and ease with which it complexes metals associated with catalytic activity. Trialkyl- or mixed alkyl-/arylphosphines are less-commonly associated with homogeneous catalysis. Although this may in part be due to a reluctance to study them as ligands in this application since they are typically air sensitive and relatively more expensive, there are examples where they generate less active, or even inactive, analogues of arylphosphine-based catalysts. An exception to this is in the carbonylation of unsaturated hydrocarbons catalyzed by palladium phenylphosphabicyclonane (PPBN) complexes. Here the ligand is a dialkylphenylphosphine where the dialkyl function is a cycloalkane with the phosphorus atom in a bridgehead position. Due to its method of synthesis, it is prepared as a mixture of two isomers (Figure 1), phenylphosphabicyclo[3.3.1]nonane (a) and phenylphosphabicyclo[4.2.1]nonane (b).

Some observations concerning palladium PPBN complexes are of interest. First, they are more active catalysts for the carbonylation of alkynes than are the corresponding triphenylphosphine complexes,¹ or the analogous model dialkylphenylphosphine (PMe₂Ph), which forms complexes that are far less active under the same conditions. Secondly, there is a

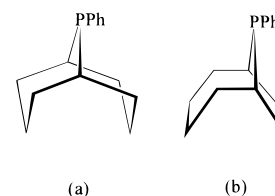


Figure 1.

significant difference in activity between complexes of the two isomers such that [4.2.1]-PPBN generates the more active catalyst by a several-fold rate enhancement under the same conditions.

In addition there is a marked difference of reactivity between triphenylphosphine complexes in comparison with 2-pyridyldiphenylphosphine complexes in similar reactions. For example, in the carbonylation of acetylenes, pyridylphosphines have been claimed to increase rates by two orders of magnitude in comparison to analogous phenylphosphines.²

Clearly there may be subtle influences of both steric and electronic factors on these reactions. One way to explore these influences is through quantum mechanical calculations. Only recently has it become feasible to apply suitably high-level methods to such compounds; hence, there are few such studies of arylphosphines and pyridylphosphines reported in the literature.³ While the most useful studies would probably involve whole metal–phosphine catalysts, for reasons of computational expediency the quantum-chemical literature on metal–phosphines is essentially limited to PH₃–metal complexes.⁴ Such calculations give useful insight into the nature of the metal–phosphorus bond,⁵ but they also indicate that the effect of electron correlation is crucial for reliable predictions of both structures and charge distributions in such complexes.⁶ High-

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level calculations on model complexes with more "realistic" ligands such as those studied here are therefore currently out of range (except perhaps for density functional methods).

Until now, there appears to have been no systematic analysis of the electronic charge distribution in the free bases, which should be instructive. This is now facilitated by the application of more "rigorous" tools for analysis of quantum-mechanical densities and wave functions, such as those developed by Bader and co-workers⁷ or Cioslowski.^{8,9} The recent study by Howard and Platts¹⁰ concentrated on the link between alkyl- and halophosphine basicity and the charge distribution around phosphorus, particularly the lone pair (LP) properties. Here, we report an analysis of aryl- and alkylphosphines along the lines of Howard and Platts, including the two PPBN ligands described earlier. We will pay particular attention to characterizing the phosphorus lone pair and the extent of its delocalization as a function of the number of substituents present, which has been reviewed in the context of spectroscopic data.¹¹

Computational Details

The geometries of $\text{PPh}_n\text{H}_{3-n}$ ($n = 0-3$), $\text{PMe}_n\text{H}_{3-n}$ ($n = 0-3$), n - PyPH_2 ($n = 2, 3, 4$), [3.3.1]-PPBN, [4.2.1]-PPBN and PMe_2Ph were optimized at the restricted Hartree-Fock (RHF) level with the 6-31G(d,p) basis set.¹³ These calculations, and the determinations of the electron distributions at the same HF/6-31G(d,p) level, employed direct SCF techniques with GAMESS¹⁴ running on DEC Alpha RISC workstations. Geometries were optimized to tolerances of 1×10^{-4} au (maximum force on any nucleus) and $<3.3 \times 10^{-5}$ au (rms force for all nuclei). The following point group symmetries were assumed: C_1 (PPh_2H and [4.2.1]-PPBN), C_{3v} (PH_3 , PMe_3), C_s (PH_2Ph , PH_2Me , PHMe_2 , n - PyPH_2 , [3.3.1]-PPBN and PMe_2Ph), and C_3 for PPh_3 . The X-ray crystal structure of PPh_3 ²¹ contains molecules with conformations somewhat distorted from C_3 symmetry; nevertheless, this symmetry was imposed for computational expediency. In the X-ray crystal

structure of [3.3.1]-PPBN²² the molecules are very close to having an effective point-group symmetry of C_s , with the phenyl ring perpendicular to the mirror plane. Hence our *ab initio* geometry optimization of this compound imposed C_s symmetry. In the case of [4.2.1]-PPBN, the geometry was essentially unknown and no symmetry constraints were applied (the optimized geometry had no symmetry).

