

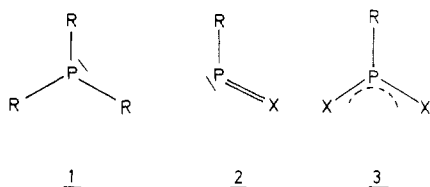
Dicoordination and Tricoordination at Phosphorus. Ab Initio Study of Bonding in Bis(imino)phosphoranes and Related Compounds¹

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Ab initio calculations at various basis set levels (double- ζ quality augmented by polarization functions) were performed at a SCF level for the molecules HPCH₂, *trans*-HPNH, HPO, HP(CH₂), HP(NH)₂, and HPO₂. Accordingly the d-orbital population is negligible in the dicoordinated phosphorus compounds and only slightly larger in the tricoordinated phosphorus compounds. There are essential differences between the HPX and HPX₂ structures (X = CH₂, NH, O). The latter type of structures refers to a heteroallyl system with a strong dipolar character rather than with multiple bonding at phosphorus. The bis(imino)phosphoranes prefer a *cis* conformation of the hydrogens (at the nitrogens) due to the smaller dipole moment in comparison to its *trans* isomer. The *cis*-*trans* conformational equilibrium depends on substituents.

While the chemistry of phosphine **1** and its derivatives (R = H, alkyl, etc.) has been explored in very much detail, the synthesis and structural elucidation of methylene-, imino, and oxophosphanes **2** (X = CR₂, NR, O) and of bis(methylene)- and bis(imino)phosphoranes **3** (X = CR₂, NR) are still under active



R = alkyl, amino etc.



investigation among various research groups in the field of low-coordination phosphorus chemistry.²⁻⁵ Structures of **2** and **3** can be derived from **1** by subsequent attachment of a π -center to a phosphorus atom. The type **2** structures are one of the first examples of double-bond systems containing second-row elements.⁶

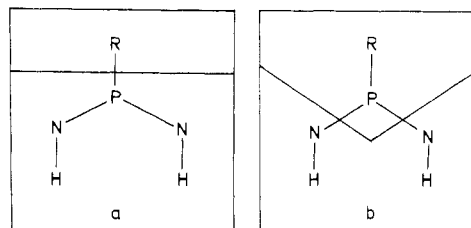
In the present publication we analyze the structure **3** and relate it to **2**. We will describe the basic features of this new class of compounds, the effects of substituents on its geometry, and some

aspects of its reactivity. Our analysis relies on semiempirical and ab initio quantum chemical calculations.

Results and Discussion

(a) Parent Diiminophosphorane and Derivatives. Let us first consider the orbital system of parent **3** (R = H; X = NH). A crystal structure of its derivative has been published.⁷ The bonds at phosphorus are perfectly in one plane, despite the strongly pyramidalized central atom in phosphines.⁸ Surprisingly, the substituents at the nitrogens are in a *cis* position to each other, adopting the most sterically hindered position. The P-N distance (toward the imino groups) is 1.503 Å in contrast with 1.55 Å in aminoiminophosphane⁹ (**2** (R = N(SiR₃)₂; X = N-*t*-Bu)). Hence the PN bond in **3** (X = NR) is about 5% shorter than in **2**. For the case X = CR₂, the PC bond in **3** is almost comparable with the one in **2**.¹⁰

A fragment analysis of bonding can be made in two ways. Either we let interact R with P(NH)₂ (**4a**) or PR step by step with NH (**4b**). There are advantages to both—the former makes



clear the role of substituents R on bonding in the P(NH)₂ allylic system; the latter allows us to discuss bonding at phosphorus.

