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Phosphoranes: Multiple Bonding and Substituent Effects

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Abstract: The bonding between carbon and phosphorus in trivalent and pentavalent alkylidenephosphoranes is examined and related to questions of structure and reactivity. The effects of electron donating and withdrawing on carbon and phosphorus are studied and their effect on PC bond lengths and rotational barriers determined. Substitution-induced changes in phosphorus–carbon π bonding are likewise evaluated. Several unexpected results are obtained and comparisons are drawn between the normal valent phosphoranes and their nitrogen congeners. Ab initio wave functions with split-valence and polarized basis sets are employed. Charge distribution is analyzed with charge density difference plots, molecular orbital plots, and atomic radii fit to total electron density surfaces.

A plethora of stable species exists containing multiple bonds between carbon and other members of the first period, but far fewer examples of the period II congeners have been characterized.[3] Though isolable molecules are relatively uncommon, unsaturated silicon and phosphorus species have been proposed as intermediates in many reactions. One of the more important reactions in which such species participate is the Wittig carbon–carbon bond-forming reaction.[4] The reactivity of alkylidene phosphoranes in this reaction is thought to stem from the large contribution of ylide resonance forms to the electronic structure, i.e.

$$L_3P{=}CR_2 \leftrightarrow L_3P^{+}{-}CR_2^{-}$$

While experimental data are ambiguous, theoretical investigations into the nature of the phosphorus–carbon bond strongly suggest that it is at least partially zwitterionic.[5] Analogous trivalent phosphorus molecules ($RP{=}CH_2$) have been experimentally characterized and are structurally similar to the phosphoranes but do not share their reactivity.[6] The present study uses ab initio molecular orbital theory to compare the bonding in these trivalent and pentavalent phosphorus species and explore the changes in electronic structure upon substitution at both phosphorus and carbon.

Table I. Phosphorus–Carbon Bond Lengths (Å) at 3-21G$^{(*)}$

molecule	r(PC) calcd	r(PC) exptl
$HP{=}CH_2$	1.645	1.670[a]
$FP{=}CH_2$	1.623	
$MeP{=}CH_2$	1.640	
$HP{=}CF_2$	1.656	1.671[a]
$H_3P{=}CH_2$	1.646	
$F_3P{=}CH_2$	1.590	
$H_3P{=}CF_2$	1.635	
$Me_3P{=}CH_2$	1.651	1.640[b]

[a] Reference 6a. [b] Reference 12.

Methods

All calculations were performed with GAUSSIAN 82[7] and the 3-21G$^{(*)}$ basis set.[8] This split-valence basis includes a set of 6 d functions on all second period elements, which has been found to be necessary to properly describe hypercoordinate molecules, such as the alkylidene phosphoranes examined here. Likewise, previous studies also have demonstrated that fully polarized bases are not required to qualitatively account for their bonding.[8b] Results obtained from 3-21G$^{(*)}$ have been shown to closely mimic those of the larger, fully polarized 6-31G* basis. Single points at MP2/6-31G*//HF/6-31G* were used to construct potential energy surfaces. All geometries were fully optimized subject only to the constraint of C_s symmetry. Normal mode analyses confirmed that these structures are minima on the potential energy surfaces in question.

Charge distributions were analyzed with use of molecular orbital plots, deformation density contours, and atomic radii. Molecular orbital plots

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(3) See, for example: Gordon, M. S. *J. Am. Chem. Soc.* **1982** *104*, 4352. Allen, L. C.; Cook, C. *Organometallics* **1982**, *1*, 246. Schaefer, H. F., III; Goddard, J. S.; Yoshioka, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7644. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley: New York, 1980.

(4) See, for example: Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, Part B; Plenum Press: New York, 1977.

(5) (a) McDowell, R. S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 4047. (b) Lischka, H. *Ibid.* **1977**, *99*, 353. (c) Gordon, M. S.; Boatz, J. A.; Schmidt, M. W. *J. Phys. Chem.* **1984**, *88*, 2998. (d) Mitchell, D. J.; Wolfe, S.; Schlegel, H. B. *Can. J. Chem.* **1981**, *59*, 3280. (e) Schmidt, M. W.; Yabushita, S.; Gordon, M. S. *J. Phys. Chem.* **1984**, *88*, 382. (f) Dixon, D. A.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 7172.

(6) Hopkinson, M. J.; Kroto, H. W.; Nixon, J. F.; Simmon, N. P. C. *J. Chem. Soc., Chem. Commun.* **1976**, 513. Kroto, H. W.; Nixon, J. F.; Ohno, K.; Simmon, N. P. C. *Ibid.*, **1980**, *709*. Lohr, L. L.; Schlegel, H. B.; Morokuma, K. *J. Phys. Chem.* **1984**, *88*, 1981. Lohr, L. L.; Ponas, S. H. *J. Phys. Chem.* **1984**, *88*, 2992. Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731.

(7) GAUSSIAN 82, release H: Binkley, J. S.; Frisch, M.; Krishnan, R.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A.; ca. 1982, Carnegie-Mellon University.