Separate optimizations on phenylphosphine with the mirror plane (i) in the plane of the ring and (ii) perpendicular to the plane of the ring indicated that (i) is the lowest energy form, although the difference in energy (ignoring vibrational energy changes) is small at this level ($\approx 5 \text{ kJ mol}^{-1}$). Nyulaszi *et al.*¹² found this difference to be even lower at the MP2 level of theory ($\approx 1.5 \text{ kJ mol}^{-1}$). We also carried out a similar analysis on dimethylphenylphosphine which again showed that conformer i is preferred, by $\approx 7 \text{ kJ mol}^{-1}$. However, the structure and charge distribution analysis reported shortly for dimethylphenylphosphine corresponds to conformer ii because this more closely resembles the conformation of the PPBNs (see Figure 1).

The set of stationary or "critical" points $\{\rho_c\}$ were located and analyzed using the program SADDLE, part of the AIMPACK suite of programs.²⁴ The analogous CP analyses of $\nabla^2\rho$ were carried out using Laidig's program BUFFALO, a recent addition to this package. The program PROAIMV²⁴ was used to compute integrated atomic properties (energies, charges, dipoles, and quadrupoles) for the phosphorus atom in all molecules.

Results and Discussion

Structures. The main structural parameters (and associated electronic energies) at the optimized geometries are shown in Figure 2. Gas-phase structures are available for PH_3 ,¹⁵ PPh_2 ,¹⁶ PPh_2H ,¹⁷ PMe_2Ph ,¹⁸ PMeH_2 and PMe_2H ¹⁹ and PMe_3 .²⁰ X-Ray crystal structures are available for PPh_3 ²¹ and [3.3.1]-PPBN.²²

In the series $\text{PPh}_n\text{H}_{3-n}$ ($n = 0-3$), P-H distances vary between 1.402 and 1.403 Å and P-C distances between only 1.842 and 1.848 Å, so both parameters are quite insensitive to the number of phenyl rings. In the pyridylphosphine series, the 3-position gives the lowest energy, but the difference relative to 2- and 4-pyridylphosphine is small ($\approx 7 \text{ kJ mol}^{-1}$). Where comparable, bond lengths and angles around phosphorus also vary negligibly with the position of the heteroatom. In the series $\text{PMe}_n\text{H}_{3-n}$ ($n = 0-3$), P-H distances vary between 1.406 and 1.407 Å and P-C distances between 1.852 and 1.859 Å, so as above both parameters are insensitive to the number of methyl groups.

By including dimethylphenylphosphine (PPhMe_2) in our study, we are able to establish, in the case of the PPBN compounds, whether any results depend on having a phosphorus atom bridging an octane ring, or whether two nonbridging alkyl groups could reproduce the same effect. The P-C(octane ring) bond lengths in the PPBNs are slightly longer than the comparable P-C(methyl) bond length found in PMe_2Ph , suggesting that the molecule is somewhat strained around phosphorus. The P-C bond lengths vary by 0.026 Å across all of the compounds (including the PPBNs), which is perhaps surprisingly small given the widely-varying nature of the substituents being studied.

The C(octane ring)-P-C(octane ring) bond angle in the PPBNs is 9° smaller than the typical C(alkyl)-P-C(alkyl) angle (in PMe_2Ph), which is also suggestive of strain around phosphorus. The HF/6-31G(d,p) optimized geometry of [3.3.1]-PPBN is in good agreement with the corresponding X-ray crystal structure.²²

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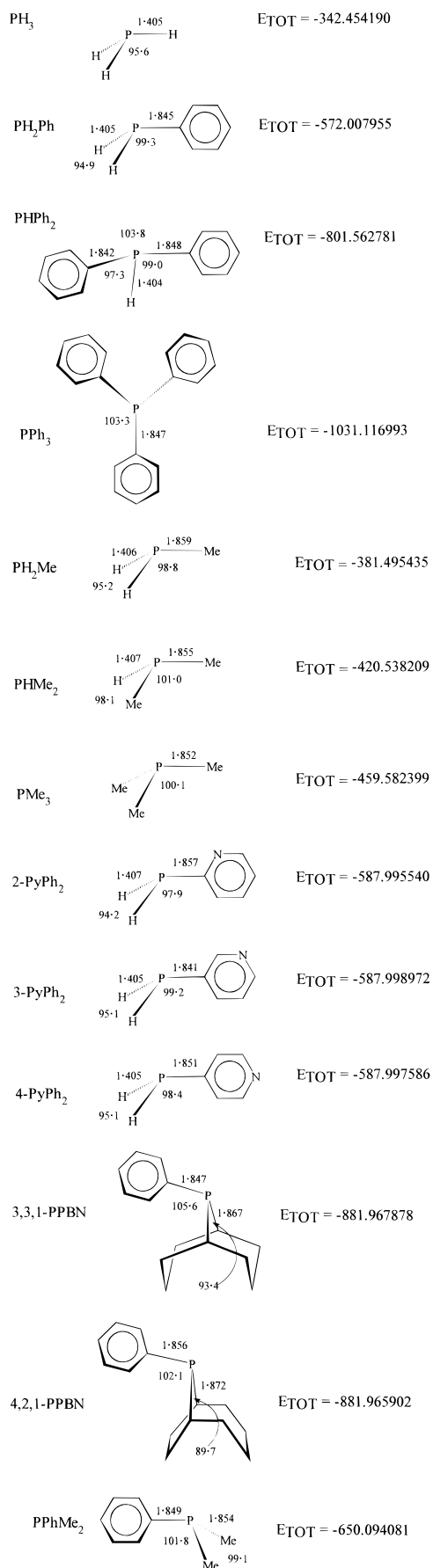


Figure 2. Optimized geometries (Å, deg) and energies (au).