- (1) For previous studies on low-coordination phosphorus compounds see: (a) Schoeller, W. W.; Niecke, E. *J. Chem. Soc., Chem. Commun.* **1982**, 569. (b) Schoeller, W. W.; Dabisch, T. *J. Chem. Soc., Dalton Trans.* **1983**, 2411. Schoeller, W. W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1635; **1984**, *39B*, 1767. Schoeller, W. W. *J. Chem. Soc., Dalton Trans.* **1984**, 2233. Schoeller, W. W.; Lerch, C. *Inorg. Chem.* **1983**, *22*, 2992. Schoeller, W. W.; Staemmler, V. *Ibid.* **1984**, *23*, 3369. Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1985**, 334. Schoeller, W. W.; Niemann, J. *J. Am. Chem. Soc.* **1986**, *108*, 22.
- (2) (a) Methylene phosphanes: Becker, G. Z. *Anorg. Allg. Chem.* **1976**, *423*, 242. For a review see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731; (b) Iminophosphanes: Niecke, E.; Flick, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 585. Scherer, O. J.; Glässel, W. *Chem. Ber.* **1977**, *110*, 3874. Niecke, E.; Rüger, R.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1034. For a review see: Fluck, E. *Top. Phosphorus Chem.*, **1980**, *10*, 193. (c) Oxophosphanes have been identified by spectroscopy: Binnewies, M.; Solouki, B.; Bock, H.; Becherer, R.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 731. See also ref c in Table II.
- (3) Bis(methylene)phosphoranes: Appel, R.; Peters, J.; Westerhaus, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 80. Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1982**, 2017. Niecke, E.; Leuer, M.; Wildbrecht, D. A.; Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1983**, 1171.
- (4) Bis(imino)phosphoranes: Niecke, E.; Flick, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 134; Scherer, O. J.; Kuhn, N. *Chem. Ber.* **1974**, *107*, 2123; Niecke, E.; Schwichtenhövel, K.; Schäfer, H.-G.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 963; Markovski, L. N.; Romanenko, V. D.; Ruban, A. V. *Synthesis* **1979**, 811. For a recent quantum chemical study on various PN₂H₂ isomers see: Ahlrichs, R.; Schiffer, H. *J. Am. Chem. Soc.* **1985**, *107*, 6494.

- (5) For a review of dioxophosphorane intermediates: Regitz, M.; Maas, G. *Top. Curr. Chem.* **1981**, *97*, 71. Dithiophosphorane: Navech, J.; Majoral, J. P.; Meriem, A.; Kraemer, R. *Phosphorus and Sulfur* **1983**, *18*, 27. Appel, R.; Knoch, F.; Kunze, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1004. Unsymmetrical bis(ylene) derivatives: Scherer, O. J.; Kuhn, N. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 811. Niecke, E.; Wildbrecht, D. A. *J. Chem. Soc., Chem. Commun.* **1981**, 72. Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Chem. Soc., Chem. Commun.* **1983**, 862. Yoshifuji, M.; Ando, K.; Toyota, K.; Shima, I.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1983**, 419. Niecke, E.; Rüger, R.; Lysek, M.; Schoeller, W. W. *Phosphorus Sulfur* **1983**, *18*, 35. Niecke, E.; Wildbrecht, D. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 199. Appel, R.; Knoch, F.; Kunze, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 157.
- (6) Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. *Acc. Chem. Res.* **1975**, *8*, 18. See also ref 2a.
- (7) Pohl, S.; Niecke, E.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 261.
- (8) Lehn, J. M.; Munsch, B. *J. Chem. Soc., Chem. Commun.* **1969**, 1327.
- (9) Pohl, S. *Chem. Ber.* **1979**, *112*, 3159.
- (10) The P-C bond lengths in methylene phosphanes are 1.64-1.67 Å as compared with 1.64 Å in bis(methylene)phosphoranes: See ref 2 and 3. Appel, R., personal communication.