(8) (a) First-row elements: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Ch. Soc.* **1980**, *102*, 939. (b) Second-row elements: Pietro, W. J.; Francl, M. M.; Hehre, W. J.; Binkley, J. S.; DeFrees, D. J.; Pople, J. A. *J. Am. Ch. Soc.* **1982**, *104*, 5039.

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were obtained at a contour level of 0.10 e$^-$/au^3 with a modified version of Jorgensen's plotting algorithm.[9] Charge density difference contours were constructed by subtracting the sum of spherical atom densities from the total molecular electron density. The radii of atoms within molecules were obtained from spheres fit to the 0.002 e$^-$/au^3 total electron density surface.[10] (The 0.002 e$^-$/au^3 contour has been shown to correspond well to the van der Waals surface of a molecule.[11])

Results and Discussion

A. Structures. Optimized phosphorus–carbon bond lengths obtained with the 3-21G$^{(*)}$ basis for all the compounds discussed below are presented in Table I. The limited data contained in Table I suggest that 3-21G$^{(*)}$ geometries adequately reproduce the known structures of the unsaturated phosphorus molecules considered here, as well as the trend upon increasing saturation. Structures are also in good agreement with those obtained in a recent study by Dixon and Smart.[5f] Note that both the experimental and calculated PC bond lengths in the parent normal and hypervalent species, $HP{=}CH_2$ and $H_3P{=}CH_2$, are nearly identical. All PC distances are within the range expected for a double bond given the single and triple bond distances are 1.855 and 1.513 Å, respectively, at 3-21G$^{(*)}$. The PC bond shortens with respect to a single bond by 11.3% in $HP{=}CH_2$, while in the hypervalent $H_3P{=}CH_2$ the linkage is 13.9% shorter. The latter shortening is comparable to that observed in typical carbon–nitrogen molecules (13.4%). Thus the existence of a substantial PC double bond is not precluded in either case.

Except for the planarity of the methylene carbon and the LPC angles, the other geometrical parameters are not noteworthy. The methylene fragment in methylidenephosphorane has been found to be slightly nonplanar at some levels of theory. Although the existing gas-phase structure of $Me_3P{=}CH_2$[12] did not determine the positions of the hydrogens, it has been suggested that pyramidalization at the methylene carbon is an artifact of the basis set.[13] The methylene carbon in the parent compound $H_3P{=}CH_2$ is found to be planar at 3-21G$^{(*)}$, and therefore we have forced planarity in the remaining molecules. The structure of the L_3P fragment in the phosphoranes deviates somewhat from local C_{3v} symmetry, and Mitchell et al.[13] have suggested that this distortion is a result of secondary overlap between the PH bonds and the methylene lone-pair fragment. Geometry optimization shows that the deviation from local symmetry is 11.5° for the parent methylidenephosphorane and somewhat larger and smaller for molecules perfluorinated at phosphorus and carbon, respectively.

B. Bond Strengths. Strengths of π bonds have customarily been assessed by measuring, experimentally or theoretically, the barrier to rotation. This method assumes that a 90° rotation about the bond completely destroys all π overlap. Although for carbon–carbon bonds this definition is legitimate, it is inappropriate for π bond formation not restricted by symmetry or the availability of atomic functions to a single plane. Such is the case for the hypervalent molecule $H_3P{=}CH_2$, due to the local (C_{3v}) symmetry of the phosphorus center. Regardless of the existence of a multiple bond between phosphorus and carbon, the expected barrier to rotation about the PC axis would be zero. (The slight deviation from local C_{3v} symmetry does, of course, lead to a small barrier.) The absence of barrier in this molecule has previously been interpreted as a lack of π character in the bond, but it is clear that this is not necessarily so and that other criteria must be used to assess PC π bond energies in such systems.

Table II. Molecular Dipole Moments (D) at 3-21G$^{(*)}$

molecule	μ	molecule	μ
$HP{=}CH_2$	1.13	$H_3P{=}CH_2$	2.36
$FP{=}CH_2$	1.54	$F_3P{=}CH_2$	0.37
$CH_3P{=}CH_2$	1.23	$H_3P{=}CF_2$	4.72
$HP{=}CF_2$	1.19	$(CH_3)_3P{=}CH_2$	

An approach using isodesmic reactions, in which the number of bonds between atoms remains constant, has been used successfully to assess relative stability of multiple bonds.[14] Since there is no net change in the number of bonds, reaction energies derived from uncorrelated wave functions are in reasonable agreement with experimental values. The isodesmic reaction

$$H_3P{=}CH_2 + PH_3 \rightarrow HP{=}CH_2 + PH_5$$

has a reaction energy of 33 kcal/mol at HF/3-21G$^{(*)}$. This suggests, surprisingly, that the PC bond in the hypervalent molecule is stronger than that in the normal valent compound. Since the PC bond lengths differ by only 0.001 Å, the σ bond energies of the two molecules should not be very different. With this assumption, the difference is then principally attributable to π or zwitterionic contributions to the bonding except that this value is artificially high due to the inequivalence of the PH bond energies in hypervalent and normal valent molecules. By taking into account the face that the PH bond in hypervalent systems is approximately 15 kcal/mol weaker than that in analogous normal valent species,[15] the difference is reduced to only 3 kcal/mol. Qualitatively then, the strength of the bond ($\sigma + \pi$ or $\sigma +$ zwitterionic) between phosphorus and carbon is similar in both molecules. This is not impossible, as it has been pointed out that the energy of an ionic interaction may equal or exceed that of the analogous π system.[16] Since PH_5 is not a known species, and maybe quite unstable, it is possible that this reaction overestimates the stability of $H_3P{=}CH_2$ relative to $HP{=}CH_2$. A similar reaction can be written

