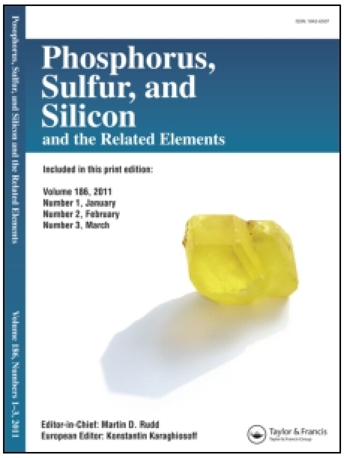


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# General Approaches to Phosphinidenes Via Retroadditions

Xinhua Li[a]; Deqing Lei[a]; Michael Y. Chiang[a]; Peter P. Gaspar[a]
[a] Department of Chemistry, Washington University, Saint Louis, MO, USA

**To cite this Article** Li, Xinhua , Lei, Deqing , Chiang, Michael Y. and Gaspar, Peter P.(1993) 'General Approaches to Phosphinidenes Via Retroadditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 76: 1, 71 — 74
**To link to this Article: DOI:** 10.1080/10426509308032361
**URL:** http://dx.doi.org/10.1080/10426509308032361

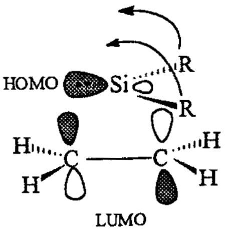
*Phosphorus, Sulfur, and Silicon,* 1993, Vol. 76, pp. 71–74
Reprints available directly from the publisher
Photocopying permitted by license only

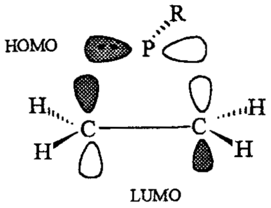
# GENERAL APPROACHES TO PHOSPHINIDENES VIA RETROADDITIONS

XINHUA LI, DEQING LEI, MICHAEL Y. CHIANG and
PETER P. GASPAR*
Department of Chemistry, Washington University,
Saint Louis, MO 63130, USA

Abstract Retroadditions - thermal and photochemical decomposition of phosphiranes and 3-phospholenes - offer general routes to free phosphinidenes.

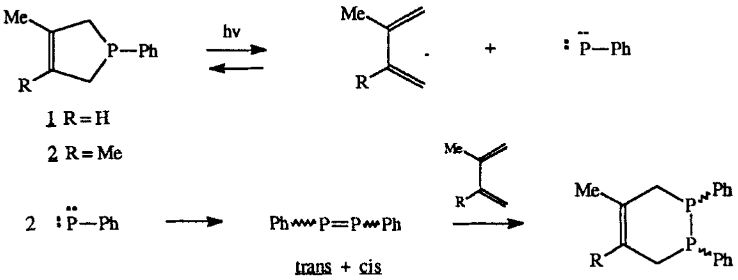
Our interest in the reactions of free phosphinidenes R-P stems from the recognition that differences in frontier orbital symmetry between singlet carbenes and silylenes, on the one hand, and singlet nitrenes and phsophinidenes on the other, might lead to differences in reaction pathways. As an example, the transition state for addition of a silylene to ethylene that maximizes frontier orbital overlap is clearly that for a "non-least-motion" pathway. The substituents on the silicon atom are not in the positions that they will occupy in the silirane product. For the analogous addition of a singlet phosphinidene, the "pi" HOMO allows "least-motion" addition. Is transition state stabilization by frontier orbital overlap important for species whose reactions have very low energy barriers?



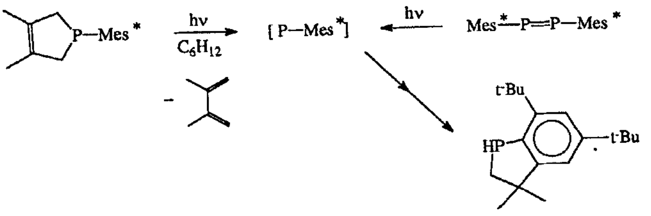


One first had to learn how to generate free phosphinidenes, an enterprise which has not met with much previous success.[1] Our experience in generating silylenes[2,3] and germylenes[4] by retroadditions led us to attempt the generation of free phosphinidenes by the thermal and photochemical decomposition of phosphiranes and 3-phospholenes.