Topology of the Charge Distributions. (i) Bonds to Phosphorus. Following Bader *et al.*⁷ we use the following nomenclature to classify CPs in ρ and $\nabla^2\rho$: (n , m), where n is

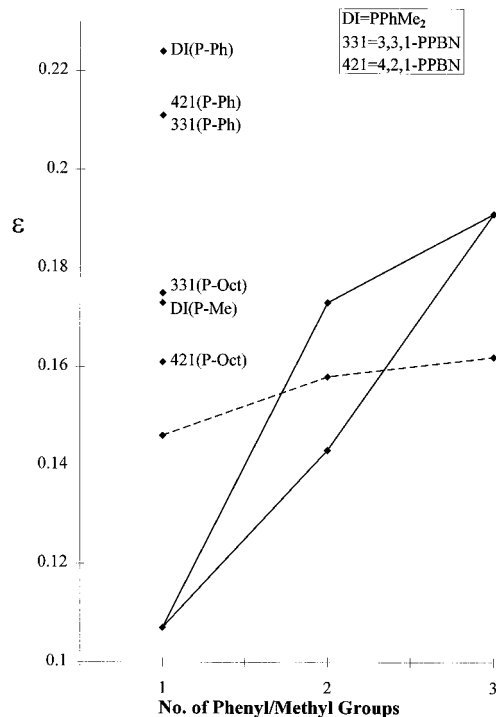


Figure 3. Relationship between P–C bond ellipticity and the number of substituents (solid = phenyl; dotted = methyl).

the number of nondegenerate Hessian eigenvalues at the CP and m is the sum of the eigenvalues signs. The results of the CP analysis of ρ for bonds to phosphorus are presented in Table 1. The ellipticity ϵ measures the asymmetry between the two principal curvatures (λ_1 , λ_2) of ρ perpendicular to the bond ($\epsilon = \lambda_2/\lambda_1 - 1$). In a “perfect” single bond, such as the C–C bond in ethane, $\epsilon = 0$. Higher values of ϵ can be found for the C=C bond in ethane ($\epsilon \approx 0.4$) or the P=C bond in $\text{PH}=\text{CH}_2$ ²³ ($\epsilon = 0.480$). The exact values found depend on the level of the calculation. The use of ϵ in measuring double bond character is well-established.^{25–29} Nyulaszi *et al.*²³ reported the length of the P=C bond to be 1.65 Å and the density at its CP to be 0.188 au with the 6-31G(d) basis set. If the P–C bonds in the compounds studied *here* were “classical” double bonds, we would expect them to have similar values.

The P–C bond ϵ values (Table 1 and Figure 3) suggest a double bond character for PPh_3 which is almost twice as large as in PH_2Ph , despite having almost identical P–C bond lengths. This is in contrast to the general behavior seen in C–C bonds,²⁹ in which the bond length is very closely related to the ellipticity. Even more noteworthy is that the two PPBN compounds have higher ϵ values than PPh_3 , despite having only one phenyl ring. Comparing the ϵ results for the PPBNs and PMe_2Ph reveals that the orientation of the phosphorus LP relative to the aromatic ring is the decisive factor in imparting the large ϵ value to the P–C(phenyl) bond. The ellipticity of the P–C(phenyl) bond in the lower energy conformer of PMe_2Ph , where the ring is in the symmetry plane (not shown in Table 1), is 0.132, approximately half the value reported in Table 1 where the ring is perpendicular to the symmetry plane and the LP can delocalize into the ring. Neither the P–C bond length nor the density at

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Table 1. Critical Point Analysis for Bonds to Phosphorus in Arylphosphines (au)^a

	bond	ρ_c	$\nabla^2\rho_c$	ϵ	χ_{LP} (deg)	χ_{RING} (deg)
PH ₃	P-H	0.1628	0.087	0.136		
PPhH ₂	P-H	0.1633	0.097	0.152		
PPh ₂ H	P-H	0.1644	0.107	0.157		
PMeH ₂	P-H	0.1627	0.099	0.148		
PMe ₂ H	P-H	0.1625	0.109	0.152		
PPhH ₂	P-C	0.1557	0.051	0.107	0.0	0.0
PPh ₂ H	P-C	0.1563, 0.1553	0.071, 0.043	0.173, 0.143	2.9, 8.8	46.4, 22.3
PPh ₃	P-C	0.1557	0.051	0.191	7.6	47.0
PMeH ₂	P-C	0.1538	-0.020	0.146	0.0	
PMe ₂ H	P-C	0.1545	0.009	0.158	1.8	
PMe ₃	P-C	0.1550	0.032	0.162	0.0	
3,3,1-PPBN	P-C(Ph)	0.1536	0.078	0.211	0.0	90.0
	P-C(Oct)	0.1570	-0.031	0.175	12.5	
4,2,1-PPBN	P-C(Ph)	0.1519	0.063	0.211	10.5	87.6
	P-C(Oct)	0.1556, 0.1561	-0.036, -0.040	0.163, 0.158	14.9	
PPhMe ₂	P-C(Ph)	0.1544	0.070	0.224	0.0	90.0
	P-C(Me)	0.1555	0.013	0.173	2.6	

^a (Oct) refers to carbon atoms in the octane ring of PPBN.

the CP varies significantly with the number of phenyl rings on the phosphorus. The density at the critical point is due almost entirely to the σ electron framework, since it invariably occurs close to the nodal plane of the π orbitals. An increase in the π character of the bond (as measured by ϵ) need not therefore be accompanied by a change in the CP density. P-C bond ellipticities for the series $\text{PMe}_n\text{H}_{3-n}$ ($n = 0-3$) vary almost negligibly.

