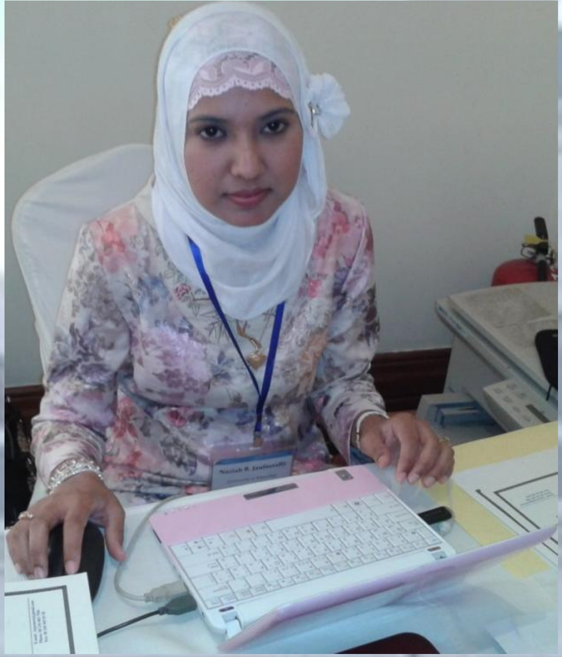
Theoretical Insights Into Novel Telluro-ketones

Myself

Miss Jaufeerally Bibi Naziah



PhD student, Computational Chemistry, University of Mauritius

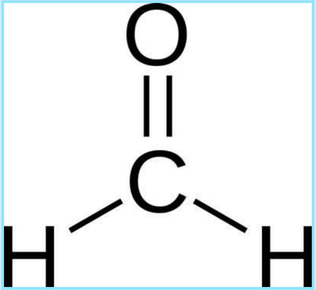
University of Mauritius

Faculty of Science | Department of Chemistry

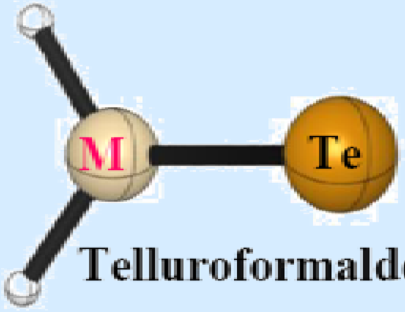
$<\Psi|H|\Psi^*> = E<\Psi|\Psi^*>$

Computational Chemistry

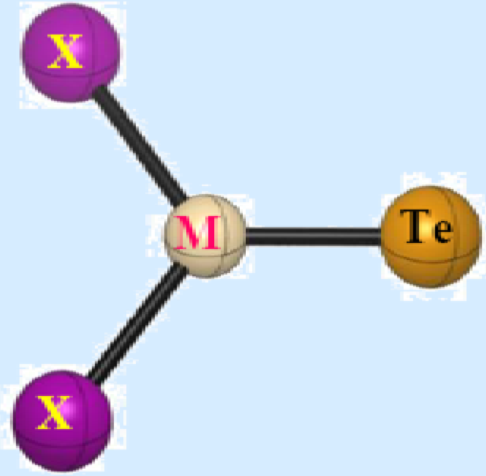
Target Molecules



Formaldehyde

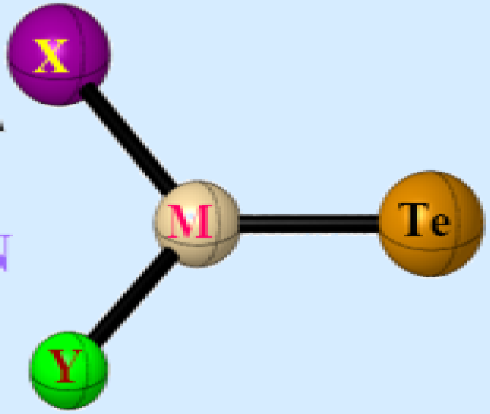


Telluroformaldehyde/
Silanetellurone
Germatellurone

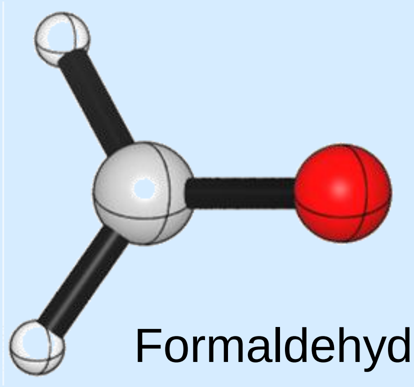


M= C, Si and **Ge**

X; **Y**= **H, F, Cl, Br, I** and **CN**



Why the study of Heavy Congeners of $H_2C=O$?

