Peter P. Gaspar

Research Interests

The overall goal of the Gaspar research group is to extend the mechanistic ideas of organic chemistry to the prediction and understanding of covalent bond-making and bond-breaking throughout the periodic table. We are mechanistic organic/main group chemists, and much of our work is near the borderline between organic and inorganic chemistry.

We study heavier analogs of reactive intermediates in organic reactions such as carbenes R₂C:. The reactivity of these intermediates is so distinctive that product studies can reveal similarities and differences between molecules based on heavier elements and those based on first-row elements.

The activities of our laboratory span much of experimental chemistry. Our group synthesizes precursors for reactive intermediates and authentic samples of products. We convert precursors into characterizeable species that are studied by solution photolysis, by gas-phase flow pyrolysis, and through the use of trapping reactions. Solution- and gas-phase flash photolysis experiments are used to detect reactive intermediates in-situ and also to study the kinetics of their reactions. Reactive intermediates carrying positive or negative charges are studied by quadrupole ion trap mass spectrometry (QITMS).

Computational modeling of reaction systems by electronic structure calculations and by kinetic simulations plays an important role in our work and has helped us to magnify the effectiveness of our mechanistic studies.

The following problems illustrate our current research interests:

1. The reaction chemistry of ground-state silylenes, germylenes, and stannylenes

A facet of the chemistry of carbenes R₂C: that has fascinated chemists for a half-century is the occurrence of two lowest energy electronic states of different spin multiplicity but nearly the same energy, singlet S and triplet T. Singlet carbenes are potent electrophiles and can form two new bonds in concert. Triplet carbenes have entirely different chemistries and behave as diradicals.

While many carbenes have triplet ground states, both S and T states of many carbenes have been found. An unexpected difference between heavier-element analogs of carbenes, silylenes R₂Si:, germylenes R₂Ge:, and stannylenes R₂Sn:, is that, until recently, only their singlet ground states were found.

In 2001 we presented the first experimental evidence for a triplet silylene, and in 2003 a triplet ground-state silylene was observed by ESR spectroscopy in Japan. Unfortunately, these first triplet silylenes were too sterically hindered for observation of intermolecular reactions, so new types of triplet silylenes were needed. One is shown below with an alkali-metal substituent.¹.
No one has previously thought about triplet germynes, but our calculations predict that \( \text{tBu}_3\text{Si-Ge-Li} \) has a triplet ground state lying a healthy 6.7 kcal/mol below the lowest singlet state, and we have designed a synthesis for a promising precursor.\(^2\)

We believe that the chemistry of ground-state triplet heavy-element analogs of carbenes (\( \text{R}_2\text{Si} : , \text{R}_2\text{Ge} : , \text{R}_2\text{Sn} : \)) will be most effectively explored employing novel, new unsaturated molecules \( \text{X}_2\text{M} = \text{M} : \) (\( \text{M} = \text{Si, Ge, Sn} ; \ \text{X} = \text{N, halogen} \)), the silylene having been suggested by Iranian theoretical chemists.\(^3\) We have carried out calculations on unsaturated stannylenes \( \text{X}_2\text{Sn} = \text{Sn} : \) that support the prediction of a triplet ground state.\(^4\)

2. **Can heavy-atom heteroaromaticity surmount adverse steric factors – is phosphatropylium ion planar?**

We have prepared the phosphirenylium ion and demonstrated its aromaticity through gas-phase mass-spectrometric reaction studies in our desktop QITMS apparatus.\(^5\)

Despite the mismatch in size between \( \text{C}_2\text{p} \) and \( \text{P} 3\text{p} \) atomic orbitals, the \( \text{C}_2\text{H}_2\text{P}^+ \) ion, like the \( \text{C}_3\text{H}_3^+ \) ion, is aromatic, with \( \text{E}_{\text{resonance}} \) ca. 38 kcal/mol, compared with 59 kcal/mol for \( \text{C}_3\text{H}_3^+ \). \( \text{Pi} \)-electron delocalization in \( \text{C}_2\text{H}_2\text{P}^+ \) reduces its carbene-like reactivity.

