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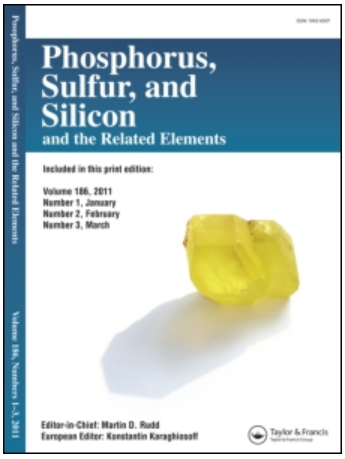

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Interaction of Donors with Electron Deficient Low-Coordinated Phosphorus Compounds

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Mono-and bis-donor-acceptor formation (donor=AH_3, Y = N, P, As, Sb, Bi and AH_2, O, S, Se, Te) is discussed on the basis of quantum chemical (*ab initio*) calculations for π-bonded low-coordinated phosphorus cations, evaluating new types of bis-donor adducts.

Keywords: donor-acceptor formation; quantum chemical calculations

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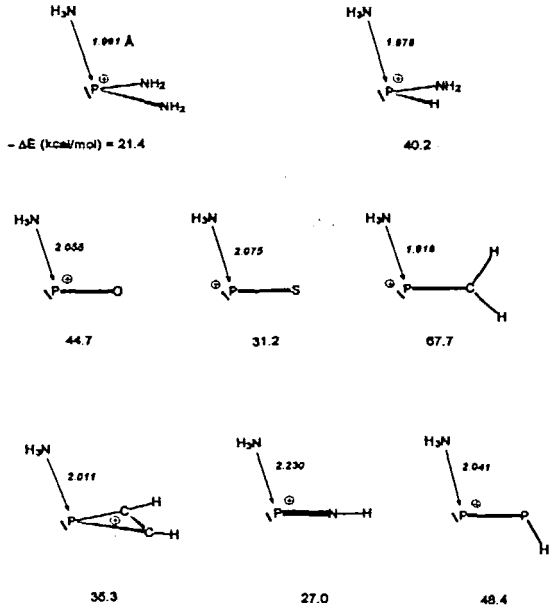
While the formation of donor-acceptor adducts between a Lewis base (amine, etc.) and silyl and germyl cations have been experimentally well explored[1] those of the π-bonded low-coordinated phosphorus cations are much less understood[2]. The donor-acceptor formation can be rationalized within a dual-parameter equation[3].

Here we report quantum chemical studies on mono- and bis-donor addition to low-coordinated π-bonded phosphorus cations.

The **mono-donor** addition of a Lewis base to a Lewis acid was studied for the cases of (a) variation of the donor (amine, phosphine, etc.), keeping the acceptor (phosphenium cation) constant and alternatively (b) for the same donor (amine) with various acceptors (borane, silylene, silyl and phosphenium cations). The electron affinities of the acceptor fragments can be differentiated into two groups: (1) Cations with strong electron affinities ($CH_3^{(+)}$ 9.5, $SiH_3^{(+)}$ 7.8, $PH_2^{(+)}$ 9.5 eV, CCSD(t)/TZP) plus ZPE correction) and (2) neutral acceptors with weak electron affinities (SiH_2 0.7, GeH_2 0.9, BH_3 0.3). Consequently the

Figure 1.



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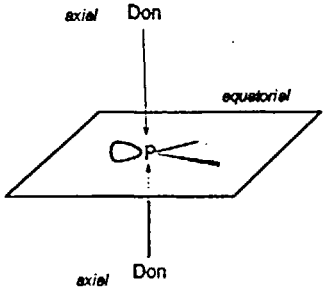
amine adducts to the various acceptor fragments yield strong binding energies for the cations (H_3N-$CH_3^{(+)}$ 103.8, H_3N-$SiH_3^{(+)}$ 75.5, H_3N-$PH_2^{(+)}$ 85.7 kcal/mol) and modest energies for the neutral acceptors (H_3N-SiH_2 24.7, H_3N-GeH_2 20.9, H_3N-BH_3 24.5 kcal/mol, at MP2/ECP-31g(d,p) level + ZPE correction). For the borane adducts the stabilities are in agreement with measured values[4]. The covalencies of the resulting donor-acceptor bonds increase with increasing electron affinity of the acceptor fragment, the adduct energies of the phosphenium cation are in accord with the dual-parameter equation[3]. The mono-amine adducts yield structures with varying stabilities (D + A ---> D-A - ΔE) (Figure 1)[5].

The **bis-donor** addition to the phosphenium cation leads to a trigonal bipyramide, I. Such structures have recently been verified[2]. The stabilities of the axial bonds are weaker than the equatorial bonds and increase in stability with increasing electronegativity of the ligating atoms; e.g., H_3N-$PH_2^{(+)}$ + NH_3 --> H_3N-PH_2-$NH_3^{(+)}$ - 26.0 kcal/mol. Acceptors with two orthogonal π-systems, such as $PNH^{(+)}$, $PS^{(+)}$ and $PO^{(+)}$ add also two donors, but in an essentially different manner, II.



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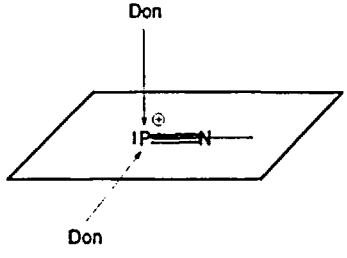

II

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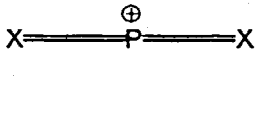
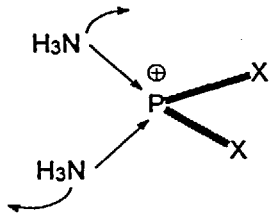
The angle < N (donor)PN (donor) is approximately 90 degrees, for the iminophosphenium cation adduct[6] in accord with our results. The binding energies are for mono-donor addition ($NH_3 + PNH^{(+)}$ ---> H_3N--$PNH^{(+)}$ - 30.6 kcal/mol), for bis-donor addition (H_3N--$PNH^{(+)}$ ---> H_3N--PNH--$NH_3^{(+)}$ - 18.9 kcal/mol). $PO_2^{(+)}$ and $PS_2^{(+)}$, **III** (X = O, S), possess linear (allenic) structures, in contrast to X = CH_2 (C_{2v} symmetry, allylic) and X = NH (C_2 symmetry, helical). For the bis-donor adducts, **IV**, (X = CH_2 and NH) the tetrahedrons are twisted (as indicated by the arrows); absent for **IV**, X = O, S; (exp. **III**, X = S[7], NR (R = tri-^{t}But-phenyl)[6].



III



IV

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