The scalar function $\nabla^2\rho$ measures the local concentration of charge (a negative value of the function at some point implies a higher value of the density compared to the immediate surroundings, and *vice versa* for positive values of $\nabla^2\rho$). Covalent bonds imply a build-up of charge at the bond CP, and therefore have "large" ($|\nabla^2\rho| \geq 1$) negative values of $\nabla^2\rho$, whereas large positive values at the bond CP are characteristic of ionic bonds. The results in Table 1 for the P-H bond series shows a regular (but essentially negligible) change in the bond CP properties with increasing number of substituents, so the character of this bond is not significantly affected by substitution of hydrogen by phenyl or methyl. Neither ρ nor $\nabla^2\rho$ registers significant change in the P-C bond on phenyl or methyl substitution.

$\nabla^2\rho$ values in the P-C bonds are all rather small in magnitude, indicating a bond of "intermediate" (ionic/covalent) character. In the *n*-pyridylphosphine compounds, a bond CP analysis (not tabulated) shows a near-negligible effect on the P-C bond character of the position of the nitrogen atom in the ring. Only ϵ changes slightly, from 0.087 (2-PyPhH₂) to 0.113 and 0.116 (3- and 4-PyPhH₂). Thus the double bond character is most like that of PH₂Ph ($\epsilon = 0.0106$) when the heteroatom is furthest from the 1- position.

The "bond path" is defined as the line of maximum charge density between two nuclei,⁷ and this generally will not coincide with the "geometrical bond path"—a straight line drawn between the nuclei. The difference between the geometrical bond angle α_e at some nucleus and the limiting angle α_b between tangents to the bond path at that nucleus may be used to quantify strain⁷ or the degree of lone pair-bonded pair (LP-BP) repulsion.^{30,31} Values of $(\alpha_b - \alpha_e)$ are given for the C-P-C arylphosphine bonds in Table 2. Nearly all the values are positive, so the bond path angles are consistently bigger than the geometric bond angles; *i.e.*, the path of maximum charge density bows outward

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Table 2. Bond Path Angles^a for Bonds to Phosphorus

	bond	$\alpha_b - \alpha_e$ (deg)
PH ₃	H-P-H	3.4
PPhH ₂		3.1
PMeH ₂		3.3
PPh ₂ H	C-P-H	1.9
PMeH ₂		2.3, 1.6
PMe ₂ H		2.1
PPh ₂ H	C-P-C	0.4
PMe ₂ H		1.3
PPh ₃		0.4
PMe ₃		1.5
3,3,1-PPBN	C(Oct)-P-C(Ph)	-0.9
	C(Oct)-P-C(Oct)	4.5
4,2,1-PPBN	C(Oct)-P-C(Ph)	0.8
	C(Oct)-P-C(Oct)	4.6
PPhMe ₂	C(Me)-P-C(Ph)	0.7
	C(Me)-P-C(Me)	2.5

^a Given as differences between the limiting bond path angles and the "geometrical" bond angle, as described in the text.

slightly from the line between the nuclei. The one exception is [3.3.1]-PPBN, where $(\alpha_b - \alpha_e)$ is negative for the C(Oct)-P-C(Ph) bonds.

In the *n*-pyridylphosphines, the C-N-C ($\alpha_b - \alpha_e$) values, not tabulated, are -14.1, -13.6, and -13.6° respectively for $n = 2-4$, so the bonds to nitrogen are markedly "bent" into the ring. Such large and negative values of $(\alpha_b - \alpha_e)$ in azines were first reported by Wiberg.³² This indicates the much weaker nature of LP-BP repulsion in phosphines as compared with azines/amines.

Finally in this section, we use the critical point analysis to gain further insight into the shape of the charge distribution in the P-C bonds and, in particular, the degree of interaction between the phosphorus LP and the π system in the aryl rings. (The next section deals with the definition of the phosphorus LP direction). At the bond critical point, two eigenvectors (v_1 , v_2) of the Hessian of ρ point in directions perpendicular to the bond, and the third (v_3) points along the bond. The vector with the least negative eigenvalue, v_2 , indicates the direction in which π density in the bond is preferentially concentrated. Hence the dihedral angle which v_2 makes with the phosphorus LP and/or the aromatic ring is indicative of the phosphorus LP/aromatic ring interaction. We will denote these two angles of χ_{LP} and χ_{RING} , respectively (see Figure 4), and these values are tabulated

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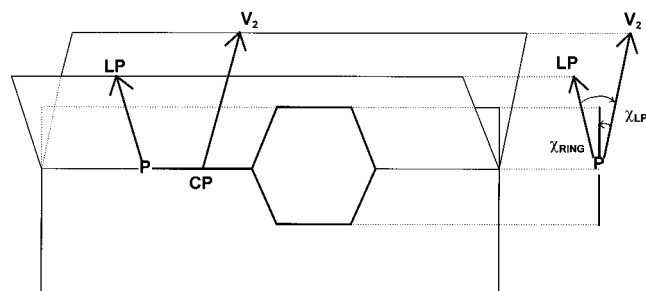


Figure 4. Diagram defining χ_{LP} and χ_{RING} .