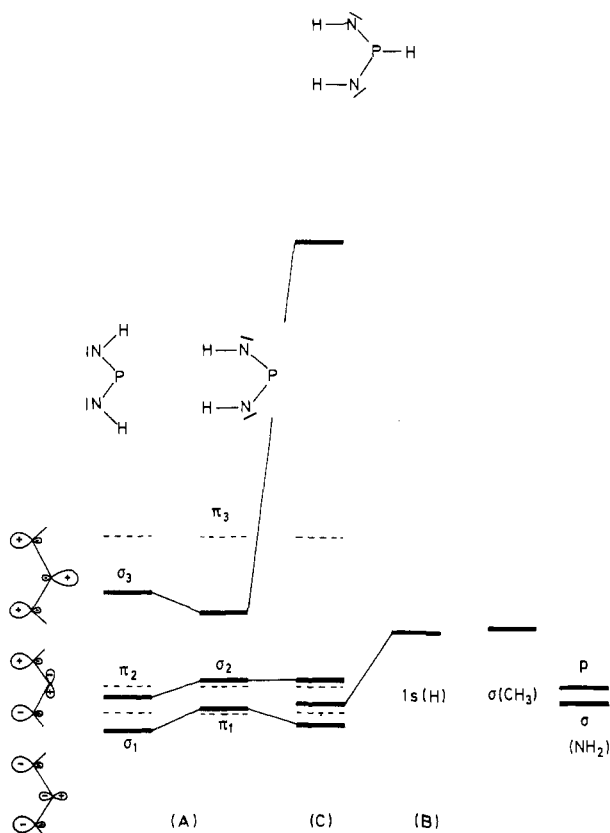
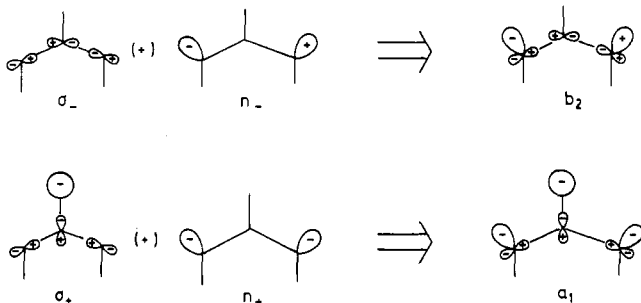


Figure 1. Interaction diagram for the composition of the molecular orbital system of bis(imino)phosphorane (C) from the fragment orbitals of P(NH)₂ (A) and the substituent R (B), as obtained from EH calculations.

An interaction diagram for the former, **4a**, is shown in Figure 1. The orbitals of the fragment P(NH)₂ (part A in Figure 1) are easily derived. The π-system refers to an allylic system, represented by the orbitals π₁–π₃ (dashed lines in the Figure). Similarly the σ-system is represented by the three orbitals σ₁–σ₃.

Consider next the fragment P(NH)₂ (part A) in its various conformations. In the trans conformation (with respect to cis) the orbital σ₃ is raised while the orbital σ₁ and σ₂ are lowered in energy. In comparison, the changes in the energies of the π-orbitals are negligible. The orbitals at B refer to a hydrogen is orbital.

Finally, both sets of orbitals will interact to C, i.e. to parent bis(imino)phosphorane. In case the hydrogen is replaced by a substituent R (part B) the corresponding fragment orbitals are a σ orbital (as in CH₃) or in addition a nonbonding P orbital (as in NH₂). For the latter case the orbital system is similar to that in methylene.¹¹ In our picture, orbital interaction takes place between σ₃ and σ₁ (at A) and 1s (at B). Due to the better overlap of 1s with σ₃ (compared with σ₁) its interaction is stronger. The composition of the resulting σ-type frontier orbitals will now be analyzed in detail for the cis structure.



The b₂ orbital is a mixture of the lowest σ₋ orbital with an out of phase combination, n₋, of nonbonding orbitals at the nitrogens.

(11) Gimarc, B. M. "Molecular Structure and Bonding"; Academic Press: London, 1979; p 23.

Table I. Optimized Bond Angles ∠NPN (deg) and Relative Energies (kcal/mol) of Various Substituted Structures **3** (X = NH), Obtained from ab Initio STO-3G Calculations^a

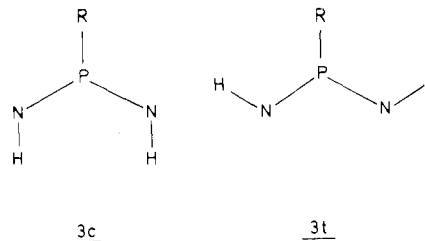
R	∠NPN	ΔE _{rel}	R	∠NPN	ΔE _{rel}
H	140.8	0	SiH ₃	134.9	0
	122.4	7.6		118.5	7.9
F	145.6	0	NH ₂ (p)	144.0	0
	124.9	2.9		123.6	4.9
Cl	144.0	7.1	NH ₂ (o)	139.5	0
	122.9	0		122.4	0.6
CH ₃	138.4	0			
	121.0	7.3			

^aUpper values (first entries) correspond to the cis conformers and the lower values (second entries) to the trans conformers. (p) refers to a planar and (o) to an orthogonal arrangement of the p orbital at the amino group with respect to the π-system.