$$H_3P{=}CH_2 + PH \rightarrow HP{=}CH_2 + PH_3$$

At HF/3-21G$^{(*)}$ this reaction is found to be exothermic by 97 kcal/mol. Again taking into account the relative stabilities of the PH bonds in the differential environments, one finds the π bond in $HP{=}CH_2$ is 142 kcal/mol less stable than the corresponding bond in the hypercoordinate system! Once again, however, the relative stabilities of the species involved are quite different. PH is a much higher energy species than phosphine. Thus, one suspects that the difference in π bond energy between the species is overestimated. For the reasons delineated above, it is apparent that these types of reactions are not appropriate measure of the π bond energies in hypercoordinate systems due to the substantial differences in bonding throughout these molecules.

Since neither of the caveats noted above apply to the roational barrier in the *trivalent* $HP{=}CH_2$, it is possible to directly assess its π bond energy in this manner. The relaxed barrier to rotation in $HP{=}CH_2$ is nearly 100 kcal/mol at 3-21G$^{(*)}$, almost twice that of the analogous nitrogen species. Taking into account correlation effects does not appreciably alter the barrier, which remains some 30 kcal/mol higher than that in ethylene. Assuming that the barrier is equivalent to the π bond strength, it would appear that $HP{=}CH_2$ contains an extremely strong double bond. This is not expected because the presumed disparity in size of the p orbitals should reduce the overlap. An examination of the spatial distribution of electron density in these systems will provide some insight into this anomalous behavior.

C. Charge Distributions. Both the Mulliken populations and dipole moments indicate a significantly larger separation of charge in the hypervalent species than in the normal valent molecules.

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[9] Jorgensen, W. L. Program 340, Quantum Chemistry Program Exchange.

[10] Francl, M. M.; Hout, R. F., Jr.; Hehre, W. J. *J. Am. Ch. Soc.* **1984**, *106*, 563.

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[13] Mitchell, D. J.; Wolfe, S.; Schlegel, H. B. *Can. J. Chem.* **1981**, *59*, 3280.

[14] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

[15] The PH bond energies were calculated at 3-21G$^{(*)}$ from the reaction energy of $PH_n \rightarrow P + nH$, where $D(PH) = E_{rxn}/n$. The bond energies were found to be 40 and 55 kcal/mol for $n = 5$ and 3, respectively. Calculations on PCl and PF bonds in analogous molecules show similar differences in energy. Experimental data (*JANAF Thermochemical Tables*; Stull, D. R., Prophet, H., NSRDS-NBS 37, National Bureau of Standards: Washington, D.C., 1971) confirm the differences in bond energies for PCl and PF systems.

[16] Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983.

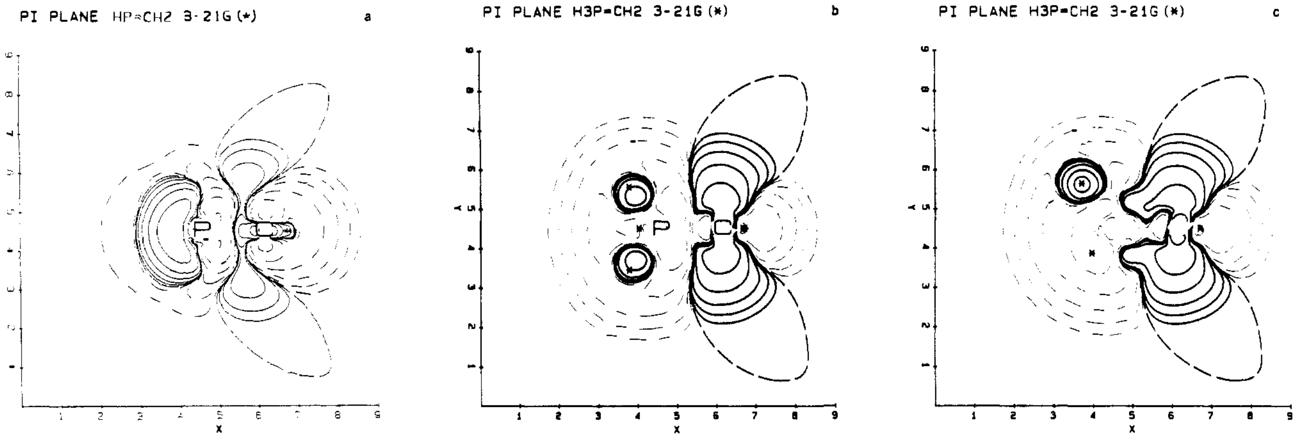

Figure 1.