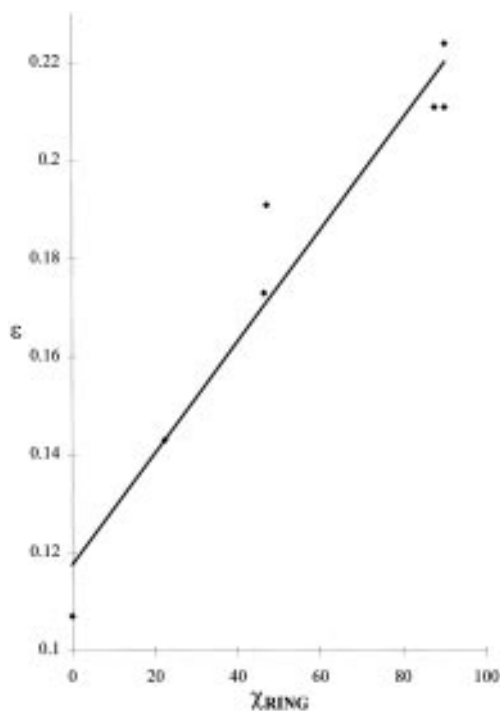


Figure 5. Relationship between the P-C bond ellipticity and χ_{RING} .

in Table 1. In some cases the values of χ_{LP} or χ_{RING} are 0.0° or 90.0° by symmetry. It is clear that χ_{RING} and ϵ are almost linearly related (see Figure 5). Furthermore, v_2 and the phosphorus LP make essentially the same dihedral angle with the ring in all compounds (the biggest discrepancy being 15° in [4.2.1]-PPBN). It follows that the dihedral angle between the phosphorus LP and the ring can be considered as the controlling parameter for the P-C(phenyl) double bond character.

(ii) The Phosphorus Lone Pair. The $\nabla^2\rho$ function reveals the electronic shell structure of atoms in molecules,⁷ and the local maxima in $-\nabla^2\rho$, or (3,-3) CPs, effectively characterize the centroids of LP and BP electrons.³³⁻³⁵ Moreover, the values of ρ and $\nabla^2\rho$ at these points associated with basic nitrogen and phosphorus atoms often correlate with (for example) proton affinity (PA),^{10,36} lithiation energy,³⁷ and the bond strength in hydrogen-bonded complexes.³⁷ Hence this type of analysis may show how the phosphorus LP responds to aryl and alkyl substituents.

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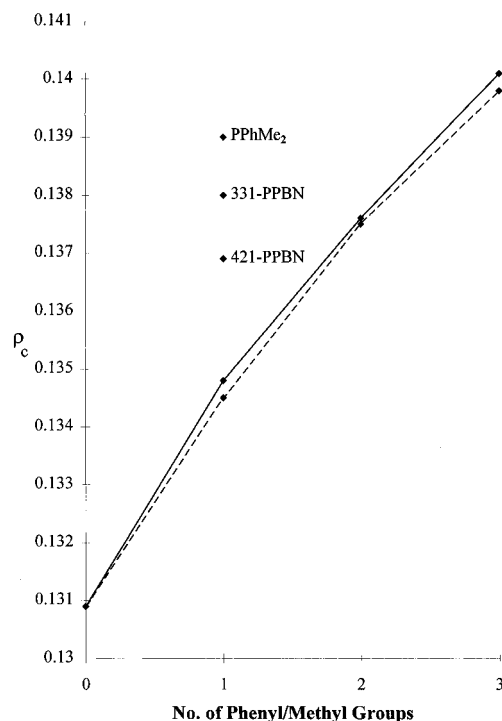


Figure 6. Relationship between the lone pair density and the number of substituents (solid = phenyl; dotted = methyl).

Table 3. $\nabla^2\rho$ Lone Pair Analyses for Phosphorus (au)

	ρ	$\nabla^2\rho$	μ_1, μ_2, μ_3
PH ₃	0.1309	-0.319	-0.40, -0.40, -8.85
PPhH ₂	0.1348	-0.341	-0.44, -0.46, -9.26
PPh ₂ H	0.1376	-0.357	-0.47, -0.50, -9.54
PPh ₃	0.1401	-0.370	-0.51, -0.51, -9.75
PMeH ₂	0.1345	-0.339	-0.44, -0.46, -9.18
PMe ₂ H	0.1375	-0.357	-0.48, -0.49, -9.46
PMe ₃	0.1398	-0.371	-0.52, -0.52, -9.67
2-PyPH ₂	0.1344	-0.337	-0.42, -0.44, -9.34
3-PyPH ₂	0.1348	-0.341	-0.44, -0.46, -9.29
4-PyPH ₂	0.1348	-0.341	-0.44, -0.45, -9.31
3,3,1-PPBN	0.1380	-0.358	-0.47, -0.52, -9.39
4,2,1-PPBN	0.1369	-0.352	-0.45, -0.50, -9.32
PPhMe ₂	0.1390	-0.365	-0.50, -0.51, -9.60