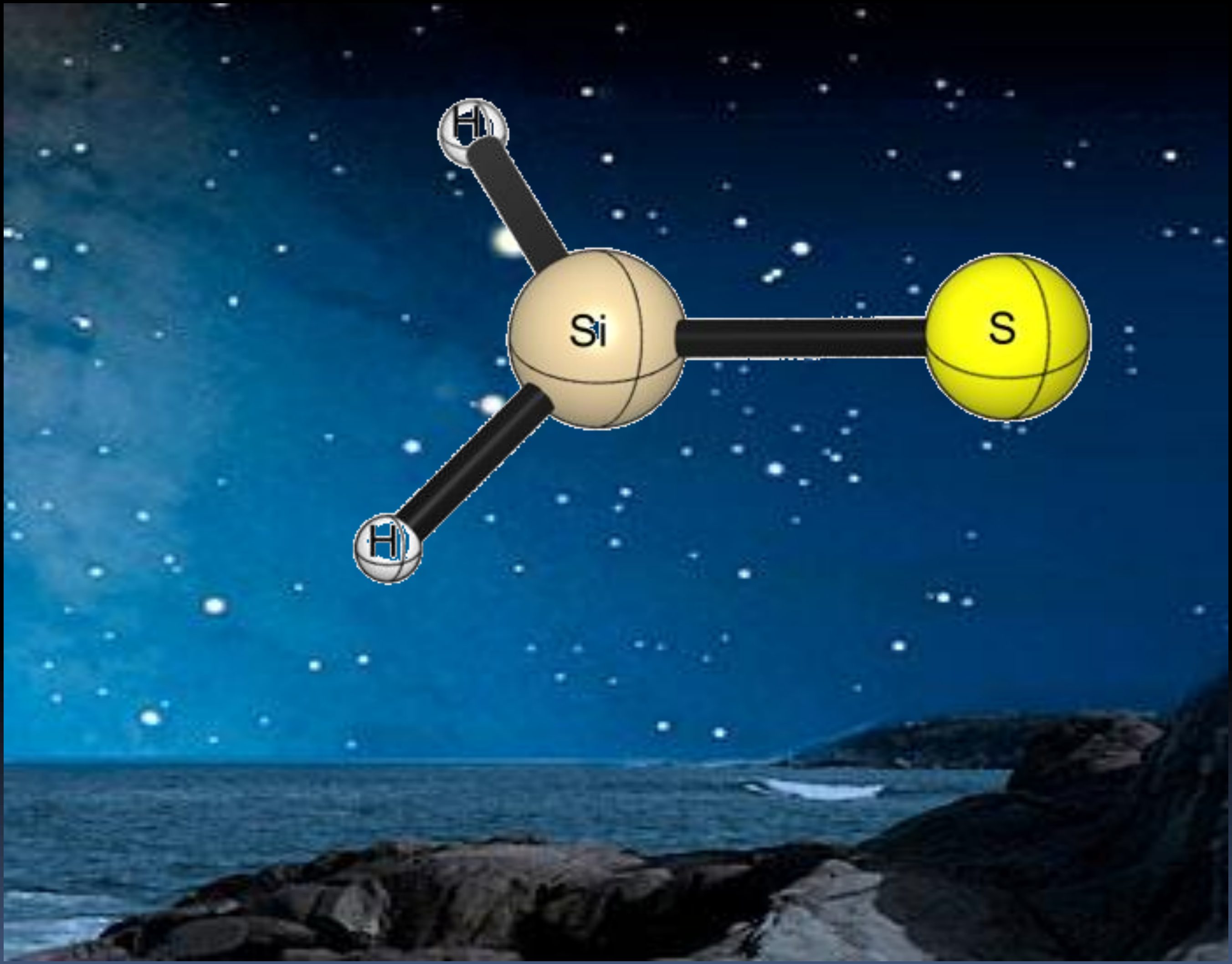


Formaldehyde

C=O group- important organic moiety in industry and biology.

