The (4 + 2) Cycloaddition Properties of Heteroatom Double Bond Systems. A Frontier Orbital Approach to Reactivity

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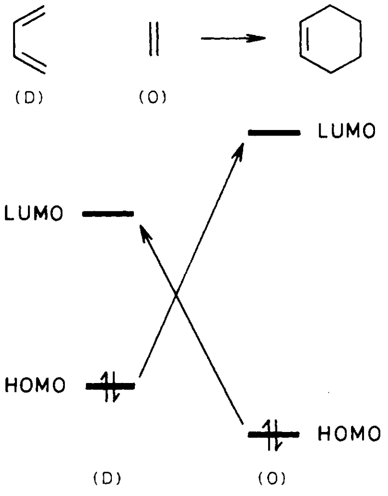
The electron demand in the (4 + 2) cycloaddition reaction of double bond systems containing the heavier elements Si and P (*vs.* C and N) is analysed using frontier orbital theory and *ab initio* SCF calculations.

The syntheses of compounds containing (p–p) π-bonds with elements of the second and following long rows are of current interest.[1] As a common feature these compounds tend to undergo cycloaddition reactions. Hence we have analysed the archetypal (4 + 2) cycloaddition reaction for this new class of 'inorganic double bond systems'.

We report a frontier orbital model which characterizes the electron demand of double bond systems containing Si and P by comparison with the π-systems of their first row analogues, C and N.

Consider the (4 + 2) reaction of *cis*-buta-1,3-diene with ethylene. Within the concept of frontier orbital theory[2] electron density is transferred (a) from the HOMO of the diene (D) into the LUMO of the olefin (O) and *vice versa,* (b) from the HOMO of the olefin into the LUMO of the diene. Using the concept of electron demand[2b] one can differentiate between three types of Diels–Alder reactions: (i) $\Delta E_1 < \Delta E_2$, normal electron demand, (ii) $\Delta E_1 > \Delta E_2$, inverse electron demand, and (iii) $\Delta E_1 \sim \Delta E_2$, the borderline case between (i) and (ii), where $\Delta E_1 = E^{(O)}_{\text{LUMO}} - E^{(D)}_{\text{HOMO}}$, $\Delta E_2 = E^{(D)}_{\text{LUMO}} - E^{(O)}_{\text{HOMO}}$. The smaller the energy gap between the frontier orbitals in a particular case, the faster is the reaction.[2]



Scheme 1

For a variety of representative double bond systems the frontier orbital energies were computed with *ab initio* SCF-MO calculations using the STO-3G basis set.[3] The electron demand of each olefin with respect to *cis*-buta-1,3-diene as the reference diene was determined from the corresponding HOMO–LUMO energy differences (Figure 1).† The dashed line corresponds to equal electron demand, with equal HOMO–LUMO energy differences between both pairs of interacting frontier orbitals [case (iii)]. Thus, olefins placed on this diagonal line are equally electron accepting and electron donating towards butadiene, while the off-diagonal species fall into type (i) or type (ii) classes of Diels–Alder reactions.

Consider some of the examples shown in Figure 1. Diimine and to a greater extent iminophosphane[4] are strongly electron accepting (compared to ethylene) but simultaneously iminophosphane is a stronger electron donor than diimine. Accordingly diimine reveals a normal electron demand [case (i)] in the Diels–Alder reaction.[2b] On the contrary, disilene, representative of Si=Si systems, shows an inverse electron demand; it is strongly electron donating rather than electron accepting towards butadiene. On this basis it should add predominantly to electron poor dienes [case (ii)]. A limiting case (iii) is methylenephosphane. It is equally electron accepting and donating towards butadiene. As in the case of enamines,[5] aminomethylene- and aminoimino-phosphanes are more electron rich than their parent systems. The amino group at C or N is more effective for conjugation than at P. Similar considerations hold for planar tetrazene and diaminodiphosphene.[6]

A more stringent test of the electron demand of the limiting case of methylenephosphane is provided by a Mulliken population analysis (Figure 2), obtained at an *ab initio* double-zeta level.‡ In the π-orbital, the phosphorus is only

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† For the calculations the geometries were taken from experimental data. The orbital energies (in eV) for the reference diene *cis*-buta-1,3-diene are: π_1 −10.7, π_2 −7.1, π_3 6.7, and π_4 11.3.

‡ The basis set consists of Gaussian lobe functions (R. Ahlrichs, *Theor. Chim. Acta,* 1974, **33**, 157) constructed from the following bases, S. Huzinaga, 'Approximate Atomic Functions II,' Technical Report, The University of Alberta, 1971: C (5,2 × 1/3,1/1), ς(d) = 0.30; P (4,6 × 1/3, 3 × 1/1), ς(d) = 0.50; H (3,1/1), ς(p) = 0.65. The structure is chosen according to ref. 7.