The results of this analysis for all compounds are reported in Table 3. There are significant and regular enhancements of ρ_c and $|\nabla^2\rho_c|$ with respect to phenyl substitution in the series PPh_nH_{3-n} ($n = 0-3$) (see Figure 6 and 7). This is suggestive of a cumulative 'donation' effect from successive phenyl groups, and it mirrors the effect shown here (and previously in ref 10) for alkylphosphines. Near-linear relationships are found for the variation of ρ and $\nabla^2\rho$ with respect to the number of phenyl groups present (Figures 6 and 7). Since the PA/basicity of these compounds is known to increase across this series, ρ and $\nabla^2\rho$ at the LP CP should also correlate with these thermodynamic quantities. The two PPBN compounds do not show exceptional behavior with respect to these LP parameters: the values of ρ and $\nabla^2\rho$ at the LP CP are similar to those of PMe₂Ph. In the *n*-pyridylphosphines, again there is little measurable effect at the phosphorus LP from this type of analysis when the heteroatom changes position.

Further insight is gained into the shape of the LP density distribution from the Hessian eigenvalues $\{\mu_i\}$ of $-\nabla^2\rho$ at the (3,-3) CP.^{10,33} The largest and most negative eigenvalue μ_3 corresponds to the curvature of $\nabla^2\rho$ in a direction approximately radially outward, on a line through the phosphorus nucleus and the (3,-3) CP. The magnitude of this curvature therefore effectively measures the radial extent of this concentration in

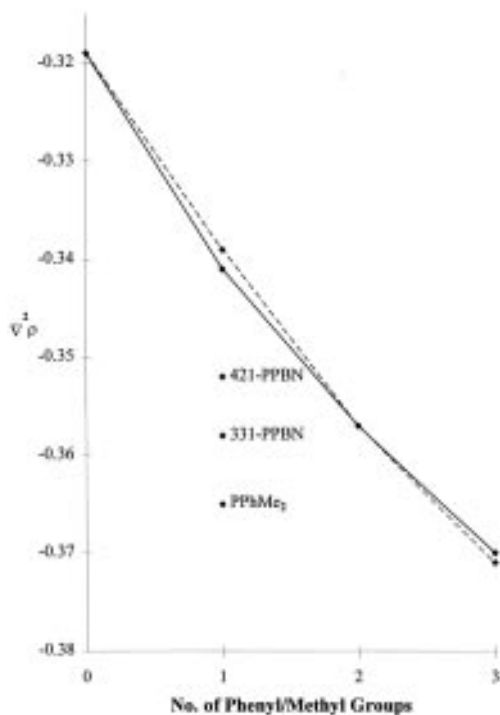


Figure 7. Relationship between $\nabla^2\rho$ at the lone pair and the number of substituents (solid = phenyl; dotted = methyl).

$\nabla^2\rho$. These μ values are listed in Table 3. In their study of alkylphosphines, Howard and Platts found a small (but regular) increase in μ_3 across the series $\text{PMe}_n\text{H}_{3-n}$ ($n = 0-3$), and similar results are found here for the $\text{PPh}_n\text{H}_{3-n}$ ($n = 0-3$) series. Thus in both types of substituted phosphine, the LP becomes “sharper” (i.e. thinner in radial extent) with increasing numbers of alkyl or phenyl substituents.

Atoms-in-Molecules Analyses for Phosphorus. We now turn to integrated properties to provide insight into the shape of the charge distribution around phosphorus. There are of course a number of practical schemes for deriving atomic charges and multipole moments.³⁸ The two most soundly-based would appear to be those due to Bader⁷ or Cioslowski,³⁹ since both utilize a density-based physical constraint to define the participating (as opposed to nonphysical partitioning of atomic orbital products). Here we apply Bader’s scheme, which utilizes nonoverlapping atomic surfaces with normal vectors \hat{n} placed such that

$$\nabla\rho\cdot\hat{n} = 0 \quad (1)$$

yielding “atoms” which individually obey the virial theorem.⁴⁰ Atomic moments (populations, dipoles, quadrupoles, *et cetera*) may be found from integration of $\rho(\mathbf{r})$ over this volume with appropriate operators. The atomic energy $E(\Omega)$ may also be obtained by integration of the kinetic energy density operator⁴¹ over the same region, and application of the atomic virial theorem.

We note that an alternative procedure to comparing the phosphorus atom charge distribution in a series of phosphines would be to compute various types of overlap density, as recently proposed by Cioslowski.³⁹ Although this could certainly provide useful information, its drawback is perhaps that it measures similarity of atoms-in-molecules by a single number

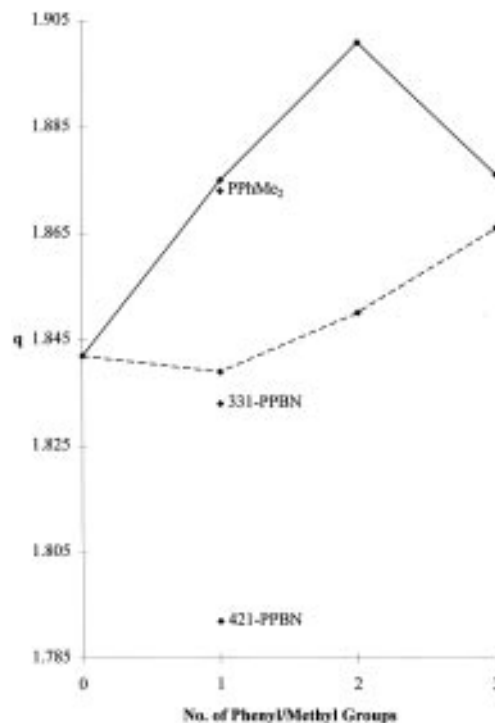


Figure 8. Relationship between the charge on phosphorus and the number of substituents (solid = phenyl; dotted = methyl).