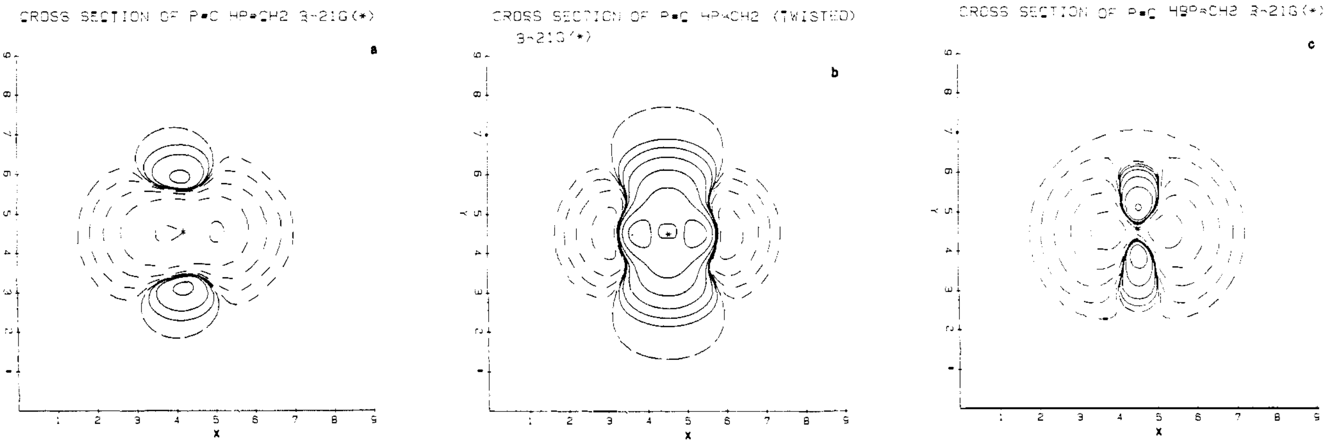

Figure 2.

The calculated dipole moment in $HP{=}CH_2$ is 1.13 D (experimentally μ = 0.87 D) compared to 2.36 D in $H_3P{=}CH_2$. The latter value is significantly larger than that calculated for the twisted isomer of $HP{=}CH_2$, 1.54 D, which presumably has a good deal of ionic character. Dipole moments for the molecules in this study are collected in Table II. Substitution at carbon by fluorine leads to a larger dipole moment, 4.72 D, but this does not necessarily indicate a more ionic PC bond. The difference between the dipole moments of the parent $H_3P{=}CH_2$ and H_3PCF_2 is due almost entirely to the polarity of the CF bonds. Though one would expect the zwitterionic character of the PC linkage to be enhanced by substitution of electron-withdrawing group this is not reflected in the 0.37 D dipole moment of $F_3P{=}CH_2$ because the highly negative fluorine atoms compensate for the negative charge on the opposite end of the molecules. Dipole moments of the trivalent molecules are within a much smaller range than those of their hypervalent counterparts and indicate much less separation of charge.

Mulliken populations indicate a significant charge separation between carbon and phosphorus in all the molecules considered (Table III). Carbon is found to be most highly charged in $F_3P{=}CH_2$, where it bears a full negative charge. In contrast, the Mulliken charge on carbon in $H_3P{=}CH_2$ is slightly positive ($0.28e^-$) due to electron withdrawal by fluorine at this center. Carbon in the hypervalent systems considered here is always more negative than that in the analogous trivalent systems, as expected for predominately zwitterionic species. However, even the normal valent molecules appear to be polarized toward carbon.

The polarity of the bond in the normal valent molecules leads to increased anionic character at the carbon center. Anionic centers are known to have a more diffuse charge distribution in comparison to analogous uncharged systems,[17] and this will produce a better overlap with phosphorus p orbitals and the increase in the π bond strength relative to the first-row congeners noted previously.

Table III. Mulliken Charges (in electrons, HF/3-21G$^{(*)}$)

molecule	q_P	q_C	molecule	q_P	q_C
$HP{=}CH_2$	+0.25	-0.67	$H_3P{=}CH_2$	+0.58	-0.92
$FP{=}CH_2$	+0.73	-0.78	$F_3P{=}CH_2$	+1.64	-1.05
$CH_3P{=}CH_2$	+0.50	-0.71	$H_3P{=}CF_2$	+0.53	+0.28
$HP{=}CF_2$	+0.17	+0.56			

Deformation density plots provide a description of the spatial aspects of the charge distribution. Figure 1 shows the charge density differences for $HP{=}CH_2$, $HP{=}CH_2$ in its twisted conformation, and $H_3P{=}CH_2$ in the π plane. All three molecules have a region of charge increase (indicated by solid contours) between the phosphorus and carbon. Note that charge is shifted significantly more toward the midline of the bond in $HP{=}CH_2$ than in either of the other two molecules. Compare the plots in Figure 2 which show the density differences in the plane bisecting the PC axis. The density increases are noticeably larger in the π direction of $HP{=}CH_2$ than in the σ direction. In contrast, the twisted isomer of $HP{=}CH_2$ and the hypervalent $H_3P{=}CH_2$ do not exhibit this buildup of charge, which is typical of π bonding. Given that the bonding between phosphorus and carbon in the twisted phosphaolefin can be formally described as σ with a zwitterionic component, this suggests that a similar situation exists for bonding in the hypervalent moiety.[18]

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[17] Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comp. Chem.* **1983**, *4*, 294.