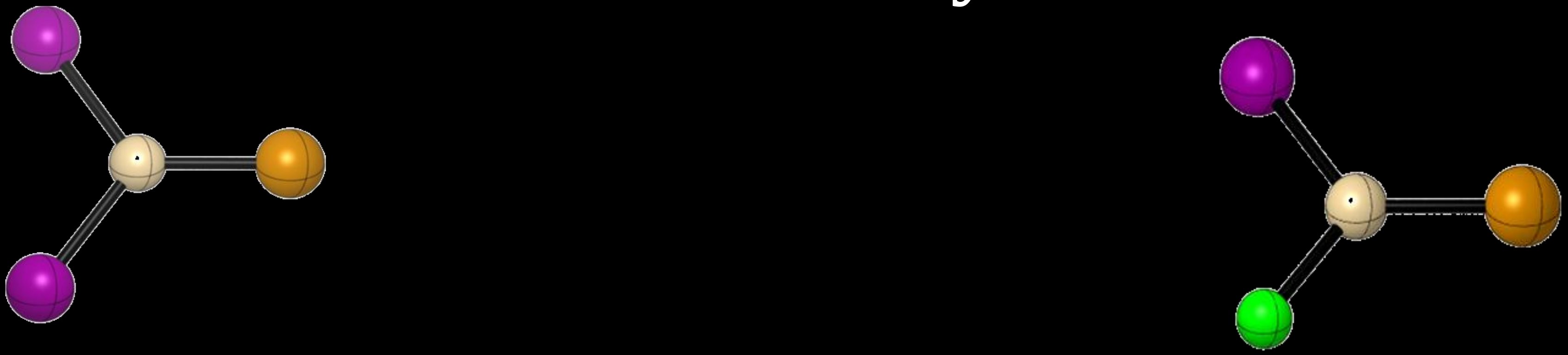
Thio- and Seleno- analogs are important intermediates in S and Se containing compounds.

Monomeric $H_2Si=S$ has reached the STARS!



http://www.scientificamerican.com/media/inline/52A1F834-FD5E-0493-FBBDE8D6A42F2DDE_1.jpg&imgrefurl=http://www.scientificamerican.com/article.cfm%3Fid%3Dthe-night-sky-will-fade-to-black&usg=__RPuI7YGKRkWEw8uIansvoBD89kM=&h=320&w=320&sz=20&hl=en&start=5&zoom=1&tbnid=V8MgZx4YbIUEOM:&tbnh=118&tbnw=118&ei=3KfqT-zkOcborQfVpNC5BQ&prev=/search%3Fq%3Dnight%2Bsky%26hl%3Den%26site%3Dimghp%26tbm%3Disch&itbs=1