Table 4. Phosphorus Atom Energy, Charge, Dipole, and Principal Quadrupole Moments (au)

	energy	charge	dipole	quadrupoles		
				aa	bb	cc
PH_3	-339.9476	1.842	2.35	+2.4	+2.4	-4.8
PPh_2H	-339.9951	1.875	2.35	+1.7	+2.2	-3.9
PPh_2H	-339.9949	1.901	2.34	+1.9	+0.7	-2.6
PPh_3	-339.9762	1.876	2.31	+3.2	+3.2	-6.3
PMe_2H	-339.9518	1.839	2.37	+1.7	+2.4	-4.1
PMe_2H	-339.9428	1.850	2.40	+0.3	+3.1	-3.3
PMe_3	-339.9249	1.866	2.43	+3.0	+3.1	-6.1
2-PyPH ₂	-340.0411	1.881	2.31	+1.5	+2.1	-3.6
3-PyPH ₂	-340.0213	1.887	2.34	+1.8	+2.2	-4.1
4-PyPH ₂	-340.0340	1.876	2.34	+1.6	+2.2	-3.8
[3.3.1]-PPBN	-340.0057	1.833	2.33	+2.4	+3.9	-6.3
[4.2.1]-PPBN	-340.0141	1.792	2.36	+1.9	+3.3	-5.2
PMe_2Ph	-339.9627	1.873	2.37	-0.1	+2.5	-2.4

(the overlap). Comparing the charge, dipole, and principle quadrupole moments of atoms gives more detailed information and is computationally simpler.

The energies and moments for the phosphorus atom in the various phosphines are reported in Table 4. In most compounds, the phosphorus atom is stabilized with respect to the phosphorus atom in phosphine (the exceptions being dimethylphosphine and trimethylphosphine). The phosphorus atom energy shows no monotonic trend across the phenyl- or methylphosphine series. Interestingly, the energies of the phosphorus atoms in the PPBNs are lower than the corresponding energies in the phenyl or methyl series, but the most stable phosphorus atoms are found in the pyridylphosphines, irrespective of the position of the nitrogen atom in the ring.

On the basis of these atomic charges, neither phenyl nor methyl substituents strongly donate or withdraw charge to or from phosphorus (Figure 8). This appears at odds with the results of the LP analysis, but it is in fact consistent with the analysis reported by Howard and Platts previously¹⁰ (a rationalization for how the phosphorus atom may even lower its electron population on substitution and yet show increased density in the LP is offered in this reference). If this slight

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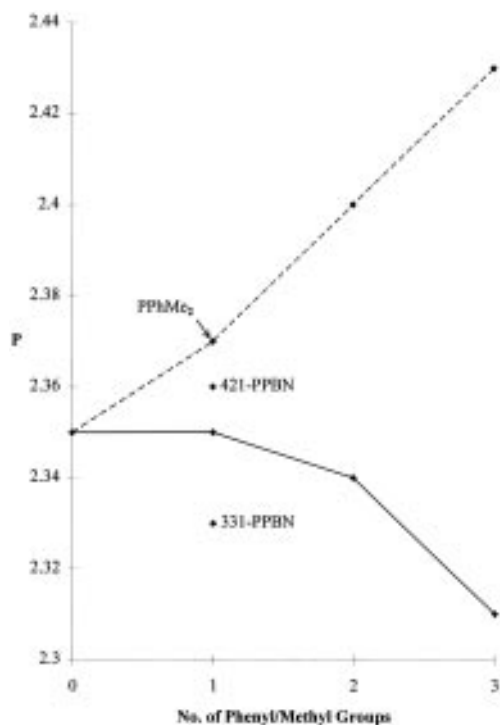


Figure 9. Relationship between the dipole moment of phosphorus and the number of substituents (solid = phenyl; dotted = methyl).

trend in the phenyl series could be considered significant, it would identify the phenyl group as a weak charge acceptor (via the π orbital system of the P–Ph fragments) when bonded to phosphorus. However, at the 6-311G(d,p) level the atomic charges of phosphorus in PH_3 and PMe_3 respectively are 1.884 and 1.885 (*c.f.* 1.842 and 1.866 at the 6-31G(d,p) level, reported in Table 4). It therefore seems likely that this trend disappears at the HF-limit.

The PPBNs are weakly electron-donating with respect to phenylphosphine (see Figure 8) which also has only one phenyl ring. From the values in Table 4, the *n*-pyridyl groups have a similar (slight) electron-withdrawing power to phenylphosphine, with little dependence on the heteroatom position.