[18] If phosphorus makes substantial use of d orbitals in bonding, it could be argued that the twisted isomer of $HP{=}CH_2$ would also have a double bond. Evidence that the formal description bears some resemblance to the actual bonding can be found by comparing the charge density difference plots for $HP{=}CH_2$ at 3-21G, without d orbitals on phosphorus, and those at 3-21G$^{(*)}$, including d orbitals in the phosphorus basis. These plots show very similar bonding patterns, suggesting that the twisted $HP{=}CH_2$ is well described as a zwitterion.

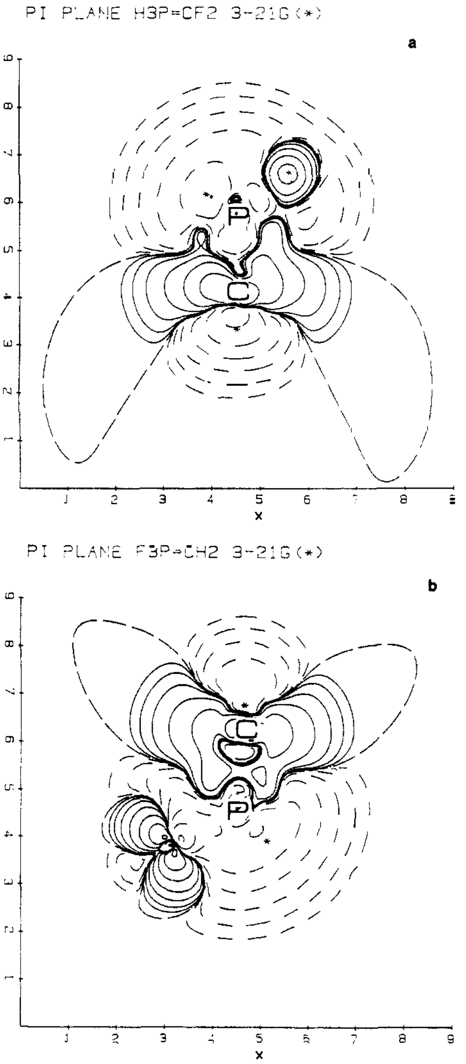

Figure 3.

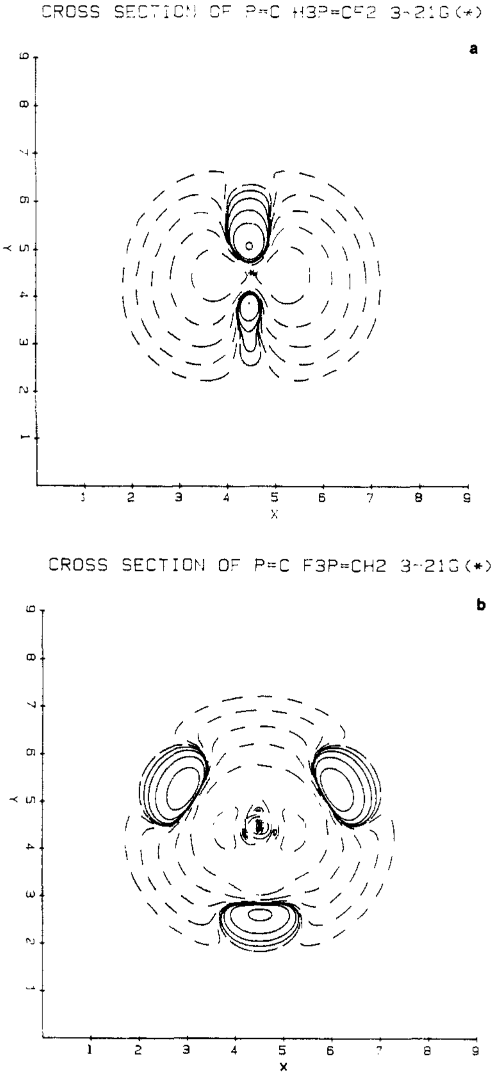

Figure 4.