The phosphirenylium ion has no choice but to be planar, thus maximizing the \( \text{pi} \)-overlap needed for aromaticity, but larger rings can be nonplanar. Thus the planarity of the tropylium ion (see below) reflects the dominance of its aromaticity overcoming the steric preference for a tub-shape of the closely-related tropilidene molecule.

If the phosphatropylium ion is planar, with reduced carbene-like reactivity, then it will be a case of heavy-atom heteroaromaticity overcoming a steric preference for a tub shape.
Planarity and heteroaromaticity are predicted for the phosphatropylium ion, and we are working on the synthesis of both substituted and unsubstituted versions of this interesting species

3. Planar vs pyramidal olefins and their heavier analogs

To test a high temperature pyrolysis system connected to a mass spectrometer we ran a reaction reported to generate disilene:6,7

\[
\begin{align*}
&\text{1} & + & \text{SiMe}_2 \quad \text{SiMe}_2 \\
&\text{1} \text{ claimed by Marchand, Mazerolles et al} & \text{as the dominant process 500-600°C with} & \\
&\text{2 and 3 found above 600°C} & \\
&\text{2} \quad \text{SiMe}_2 \quad \text{SiMe}_2 & \rightarrow & \text{Me}_2\text{Si} \quad \text{SiH}_2 & \quad \text{MeHSi} \quad \text{SiHMe} \\
&\text{5 discovered by Conlin}^8 & \\
&\text{Processes 2, 3, 4 and 5 found by Zhou at all} & \text{temperatures (>650°C sufficient for reaction}^7
\end{align*}
\]

Our experiments suggested the stepwise mechanism shown below, with a diradical intermediate, noteworthy because such a mechanism suggested by Dewar for conventional Diels-Alder (DA) reactions\(^9\) was controversial for 20 years and was finally ruled out for the simplest DA reaction.\(^{10}\) Our mechanism explains the formation of the previously unrecognized rearrangement product H from the starting 1,2-disilacycloclohex-4-ene D. The predicted reversibility of stepwise disilene extrusion has been confirmed by observation of both D and H when Me\(_2\)Si=SiMe\(_2\) was independently generated in the presence of butadiene.\(^7\)

We postulated that the dramatic difference between the forward and reverse [2+4] cycloaddition reactions of normal olefins and disila-olefins was due to differences in their \textit{shapes}! In contrast to H\(_2\)=C=CH\(_2\), Me\(_2\)Si=SiMe\(_2\) is pyramidal, and thus its frontier molecular orbitals lack left-right symmetry,\(^{11}\) discouraging concerted cycloadditions:
Our idea is that a planar dimetallaolefin might undergo concerted cycloadditions and retro-cycloadditions. 9,10-digerma and disila naphthalenes are predicted to be planar, and the M=M double bonds are delocalized to a negligible extent, as indicated by the HOMO of the Ge compound, shown above. The predicted bond lengths shown below also indicate alternating single and double bonds, including electronically isolated M=M double bonds.

We plan to synthesize 9,10-disila- and digerma-naphthalene by the method of Ashe. Strong motivation for this synthesis was provided last summer by the computational prediction that 9,10-disilanaphthalene will undergo concerted [2+4] cycloaddition and retro-cycloaddition processes, which, when experimentally realized, will validate our hypothesis.
References

Acknowledgments
Undergraduates
Daniel Ni, BS 2016, (2+4) cycloadditions of disila-olefins
Michael Boucher, BA 2014,, carbene retroadditions
Jessica Kruger, BA 2013, strained cyclopropane pyrolysis
Jenny Yeon, BA 2012, new triplet germylenes

Graduate students
Sophia Koziatek, PhD 2014, phenylsilyne cation Ph-Si:+, F-B:
Diana Ivanova, PhD 2006, QITMS, phosphonium ions R2P:+
Xinping Liu, PhD 2005, QITMS, phosphirenylium ion, phenylnitrenium ion
Dong Zhou, PhD 2004, 1,2-disilacyclohex4-ene pyrolysis, synthesis of 1-stannacyclopent-3-enes and kinetics of their pyrolysis to stannylenes
Ping Jiang, PhD 2002, tBu3Si-Si-Si(iPr)3

Postdoctoral research associates
James Harang, 2012-2014, phosphatropylium ion, stannylebne photogeneration
Mrinmoy Nag, 2005-9, Me2Si=SiMe2, computational chem.