The dipole moment of the phosphorus atom is generally found to point within a few degrees of the LP direction. (In PH_3 , PPh_3 , and PMe_3 it points exactly along this direction by symmetry). This atomic dipole is invariably oriented so that the positive pole lies in the LP region, *i.e.* this moment reflects the overall (dipolar) polarization of charge into this region. As an integrated quantity it is perhaps a better indicator of how much charge is contained the LP region as a whole, than the $(3,-3) \nabla^2\rho$ CP properties which are evaluated at just one point (the LP centroid). Interestingly, like the latter $(3,-3) \nabla^2\rho$ CP properties described in the previous section, the phosphorus dipole (Table 4 and Figure 9) indicates nothing exceptional about the LP region in the PPBNs. The phenyl series shows a very slight weak *decrease* in phosphorus dipole moment with increasing number of substituents while the methyl series shows the opposite. However, the range of atomic dipoles across all compounds studied is so small (2.31–2.43 au) that we attach little significance to these trends.

The eigenvectors of the phosphorus quadrupole tensor are one LP-directed vector with an associated (negative) eigenvalue, and two perpendicular vectors with approximately equal positive values (they may be exactly equal by symmetry). The trends in the LP-associated eigenvalue with the number of substituents are illustrated in Figure 10. Curiously, the trends for the phenyl- and methylphosphine series closely mirror each other in contrast

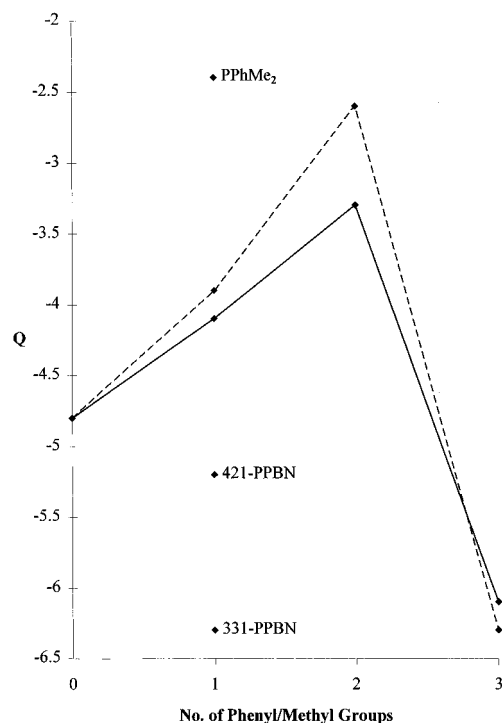


Figure 10. Relationship between the principal quadrupole moment, Q_{zz} , of phosphorus and the number of substituents (solid = phenyl; dotted = methyl).

to the dipole moment results. The PPBN compounds show significantly larger principal atomic quadrupole moments than phenylphosphine or dimethylphenylphosphine.

Conclusions

The key characteristics of the electron distribution around the phosphorus atom have been compared in a number of aryl- and alkylphosphines. Substitution of hydrogen by successive phenyl or methyl groups produces regular enhancements in lone pair properties, which would be expected to correlate with gas phase proton affinities across this series. The *ab initio* optimized structures obtained provide a useful basis for further study.

We find no evidence in any of the one-electron properties studied that the phosphorus atom electronic structure is much perturbed by the presence of a nitrogen heteroatom in an aromatic ring, nor that the position of this heteroatom has any significant consequence for the phosphorus atom. Where pyridylphosphines are superior to the analogous phenylphosphines as ligands in metal phosphine catalysts, the reason surely lies in the ability of the nitrogen heteroatoms to provide extra electron donation or basic centers, rather than any through-bond electronic influence.

The electron distribution analysis yields several key results.

(i) P–C double bond character in arylphosphines (measured via bond ellipticity) increases across the series $\text{PPh}_n\text{H}_{3-n}$ ($n = 0-3$) arylphosphines, despite the fact that the bond length remains essentially constant. This could be rationalized in terms of a larger number of “resonance” structures for PPh_3 . These results suggest that it is misleading to look only at the P–C bond length as a measure of the π -character, as some previous studies have done.¹¹ A previous study of phenylphosphine¹² concluded that conjugative effects are of “minor importance”. By considering a wider series of compounds we have revealed a more substantial conjugative effect, especially in [3.3.1]-PPBN and [4.2.1]-PPBN in comparison with simpler aryl- and alkylphosphines. Further studies are in progress on these ligands which include a determination of their basicity and an investiga-

tion of their catalytic properties in complexes with group 10 transition metals.⁴²

(ii) Two of the three indicators for the lone pair (the lone pair critical point properties, and the axial atomic quadrupole moment) show an increase of density in this region for the PPBNs, triphenyl- and trimethylphosphine relative to PH_3 . The third indicator, the phosphorus atomic dipole moment, actually shows opposite trends for the methyl and phenyl series, although the variation in the phosphorus dipole across all compounds is very small (5%).

(iii) The key parameter controlling the double bond character of the P–C(phenyl) bond is the orientation of the phenyl ring with respect to the phosphorus lone pair. This is evident in the

(42) Foreman, J. P.; Howard, S. T.; Edwards, P. G. Manuscript in preparation.

large P–C(phenyl) bond ellipticities found in the PPBN compounds and in the analogous conformation of dimethylphenylphosphine. In other words, the octane ring in the PPBNs imparts the high double P–C(phenyl) double bond character by forcing the molecule to adopt the conformation where the phosphorus lone pair is normal to the ring. This conformation is disfavored in phenylphosphine and dimethylphenylphosphine. This suggests a possible electronic basis for the high catalytic activity of the PPBNs.

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