Charge density difference plots in the plane of the π system for substituted pentavalent phosphaolefins are shown in Figure 3. All the molecules exhibit charge increase in the region between phosphorus and carbon, similar to that observed in the parent molecule. The shift in density away from phosphorus, toward carbon, is most marked in $F_3P{=}CH_2$, as expected from the Mulliken populations. Substitution of fluorine at carbon leads, in contrast, to a slight shift in density toward the midpoint of the bond, relative to its parent. One would expect the π character of the PC bond to be enhanced in this case. This is in agreement with the results of Dixon and Smart,[5f] which suggest that the zwitterionic character of the PC bond in $L_3P{=}CF_2$ molecules is minimal. The extent of the π charge density compared to the σ charge can be seen in Figure 4, for these pentavalent molecules. The enhancement of π charge density in the normal valent species is evident by comparison with Figure 5, the analogous contour plots for the substituted trivalent molecules. Even the most covalent of the $L_3P{=}CH_2$ molecules exhibit only about 80% of the increase observed in the normal valent cases. Examination of density difference contours in the π plane reveals that while substitution at phosphorus has little effect on the region of charge increase, fluorine substitution on carbon causes a significant delocalization of density over both the phosphorus and the carbon. This accounts for the short calculated bond distance and the lack of change in the dipole moment relative to the parent $HP{=}CH_2$.

Molecular orbital plots further substantiate the zwitterionic character of $H_3P{=}CH_2$. The highest occupied molecular orbital (HOMO) of $HP{=}CH_2$ is obviously a pπ–pπ bonding MO, while that in $H_3P{=}CH_2$ appears to be the MO corresponding to a carbon anion lone pair (Figure 6). The distribution of charge in the π MO can be assessed by using sphere fit radii to the total electron density. In this instance the radii have been determined with and without the HOMO included. The results (Table IV) parallel the results of the Mulliken population analysis. In the hypervalent systems the size of the carbon atom is found to be significantly larger than that of most sp^2 carbons, approaching that of a carbon α to a lithium substituent. The π MO is shown to be exclusively located on the carbon center. Differences in the calculated radii of phosphorus are well within the error limits of

Table IV. Radii of Best Fit Spheres to the Total Electron Density with and without the HOMO (Radii in Å)

	with HOMO		without HOMO			
molecule	r(P)	r(C)	r(P)	r(C)	ΔP[a]	ΔC[b]
$HP{=}CH_2$	2.04	1.90	1.90	1.55	0.14	0.35
$FP{=}CH_2$	1.99	1.90	1.88	1.69	0.11	0.21
$HP{=}CF_2$	2.04	1.81	1.88	1.58	0.16	0.23
$CH_3P{=}CF_2$	2.05	1.91	1.93	1.67	0.12	0.24
$H_3P{=}CH_2$	1.99	1.95	1.97	1.69	0.02	0.26
$F_3P{=}CH_2$	1.84	1.92	1.77	1.68	0.07	0.24
$H_3P{=}CF_2$	1.99	1.88	1.95	1.61	0.04	0.27
CH_4		1.88				
CH_3Li		2.03				
$CH_2{=}CH_2$		1.87				
$CH_2{=}CH(Li)$[c]		2.00				
PH_3	2.05					
PH_5	1.99					
PH_4^+	1.94					

[a] ΔP = r(P, with HOMO) − r(P, without HOMO) [b] ΔC = r(C, with HOMO) − r(C, without HOMO) [c] Radius of carbon α to Li.