In comparison to the a₁ orbital results from superposition of the nonbonding (σ₊) combination of p orbitals with an in phase (n₊) combination on lone pairs at the nitrogens. Likewise the σ-type frontier orbitals in the trans structure can be constructed.

A correlation diagram for the bond angle, ∠NPN deformation reveals the following picture (not published here): In the cis conformation the increase in the bond angle lowers the a₁ and b₂ components, while in the trans conformation b₂ is lowered and a₁ raised in energy.

In order to put this qualitative picture on firmer ground we performed energy-optimized ab initio STO-3G calculations on various substituted structures of **3** (X = NH), at times in a cis (**3c**) or trans (**3t**) conformation. The results of these investigations



are summarized in Table I. The first entries in the table refer to **3c** and the second entries to **3t**. Accordingly, electronegative substituents at phosphorus open the ∠NPN angle while electro-positive substituents close it, at times in reference to R = H. The trend is strong for **3c** and more weakly pronounced for **3t**. Our theoretical analysis is also in agreement with the X-ray structure reported on a derivative of **3c** (X = NSiMe₃; R = NR'₂).⁷

(b) The Role of d Orbitals in Bonding in 2 and 3 (X = CH₂, NH, O). So far our discussion does not include d orbitals in the bonding picture. Are they of importance? In order to reveal their contribution to bonding¹² we performed ab initio calculations of "double-ζ quality" on the complete palette of parent **3** (R = H; X = CH₂, NH, O). For comparison the structures of **2** (R = H; X = CH₂, NH, O) were also included in the considerations. To reveal the differential effect of d orbital participation the calculations were carried out with d orbitals at the heavy atoms P, C, N, or O (basis II) or without d orbitals in the basis set (basis I). The computational details are given in the Appendix. The geometrical parameters for the calculations were taken from the experimental structures and are collected in Table II. The resulting energies obtained from the SCF calculations are listed in Table III. With respect to the total energies the d orbital contribution is negligibly small in the P(III) double-bonded systems **2**. It is also minor in the bis(methylene)phosphorane **3** (R = H; X = CH₂). Of all investigated compounds the d orbitals contribute to the total energy most strongly in **3** (R = H; X = NH, O).

This picture is also confirmed by an analysis of the Mulliken gross populations of the d orbitals at the heavy atoms in **2** and **3** (Table IV). The numerical experiments reveal two features:

(12) Coulson, C. A. *Nature (London)* **1969**, *221*, 1106. Kwart, H.; King, K. G. "Reactivity and Structure Concepts in Organic Chemistry"; Springer-Verlag: West Berlin, Heidelberg, West Germany, 1977; Vol. 3. Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

Table II. Bond Lengths (Å) and Bond Angles (deg)

	HPCH ₂ ^a	HPNH ^b	HPO ^c	HP(CH ₂) ₂ ^d	HP(NH) ₂ ^e	HPO ₂ ^f
r(PX)	1.673	1.560	1.480	1.650	1.503	1.435
r(PH)	1.420	1.430	1.456	1.420	1.420	1.420
r(XH)	1.090	1.018		1.090	0.900	
∠(XPX)				130.0	134.0	136.0
∠(HPX)	97.4	101.0	103.5	115.0	113.0	112.0
∠(HXH)	124.4 (118.4) ^g	119.1 ^h		120.0	120.0	

^aKroto, H. W.; Nixon, J. F.; Ohno, K. *J. Mol. Spectrosc.* **1981**, *90*, 367. ^bTrans conformation; ref 9. ^cLarzillière, M.; Damany, N.; Than My, L. *Chem. Phys.* **1980**, *46*, 401. See also: Herzberg G. "Molecular Spectra and Molecular Structure"; van Nostrand: New York, 1966; Vol. 2, Table 63. ^dAppel R.; Westerhaus A., personal communication. ^eReference 7, cis conformation of the hydrogens at the nitrogens. ^fOptimized at basis II level (within C_{2v} symmetry), r(PH) assumed. ^gHydrogen trans to hydrogen at phosphorus. ^h∠PNH.

