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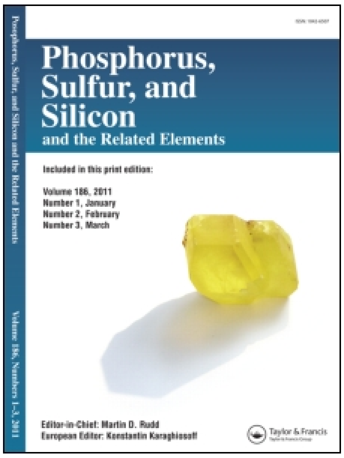

## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Phosphinidenes, Phosphiranes, and their Chalcogenides

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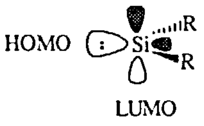
Pyrolysis and photolysis of phosphiranes and their chalcogenides provide routes for the generation of phosphinidenes R-P and their chalcogenides R-P=Z (Z = O,S). Kinetic studies of the pyrolyses allow the elucidation of the mechanisms of the addition reactions of R-P and R-P=Z. Results are in accord with predictions of frontier orbital theory, including alteration of reactivity by manipulation of frontier orbital symmetry.

*Keywords:* phosphinidenes; phosphinidene oxides; phosphinidene sulfides; phosphiranes; phosphirane oxides; phosphirane sulfides

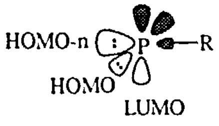
Control is the fruit of mechanistic knowledge. What drew my group to phosphorus chemistry was the opportunity to answer a fundamental question regarding chemical reactivity: does maximization of bonding in the transition state of a reaction, as embodied by frontier orbital theory, correctly predict a reaction pathway, *even in the absence of a significant energy barrier*?[1] If the answer is yes, one should, in some cases, be able to alter reaction pathways by manipulation of frontier orbital energies. It is believed that such control has now been achieved in the case of phosphinidenes R-P and their chalcogenides R-P=Z (Z = O,S).

Phosphinidenes, the third-row member of the "nitrene family" were chosen for study because the symmetry of the HOMO's of their closed-shell singlet states differs from that of singlet silylenes $R_2Si$:, the third-row member of the "carbene family" of six-valence electron reactive intermediates. In 1982 Schoeller and Niecke pointed out that an eight-valence electron P(III) system with p-p $\pi$-bonding to phosphorus would be isolobal with a carbene if its HOMO contained the s-weighted P lone pair, and the $\pi^*$ orbital was the

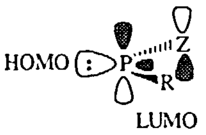
LUMO.[2] Below are seen the frontier orbitals of a silylene, phosphinidene, and a phosphinidene chalcogenide.



silylene



phosphinidene

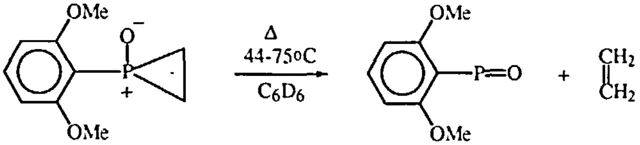


phosphinidene chalcogenide

Maximization of frontier orbital overlap would lead to a least-motion transition state for concerted addition of a closed-shell singlet phosphinidene but to a non-least motion pathway for a singlet silylene.[1,3] It has been suggested, however, that entropic factors may control pathways for highly reactive species,[4] in which case the predictions of frontier orbital theory might fail. Certainly steric effects would favor least-motion transition states for many concerted carbene-like additions. Qualitative data on the retro-addition reactions of phosphinidenes[1,3] and silylenes[5] do, however, conform to the predictions of frontier orbital theory: least-motion addition for R-P and non-least-motion addition for $R_2Si$:.

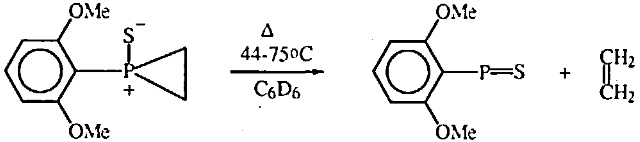
Phosphirane chalcogenides are attractive precursors of phosphinidene chalcogenides R-P=Z (Z = O, S, Se), and Quast has generated tBu-P=O in this manner.[6] 2,6-Dimethoxyphenylphosphirane has been converted to its oxide and sulfide. Characterization included x-ray crystal structures of all three molecules.[7] Both photolysis and thermolysis of the phosphirane oxide and sulfide led to the loss of ethylene and the presumed formation of the corresponding phosphinidene chalcogenide. The pyrolyses are clean first-order reactions whose rates are not accelerated by the presence of trapping agents for the R-P=Z species. From the temperature dependence of the first-order rate constants, activation parameters have been obtained and are displayed below.

The similarity between the activation parameters for the extrusion of 2,6-dimethoxyphenylphosphinidene oxide shown below and the values found by Popoff and Berry for the extrusion of dimethylsilylene from hexamethylsilirane.[8] $\Delta H^{\ddagger} = 31.6 \pm 2.7$ kcal/mol, $\Delta S^{\ddagger} = 11.2$ cal/mol deg is striking. Granted that the structural differences make the comparison tenuous, but it appears that the phosphirane oxide and the silirane undergo retroaddition by similar transition states!



$\Delta H^{\ddagger}$ = 30.3 kcal/mol

$\Delta S^{\ddagger}$ = 9.8 cal/mol deg



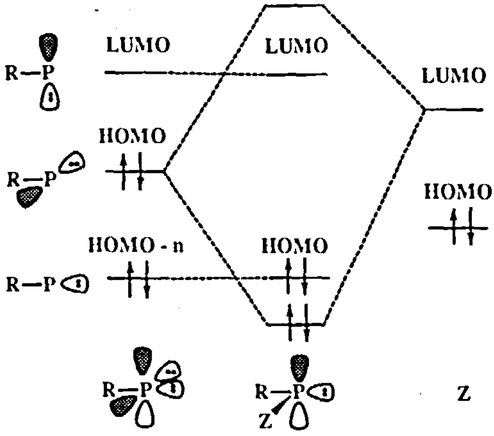
$\Delta H^{\ddagger}$ = 24.3 kcal/mol

$\Delta S^{\ddagger}$ = - 1.3 cal/mol deg

An *ab initio* calculation (HF/6-31G$^*$) on the mechanism of extrusion of methylphosphinidene oxide Me-P=O from 1-methylphosphirane oxide predicts a non-least-motion transition state, lending strong support to a non-least motion pathway for extrusion of phosphinidene chalcogenides from phosphirane chalcogenides.

In the case of 2,6-dimethoxyphenylphosphinidene oxide and sulfide, their carbene-like reactivity has been observed in trapping reactions with MeOH, EtSSEt, PhCOCOPh, and, in the case of the sulfide, 2,3-dimethylbutadiene.

It thus appears that a phosphinidene whose frontier orbital symmetry differs from that of singlet carbenes and silylenes, this difference translating into differences in reaction pathways, can be converted into a species that is isolobal with the singlet "carbene family", and resembles the "carbene family" in the transition states of its addition reactions. The altering of the energy levels of a phosphinidene by donating an electron pair to an acceptor atom or group Z is shown in the orbital interaction diagram below. This not only explains the reactivity of phosphinidene chalcogenides but of other phosphinidene derivatives such as the transition-metal complexes studied by Mathey.[9] Tuning the reactivity of the phosphinidene chalcogenides may make them as synthetically useful as their cousins, the transition metal complexes.



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