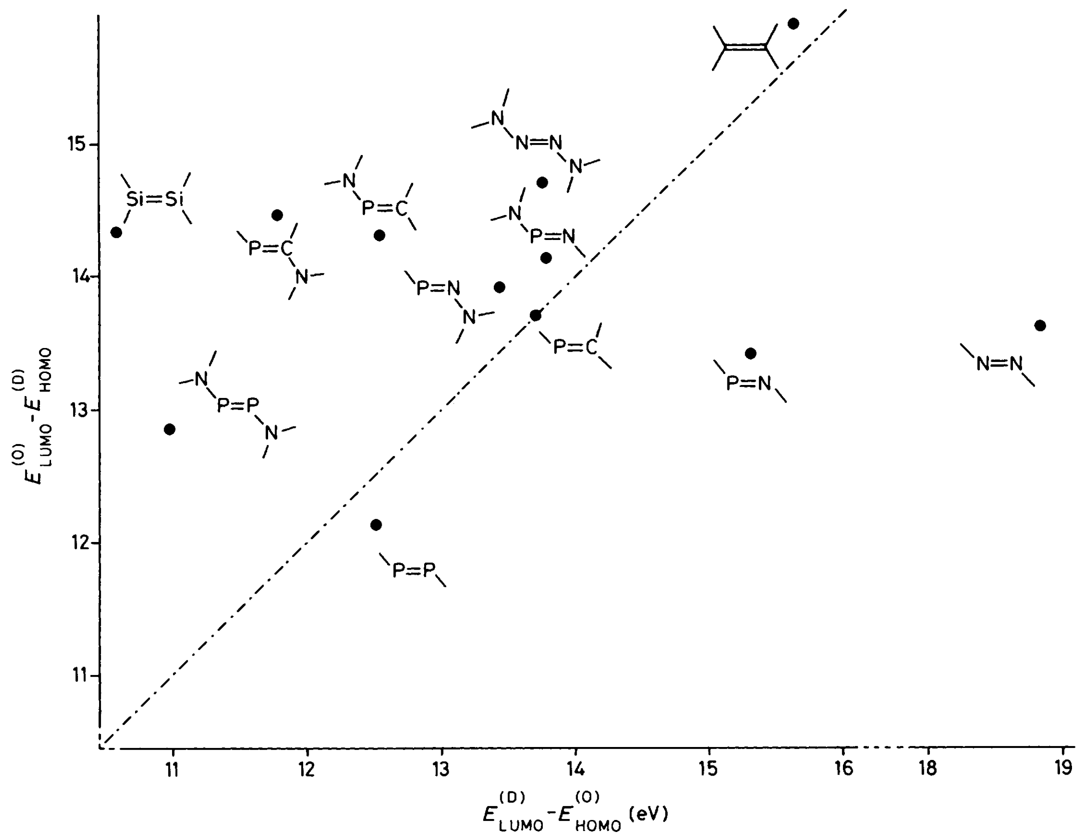

Figure 1. Differences in frontier orbital energies (in eV) for various olefins with respect to *cis*-buta-1,3-diene.

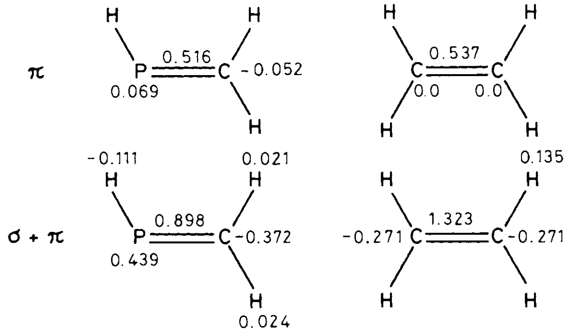

Figure 2. Mulliken population analyses of ethylene and methylenephosphane at an *ab initio* double-zeta level with polarization functions at all atoms; net charges at atoms and populations between bonds.

slightly more electropositive than carbon, while in the overall charge distribution (σ + π) charge density is considerably shifted towards carbon. On this basis the π-bond in methylenephosphane is almost unpolarised and hence phosphaalkenes should resemble olefinic species in their behaviour.

The frontier orbital considerations do not allow the distinction between a one-step or two-step (Woodward–Katz[8]) mechanism for the addition reaction.§ In addition the model does not account for possible steric effects in the addition approach of both reaction partners.

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§ Detailed quantum chemical investigations on the system butadiene–ethylene are not conclusive, rather they favour both alternatives, see ref. 9.

A complete investigation by the MNDO method on the electronic hypersurface of the system methylenephosphane–butadiene reveals that the lone pair at P is not essentially involved in the (4 + 2) addition process.

References

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