Table III. Total Energies (au)

structure	basis I	basis II	ΔE	structure	basis I	basis II	ΔE
HPCH ₂	-380.15777	-380.20246	-0.0447	HP(CH ₂) ₂	-419.03638	-419.13458	-0.0982
HPNH ^a	-396.15553	-396.22370	-0.0682	HP(NH) ₂ ^b	-415.05966	-451.21686	-0.1572
HPO	-415.88534	-415.97370	-0.0884	HPO ₂	-490.77492	-490.57740	-0.1975

^aTrans conformation. ^bCis conformation (of the hydrogen atoms at the nitrogens).

Table IV. Mulliken Gross Population of d AO's^a

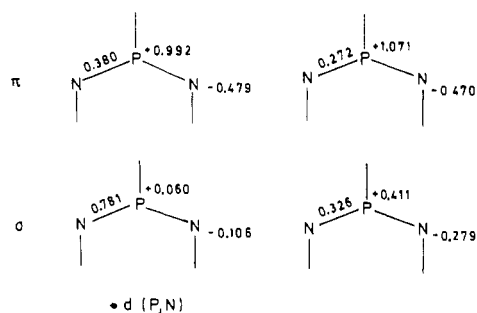
structure	on P	on C, N, O	structure	on P	on C, N, O
HPCH ₂	0.108 (0.025)	0.039	HP(CH ₂) ₂	0.249 (0.114)	0.033
HPNH ^b	0.176 (0.043)	0.023	HP(NH) ₂ ^c	0.456 (0.160)	0.025
HPO	0.226 (0.055)	0.016	HPO ₂	0.559 (0.175)	0.019

^aCorresponding values for the π-space are given in parentheses. ^bTrans conformation. ^cCis conformation of the hydrogens (at the nitrogens).

Table V. Total Effective Charges (q(X)) and Bond Populations (p(P-X)) from the Mulliken Population Analyses

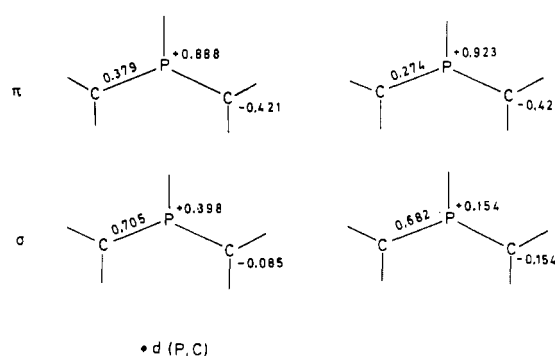
	HPCH ₂	HPNH ^a	HPO	HP(CH ₂) ₂	HP(NH) ₂ ^b	HPO ₂
			Calculated without d			
q(P)	0.526	0.748	0.960	1.077	1.481	1.776
q(C,N,O)	-0.433	-0.710	-0.750	-0.577	-0.743	-0.830
p(P-C,N,O)	0.747	0.556	0.560	0.956	0.597	0.617
			Calculated with d			
q(P)	0.461	0.506	0.749	1.286	1.052	1.347
q(C,N,O)	-0.251	-0.530	-0.589	-0.506	-0.585	-0.641
p(P-C,N,O)	0.905	0.962	0.940	1.084	1.161	1.116

^aTrans conformation. ^bCis conformation (of the hydrogen atoms at the nitrogens).

Chart I

(a) the d orbitals at C, N, and O are not populated, and (b) their participation at phosphorus increases in the order C < N < O. Further insight into the electronic structures of parent **2** and **3** is given by a complete Mulliken population analysis. The results of these investigations are collected in Table V. As already revealed from the energies (Table II) and the d-orbital populations at P (Table III), the differential changes in the populations (charge densities, bond populations), if one includes d orbitals in the quantum chemical calculations, are smallest in the structures **2**. The d-orbital participation in bonding continuously increases from X = CH₂ toward X = O, accompanied by a reduction of positive charge at P.

Some of the trends observed for **2** hold also for the structures **3**: (a) the total d-orbital populations steadily increase with increasing electronegativity of X (CH₂ < NH < O) (see Table IV),

Chart II

and the differential bond populations, i.e. with and without inclusion of d orbitals in the basis set, are most strongly pronounced for **3** (X = NH). Here the d-orbitals considerably strengthen the bond between P and N. However, there are also some essential differences in bonding in **3** with respect to **2**. At the central phosphorus, inclusion of d orbitals attenuates positive charge in **3** (X = CH₂) while it depletes positive charge in **3** (X = NH). Similar is the case **3** (X = O). The less positive character of the P in bis(imino)phosphorane compared with bis(methylene)phosphorane is confirmed by experimental observations.¹³ Further investigations indicate that in **3** the σ-bonds (P-X) are less strongly

(13) Böske, J. Diplomarbeit, Universität Bielefeld, 1983.