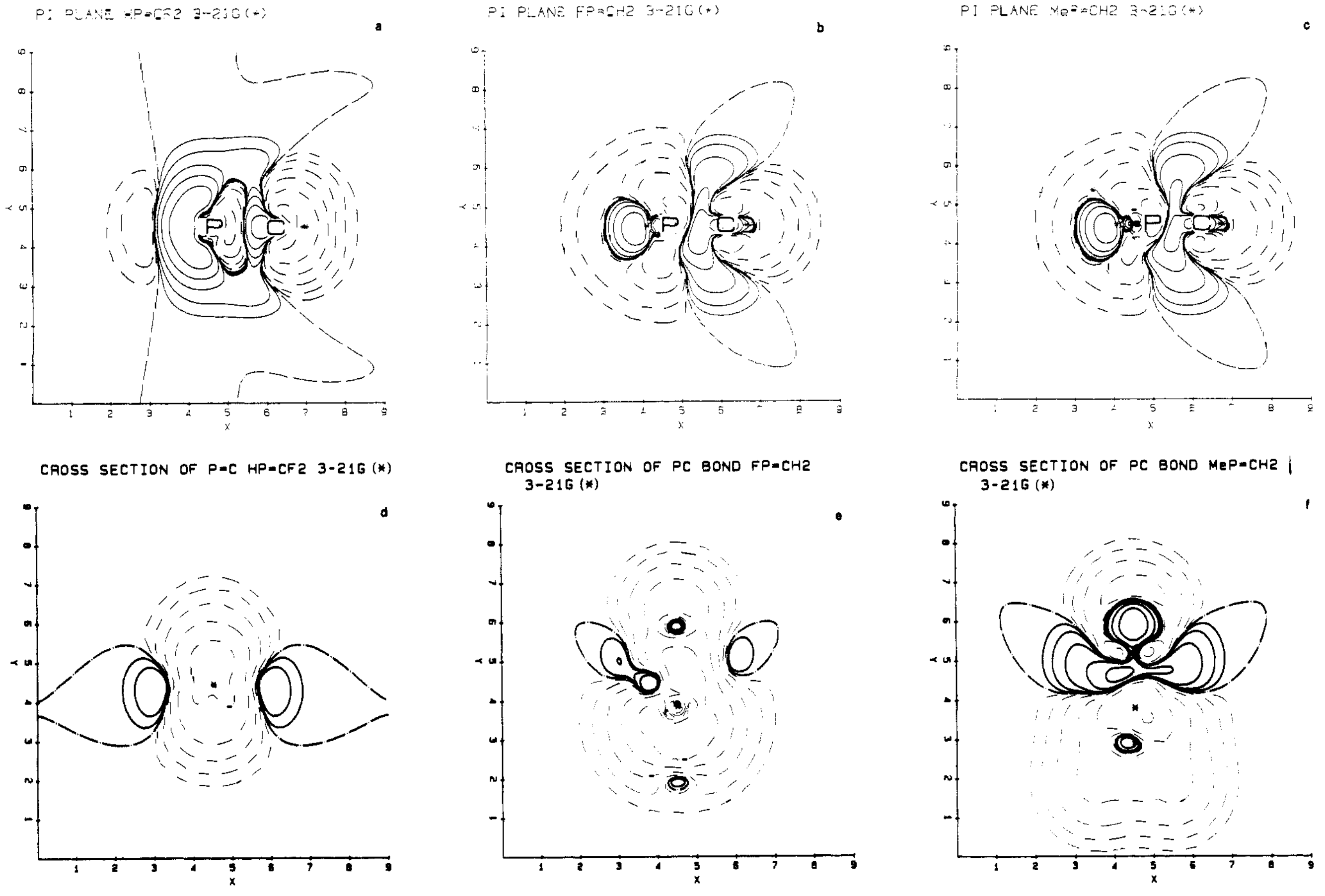

Figure 5.

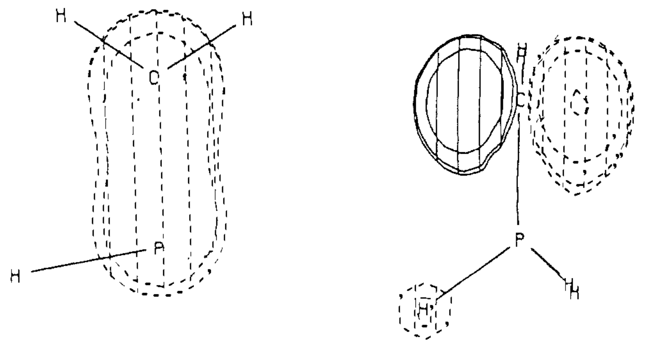

Figure 6.

Table V. Effect of Polarization Functions and Electron Correlation on the Rotation and Planar Inversion Barriers of $HNCH_2$ (kcal/mol)

molecule	basis	rigid rotation barrier	relaxed rotational barrier	planar inversion barrier	ΔE^a
$HNCH_2$	HF/3-21G	56.5		26.1	30.4
	HF/6-31G*			32.5	
	MP2/6-31G*			31.9	
$HPCH_2$	HF/3-21G*	107	100	175	-68
	HF/6-31G*	108	101	172	-64
	MP2/6-31G*	115	107	173	-58

[a] ΔE = rigid rotation barrier − planar inversion barrier.

Table VI. Rigid Rotation Barriers for LP=CR_2 at 3-21G$^{(*)}$

molecule	barrier^a	molecule	barrier^a
HP=CH_2	106.6	FP=CH_2	68.0
CH_3P=CH_2	93.9	HP=CF_2	51.0

[a] Difference in energy (kcal mol^{-1}) between the HF/3-21$^{(*)}$ optimized structure of LP=CR_2 and the corresponding structure in which the RCR plane is perpendicular to the LPC plane.

the fit. Similarly, in the normal valent molecules, the charge distribution of the π MO is skewed considerably more toward the carbon than the phosphorus (removal of this orbital does affect the sphere fit radius of phosphorus).

D. Rotation vs Inversion. While olefins have only one route open for cis/trans isomerization about the double bond, rotation; trivalent phosphaolefins, like imines, have two possible pathways, rotation and inversion through the heteroatom lone pair. The latter process, since the π bond should remain intact, is expected to be the more favorable. Our calculations find the barrier toward rotation in HN=CH_2 to be 56 kcal/mol at HF/3-21G as compared to 26 kcal/mol for the inversion pathway. Experimental values for alkyl imine inversion barriers range from 25 to 27 kcal/mol, in good agreement with these results.

Consideration of the planar inversion barrier in the phosphaolefin HP=CH_2 shows it to be greater by 75 kcal/mol than the relaxed rotational barrier at 3-21G$^{(*)}$. Including electron correlation in the calculation of the planar inversion trajectory leads to an inversion barrier that is slightly closer to that for rotation, having a difference of 66 kcal/mol.