High school student research participants
Suhas Bobba, 2013 STARS program, Marquette High School, phosphatropylium ion
Mandy Zhang, 2012, 2013 STARS program, Mary Institute, Country Day School (MICDS), carbene retroadditions
Liu, Ryan, 2010 STARS program, Ladue Horton Watkins High School, synthesis Of PhSiF2BF2.
Atlee Solomon, 2009, 2010, Ladue Horton Watkins High School, triplet germyleenes (tBu3Si)2Ge:, tBu3Si-Ge-Li
United States National Science Foundation for financial support under grants CHE-0316124 and CHE-1213696.

National Center for Supercomputing Applications (Urbana) for computer time under project CHE070050N.

Selected Publications


Mrinmoy Nag, Peter P. Gaspar, “A Computational Study of the Mechanism of Addition of Singlet Carbene Analogues to 1,3-Butadiene to Form 1,1Dimethylmetallacyclopent-3-enes [MMe₂C₄H₆, M = Si, Ge, Sn] and Their Reverse Retro-addition Reactions,” Organometallics, 2009, 28, 5612-5622.


**Appointments**

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<tr>
<td>1973 – present</td>
<td>Professor of Chemistry, Washington University, St. Louis, MO</td>
</tr>
<tr>
<td>2004</td>
<td>Visiting Foreign Research Fellow, Tsukuba University, Tsukuba, Japan</td>
</tr>
<tr>
<td>1969 – 1990</td>
<td>Research Collaborator, Department of Chemistry, Brookhaven National Laboratory, Upton, NY.</td>
</tr>
<tr>
<td>1990-1991</td>
<td>member, editorial advisory board, ACS journal <em>Organometallics</em></td>
</tr>
<tr>
<td>1988</td>
<td>Visiting Professor, Universite des Sciences et Techniques du Languedoc, Montpellier, France</td>
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<tr>
<td>1988</td>
<td>Traveling Lectureship, French Ministry of Education</td>
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<tr>
<td>1987</td>
<td>Visiting Professor of Chemistry, Princeton University, Princeton, NJ</td>
</tr>
<tr>
<td>1973</td>
<td>Fulbright Lecturer and Visiting Professor of Organic Chemistry, Instituto Superior Tecnico, Lisbon, Portugal</td>
</tr>
<tr>
<td>1973</td>
<td>NATO Traveling Lectureship, Germany, Holland, Switzerland</td>
</tr>
<tr>
<td>1969-1970</td>
<td>Visiting Associate Professor of Chemistry, Princeton University, Princeton, NJ</td>
</tr>
<tr>
<td>1968-1973</td>
<td>Associate Professor of Chemistry, Washington University, St. Louis, MO</td>
</tr>
<tr>
<td>1963 -968</td>
<td>Assistant Professor of Chemistry, Washington University, St. Louis, MO</td>
</tr>
<tr>
<td>1962-1963</td>
<td>Postdoctoral Fellow, Department of Chemistry, California Institute of Technology, Pasadena, CA</td>
</tr>
<tr>
<td>1961-1962</td>
<td>NATO Postdoctoral Fellow, Institut fuer organische Chemie, Heidelberg University, Heidelberg, Germany</td>
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## Honors

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<td>commendation for graduate student mentoring, Graduate Student Senate, Washington University, St. Louis, MO.</td>
</tr>
<tr>
<td>2003-2004</td>
<td>commendation for graduate student mentoring, Graduate Student Senate Washington University, St. Louis, MO.</td>
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<td>1986</td>
<td>Frederick Stanley Kipping Award for organosilicon chemistry, American Chemical Society.</td>
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