Table VI. Dipole Moments (D)

structure	basis I	basis II	structure	basis I	basis II
HPCH ₂	1.215	0.970 ^c	HP(CH ₂) ₂	1.771	1.385
HPNH ^a	1.525	1.422	HP(NH) ₂ ^b	0.233	0.178
HPO	2.746	2.449	HPO ₂	3.199	2.653

^a Trans conformation. ^b Cis conformation of the hydrogens (at the nitrogens). ^c 0.869 D experimentally; see ref *a* in Table II.

Table VII. MO Energies (eV) of Parent 2 and 3, Obtained at the Basis II Level

HPCH ₂ (C _v)	HPNH ^a	HPO (C _v)	HP(CH ₂) ₂ (C _{2v})	HP(NH) ₂ ^b (C _{2v})	HPO ₂ (C _{2v})
-26.49 (1a')	-31.19 (1a')	-35.95 (1a')	-27.46 (1a ₁)	-33.08 (1a ₁)	-38.28 (1a ₁)
-20.17 (2a')	-21.34 (2a')	-21.44 (2a')	-24.58 (1b ₂)	-31.02 (1b ₂)	-36.57 (1b ₂)
-16.52 (3a')	-15.83 (3a')	-16.14 (3a')	-19.98 (2a ₁)	-22.51 (2a ₁)	-21.88 (2a ₁)
-14.03 (4a')	-14.30 (4a')	-14.50 (4a')	-16.50 (3a ₁)	-18.95 (2b ₂)	-17.99 (3a ₁)
-10.41 (5a') σ(P)	-11.38 (1a'') π	-13.22 (1a'') π	-15.43 (2b ₂)	-16.43 (3a ₁)	-16.84 (2b ₂)
-9.56 (1a'') π	-9.86 (5a') σ(P)	-10.79 (5a') σ(P)	-14.25 (3b ₂)	-13.71 (4a ₁)	-16.15 (1b ₁) π ₁
			-14.15 (4a ₁)	-13.68 (1b ₁) π ₁	-14.13 (4a ₁)
			-11.29 (1b ₁) π ₁	-11.28 (3b ₂)	-13.88 (3b ₂)
			-7.15 (1a ₂) π ₂	-10.26 (1a ₂) π ₂	-13.50 (1a ₂) π ₂

^a Trans conformation. ^b Cis conformation (of the hydrogens at the nitrogens).

Table VIII. Parameters for the EH Calculations

		H _{ii} , eV	ζ			H _{ii} , eV	ζ
H	1s	-13.60	1.300	O	2s	-33.21	2.246
C	2s	-19.54	1.608		2p	-16.05	2.227
	2p	-11.20	1.568	P	3s	-18.17	1.881
N	2s	-25.51	1.924		3p	-10.74	1.629
	2p	-14.02	1.917				

polarized compared with their corresponding π-bonds. A detailed Mulliken population analysis for *cis*-3 (X = NH) is given in Chart I. The d-orbitals strongly increase σ-bonding but only to a negligible amount π-bonding. On the contrary in 3 (X = CH₂) the d orbitals tend to polarize the σ-bond toward the carbon atoms, such as to increase the positive charge at phosphorus. (For the partitioning of the populations in contributions of the σ-space and π-space it is assumed that 2 electrons at the phosphorus contribute to π-bonding while 1 electron is donated from each carbon atom.)

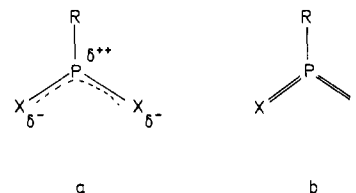
We have also calculated the dipole moments for the given structures. They are collected in Table VI. In general they are predicted as very high for the cases X = O in 2 and 3. Experimentally they are not known. Nevertheless we may compare our results with the findings for (CH₃)₃PO. It reveals a dipole moment of 4.34 D¹⁴ in agreement with corresponding quantum chemical calculations¹⁵ of comparable basis set quality. Our calculations yield for *cis*-3 (X = NH) an unusual small dipole moment. Further analysis of the localized orbitals indicates that this is due to the orientation of the lone pairs at the nitrogens. The large dipole moment of the polar PN bonds is offset by the opposite dipole vector of the nitrogen lone pairs. In order to complete the picture we have also calculated data for the trans isomer of 3 (X = NH). In accordance with the qualitative discussion of section a, it is higher in energy than the cis isomer. It reveals a much larger dipole moment (4.18 D), comparable to that of 3 (X = O).