Barriers calculated for the trivalent species considered here using the rigid rotor approximation are given in Table VI. The barrier heights do *not* parallel the bond lengths. If the barrier heights were equivalent to the π bond stengths, then shorter bond lengths would be expected for bonds with high barriers. Substitution at phosphorus with F results in a very short PC bond (1.623 Å) compared to the parent compound. However, the barrier to rotation about this bond is only about half that of HP=CH_2 (68.0 kcal/mol). Similarly, though the bond in CH_3P=CH_2 is slightly shorter than that of the parent, the barrier is also smaller by more than 10 kcal/mol. In both these instances, empty oribtals on phosphorus (d_{xz}) can accept electron density from carbon, stabilizing the twisted, zwitterionic forms. This acceptor behavior is enhanced by fluorine substitution, which depletes charge from phosphorus via σ induction. Substitution of two fluorines at carbon (HP=CF_2) leads to a relatively long PC bond and a low barrier is observed (51 kcal/mol).

Conclusions

1. Phosphorus–carbon bond strengths in trivalent and pentavalent alkylidenephosphoranes are comparable. Reactivity of the latter species does not arise from weak bonding between the phosphorus and carbon but rather from the zwitterionic character of the bond.

2. The π character of the PC bond in the pentavalent systems can be increased by fluorine substitution at C as evidenced by charge density difference plots. Substitution at phosphorus with electron withdrawing and donating groups does not significantly affect π contributions to the bond.

3. The π bond strength in $HP{=}CH_2$ is calculated to be 107 kcal/mol at MP2/6-31G*//HF/3-21G$^{(*)}$, significantly higher than that in either its nitrogen congener or ethylene.

4. Phosphorus–carbon bonds in the trivalent phosphoranes exhibit the characteristic charge distributions of π bonding. The π orbital is distributed over both centers, in contrast to the pentavalent species.

5. Barriers toward rotation for systems having accessible d orbitals must be interpreted with caution, as they may bear no relationship to bond strength. This has been shown to be the case for pentavalent alkylidenephosphoranes and we show here that it can also occur in the corresponding trivalent species.

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Registry No. $HP{=}CH_2$, 61183-53-7; $FP{=}CH_2$, 105801-75-0; $MeP{=}CH_2$, 89149-01-9; $HP{=}CF_2$, 61183-52-6; $H_3P{=}CH_2$, 36429-11-5; $F_3P{=}CH_2$, 110638-16-9; $H_3P{=}CF_2$, 104575-63-5; $Me_3P{=}CH_2$, 14580-91-7.

Chemical Origins of Substituent Effects in Alkylpentacarbonylmanganese(I) Group Migration Reactions

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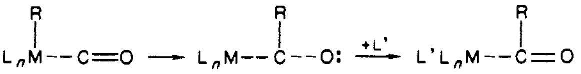
Abstract: A molecular orbital study of the effects of different alkyl substituents on the ease of group migration and the stability of the products formed in alkylpentacarbonylmanganese(I) systems ($(CO)_5MnR$, where R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH(CH_3)_2$, H, $CH_2C_6H_5$, C_6H_5, CH_2F, CF_2H, and CF_3) is presented. Isomerization energies for the group migrating step to an η^1-conformation and an η^2-conformation were calculated for the entire series of substituents. The energies of activation for both of these processes were estimated. The relative overall energy difference for the carbonylation reaction $(CO)_5MnR + CO \rightarrow (CO)_5Mn(COR)$ was also calculated for each derivative. The PRDDO method was used to obtain estimates of the geometries of the germane conformations necessary for a quantitative study of group migration. Ab initio Hartree–Fock calculations at the PRDDO optimized geometries were also carried out to provide an assessment of the calculated energies for a more limited set of the substituents. The calculated results at both levels of theory are compared to available experimental data and are found to be in good qualitative agreement. Localized molecular orbitals are used to analyze the Mn–R bond in the six-coordinate complex. A simple generalized acid–base description of the substituent effects is proposed to rationalize their observed and calculated behavior. This model may be easily extended to predict the qualitative change in migratory aptitude when CO is replaced by some other unsaturated ligand and when the transition-metal moiety is different.

The carbonylation reaction 1 remains a topic[1] of current investigation in organometallic chemistry. This reaction is typically



$$\overset{R}{L_nM}{-}C{=}O \longrightarrow L_nM{-}\overset{R}{C}{-}O: \xrightarrow{+L'} L'L_nM{-}\overset{R}{C}{=}O \qquad (1)$$

characterized by a topological rearrangement of a σ-bonded anionic group from the transition-metal center to an adjacent carbonyl group. In some transition-metal systems the process of alkyl group migration constitutes the initial step in a two-step process. The newly formed vacancy in the coordination sphere may or may not be followed by the addition of an incoming nucleophile (L′). Although this reaction occurs for a wide variety of transition metals[1b] in a large assortment of d orbital configurations, entering ligands[1a] (L′), and ancilliary ligands[1a] (L), there exists a specific trend in the migratory ability of a wide range of alkyl groups which is common to most of these systems. This basic trend has been attributed to the electron-withdrawing or electron-releasing nature of the substituent. Electron-releasing substituents facilitate the reaction, while electron-withdrawing substituents retard it. These substituent effects have been demonstrated in two ways. First, extensive kinetic studies[2,3] of the effect of the different alkyl substituents on the carbonylation reaction rate have been performed on several systems. Second, thermodynamic data[4,5] for numerous alkyl migratory systems reflect a similar trend in the stability of the products formed. One of the best experimentally

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