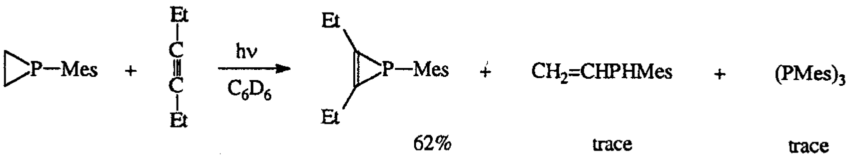
Several 1-aryl-3-phospholenes were synthesized by the route of Myers and Quin.[5] Photolysis at 254 nm of 1-phenyl-3-phospholenes produced the corresponding 1,3-diene, and 1,2-diphosphacyclohex-4-enes. In the presence of an added diene, a new 1-phenyl-3-phospholene is produced. The conversion of the initial phospholene does not depend on the concentration of added diene, although the product ratio does. The presence of another, photoinert, phospholene does not lead to the formation of a new disphosphacyclohexene. These observations are consistent with the photoextrusion of a free phosphinidene that undergoes dimerization in competition with addition to a diene reforming a phospholene. The phosphinidene dimer, a diphosphene, undergoes cycloaddition forming a diphosphacyclohexene:

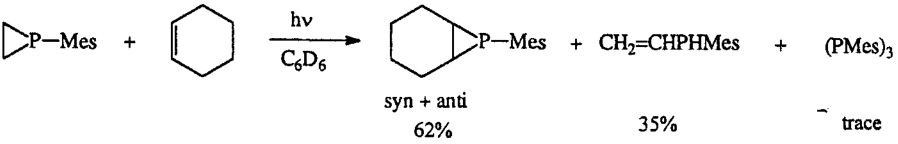


Further evidence for the photoextrusion of a free phosphinidene from a phospholene is the formation of the same phosphaindane that arises from photolysis of the Yoshifuji diphosphene, the latter process believed to involve a free phosphinidene.[6]

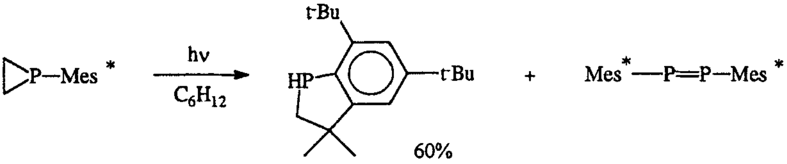


We have also studied the decomposition of phosphiranes prepared by the method of Oshikawa and Yamashita.[7] Thermal and photochemical dissociation of mesitylphosphirane produced free phosphinidene, as judged from the addition products obtained in the presence of olefins, dienes and acetylenes. The reactions shown below represent powerful new synthetic routes to phosphiranes and phosphirenes.





Irradiation of supermesitylphosphirane gives the phosphaindane attributed to intramolecular C-H attack by supermesitylphosphinidene, and a low yield of the phosphinidene dimer.



Since no direct spectroscopic detection of a free phosphinidene from decomposition of a phosphirane or a 3-phospolene has yet been successful, the mechanisms of these reactions remain to be established through careful kinetic, spectroscopic and stereochemical studies. The available information suggests, however, that these decompositions are first order, in accord with the formation of the free phosphinidene intermediates suggested by the observed reaction products. There is no doubt that the decomposition of phosphiranes and 3-phospholenes is an extremely versatile and useful reaction, giving the synthetic equivalent of a wide range of free phosphinidenes.

One may also be optimistic about nearing the answer to the original mechanistic question: do singlet phosphinidenes undergo addition reactions by a pathway different from that for singlet silylenes and related species. Stereospecific addition to cis- and trans-2-butene has been observed in the photolysis of mesitylphosphirane, implying concerted addition by what is believed to be mesitylphosphinidene. It has also been observed that the retro-addition, thermal decomposition of 1-mesitylphosphirane is accelerated by C-methyl substituents, while the retro-addition of diadamantylsilylene (thermolysis of 1,1-diadamantylsiliranes) is impeded by an increase in size of ring C-alkyl substituents. The implication is that the addition of singlet mesitylphosphinidene is a least-motion process, while addition of $Ad_2Si$: occurs by a non-least-motion pathway. That conclusion requires a number of assumptions whose validity remains to be tested experimentally.

Acknowledgment: This work receivedc financial support from the National Science Foundation under Grant No. CHE-9108130

## REFERENCES

1. For a review up to 1989, see F. Mathey in Multiple Bonds and Low Coordination in Phosphorus Chemistry, (Thieme, Stuttgart, 1990). Recently Cowley has generated arylphosphinidenes from diazidophosphines and a phosphaketene: A.H. Cowley, F. Gabbai, R. Schluter, and D. Atwood, J.Am.Chem.Soc., 114, 3142 (1992).

2. D. Lei and P.P. Gaspar, Organometallics, 4, 1471 (1985).

3. D.H. Pae, M. Xiao, M.Y. Chiang, and P.P. Gaspar, J.Am.Chem.Soc., 113, 1281 (1991).

4. D. Lei and P.P. Gaspar, Polyhedron, 10, 1221 (1991).

5. D.K. Myers and L.D. Quin, J.Org.Chem., 36, 1285 (1971).

6. M. Yoshifuji, T. Sato, and N. Inamoto, Chem.Lett., 1735 (1988).

7. T. Oshikawa and M. Yamashita, Synthesis, 290 (1985).