(c) **Orbital Energies and Ionization Potentials.** Since in the present study we performed systematic calculations on a series of related molecules with basis sets of equal and rather good quality, we regard it as worthwhile to report the orbital energies (Table VII). In view of Koopman's theorem¹⁶ they can be correlated with experimental ionization potentials, and they are useful for other purposes. Only the valence orbital energies are listed in the table. Some comments are appropriate here. The P(III) double-bond system in 2 possesses two closely spaced occupied frontier orbitals. They refer to the π orbital or σ orbital (mostly localized at P). In 2 (X = CH₂) the π orbital is above the σ orbital on the energy scale while it is the opposite for 2 (X

= NH, O).¹⁷ In agreement with experiment,¹⁸ methylene-phosphane undergoes (2 + 2) cycloaddition while iminophosphane reacts via (2 + 1) and/or (4 + 1) cycloaddition pathways. In contrast to this, in 3 the π₂ orbital of the allyl system is the frontier orbital throughout. The π₁ orbital is lowered in energy with increasing electronegativity of the ligand X (CH₂ < NH < O). In 3 (X = NH) the 3b₂ orbital corresponds to the negative combination of lone pairs at the nitrogens. Similar considerations hold for 3 (X = O).

Conclusions

In our study we have presented the first quantum chemical calculations on the tricoordinated phosphorus compounds 3 and compared them with the P(III) double-bond systems 2. The results of our investigations can be summarized as follows: (1) In the structures 2 (X = CH₂, NH, O) the amount of d-orbital participation that contributes to bonding is fairly small. Nevertheless it becomes more significant with increasing electronegativity of the ligands X (CH₂ < NH < O). The polarization of the π-system in these compounds parallels those in the σ-system. (2) In bis-(methylene)phosphorane 3 (X = CH₂) d-orbital participation is also minor. Its structure is best considered as a very polar π-system, i.e. a heteroallylic anion. In comparison to that in 3 (X = NH, O) the d-orbital participation is larger. However, in all investigated cases, d-orbital population at P is smaller than in H₃PO.¹⁵ On this basis the picture that in 3 two "limiting" structures a or b are exclusive, i.e. the bond PX is either allylic



(as in a) or multiple (as in b), cannot be drawn. The presence of back-bonding in 3 does not seem to lead to a change from a

(14) For (CH₃)₃PO: Armstrong, R. S.; Aroney, M. J.; Le Fèvre, R. J. W.; Pierens, R. K.; Saxby, J. D.; Wilkins, C. J. *J. Chem. Soc. A* 1969, 2735.

(15) The calculated dipole moment for H₃PO is 4.7 D: Demuynek, J.; Veillard, A. *J. Chem. Soc. D* 1970, 873. See also: Wallmeier, H.; Kutzelnigg, W. *J. Am. Chem. Soc.* 1979, 101, 2804.

(16) Koopmans, T. *Physica (Amsterdam)* 1934, 1, 104.

(17) Reference 1a. For detailed ab initio calculations on parent imino- and methylenephosphane see: Trinquier, G. *J. Am. Chem. Soc.* 1982, 104, 6969. Gonbeau, D.; Pfister-Guillouzo, G.; Barrans, J. *Can. J. Chem.* 1983, 61, 1371. Bruna, P. J.; Krumbach, V.; Peyerimhoff, S. D. *Ibid.* 1985, 63, 1594.

(18) Niecke, E.; Gudat, D.; Schoeller, W. W.; Rademacher, P. *J. Chem. Soc., Chem. Commun.* 1985, 1050.

to b. (3) The dipole moments of **3** ($X = \text{CH}_2, \text{O}$) are larger than those of **2**. An exception is the case of *cis*-**3** ($X = \text{NH}$), which reveals a small value. This is due to the trans orientation of the lone pairs with respect to the PN σ -bonds. The substituent attached to the phosphorus atom exerts a considerable effect on the $\angle\text{NPN}$ bond angle.

Appendix

Qualitative considerations were drawn from EH calculations.¹⁹ The H_{ij} matrix elements were computed with the Wolfsberg-Helmholtz approximation.²⁰ The parameters are listed in Table VIII. The ab initio calculations were carried out at a SCF level, utilizing the following basis sets: (1) Minimal basis set calculations were carried out with the STO-3G basis developed by Pople et al.²¹ (2) Basis I consists of Gaussian lobe functions.²² It is of

(19) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397, and subsequent publications.

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(21) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

(22) The computer program is described by: Ahlrichs, R. *Theor. Chim. Acta* **1974**, *33*, 157.

double- ζ quality, constructed from the following Huzinaga²³ bases: C, (7/3) in the contraction (4,3 \times 1/2,1); N, (8/4) in the contraction (4,4 \times 1/2,2 \times 1); O, (8/4) in the contraction (4,4 \times 1/2,2 \times 1); P, (10/6) in the contraction (4,6 \times 1/3,3 \times 1); H, (3,1). A set of p functions ($\zeta_p = 0.65$) was added to the hydrogens. (3) Basis II consists of basis I plus one set of d functions at the heavy atoms C, N, O, and P. The various exponents were chosen as follows: C, $\zeta_d = 0.30$; N, $\zeta_d = 0.95$; O, $\zeta_d = 1.25$; P, $\zeta_d = 0.50$. Hence basis I refers to a saturated s, p basis while basis II accounts in addition for d orbital participation. Localization of the orbitals was performed at basis I and basis II level by using the Boys localization criterion.²⁴

Registry No. HPC₂, 61183-53-7; *trans*-HPNH, 58734-30-8; HPO, 13817-06-6; HP(CH₂)₂, 6569-82-0; HP(NH)₂, 99686-53-0; HPO₂, 99686-54-1.

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Notes

Contribution from the Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Oligosilastylene-Supported Bis(arene)metal and -dimetal Complexes from Metal Vapor Synthesis

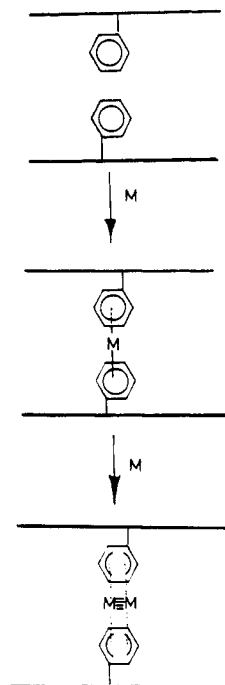
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We have recently shown that organometallic polymers containing up to three different transition metals or transition-metal clusters¹⁻⁵ can be synthesized by vaporizing the atoms Ti, V, Cr, and Mo into liquid oligoalkanes, oligo(ethylene oxides) and siloxane polymers functionalized with arenes. These preparations and characterizations were carried out via metal atomization utilizing a rotary reactor for gram-scale preparation or matrix isolation techniques modified for spectroscopy on thin quiescent liquid films.^{6,7} A key feature of these experiments is that the bis(arene) transition-metal complexes that are initially formed undergo subsequent reactions by direct addition of diffusing metal atoms (Scheme I), yielding metal clusters.^{1-5,6b,8} In reactions with polymers, the macromolecular domain restricts metal atom clustering, under specified conditions of temperature and metal loading, to spatial regions where accretion and flocculation are prevented. Thus, the bis(arene)metal complexes act as functional loci for cluster growth, also stabilizing them against aggregation by providing a more or less rigid local environment due to polymer cross-linking. The result is a selectively doped metal-containing polymer.

Because of the current interest in organic metals and transport processes in electrically conducting dispersely filled polymeric composites, we have initiated studies involving the application of metal atom preparative methods to a class of polymers based on chains of silicon atoms. In this note we report that the transi-

Scheme I



tion-metal atoms Ti, V, Cr, and Mo can be trapped as bis(arene)metal complexes in fluid cyclic oligomers of a phenyl-containing polysilane.⁹ In the one case examined, vanadium dimers

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