ChemMYSTERY behind unavailabilty of monomeric heavy ketones

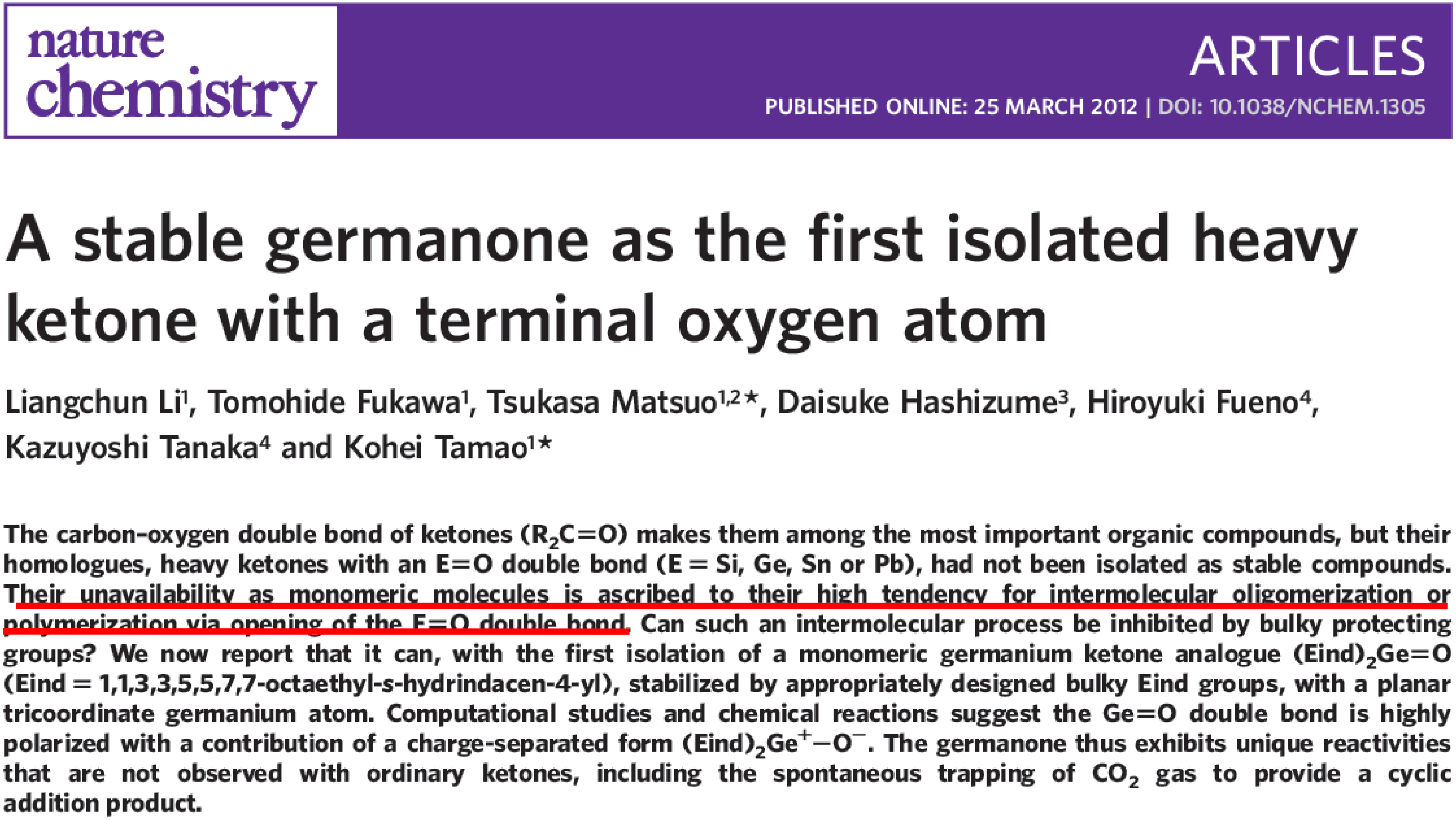


Isolating **$R_2E=X$** (X=C, Si and Ge, E=S, Se and Te) as stable monomeric molecules – real challenge!

$E=X$ very reactive

Actual **quests** for heavy ketones

Stable Monomeric Germanone



nature chemistry

ARTICLES

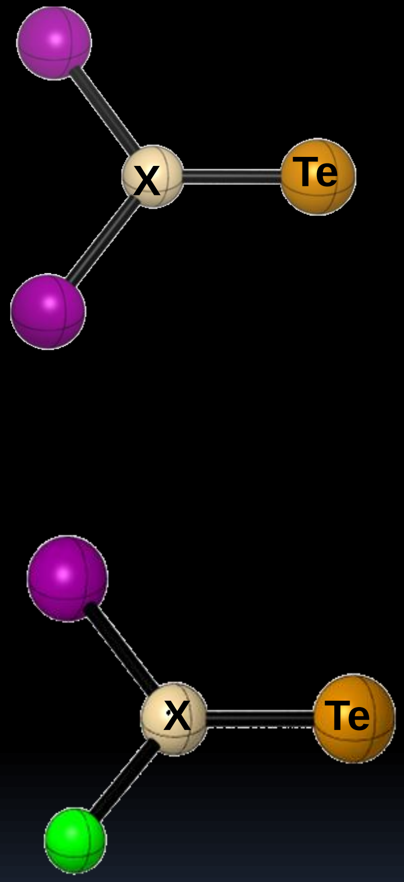
PUBLISHED ONLINE: 25 MARCH 2012 | DOI: 10.1038/NCHEM.1305

A stable germanone as the first isolated heavy ketone with a terminal oxygen atom

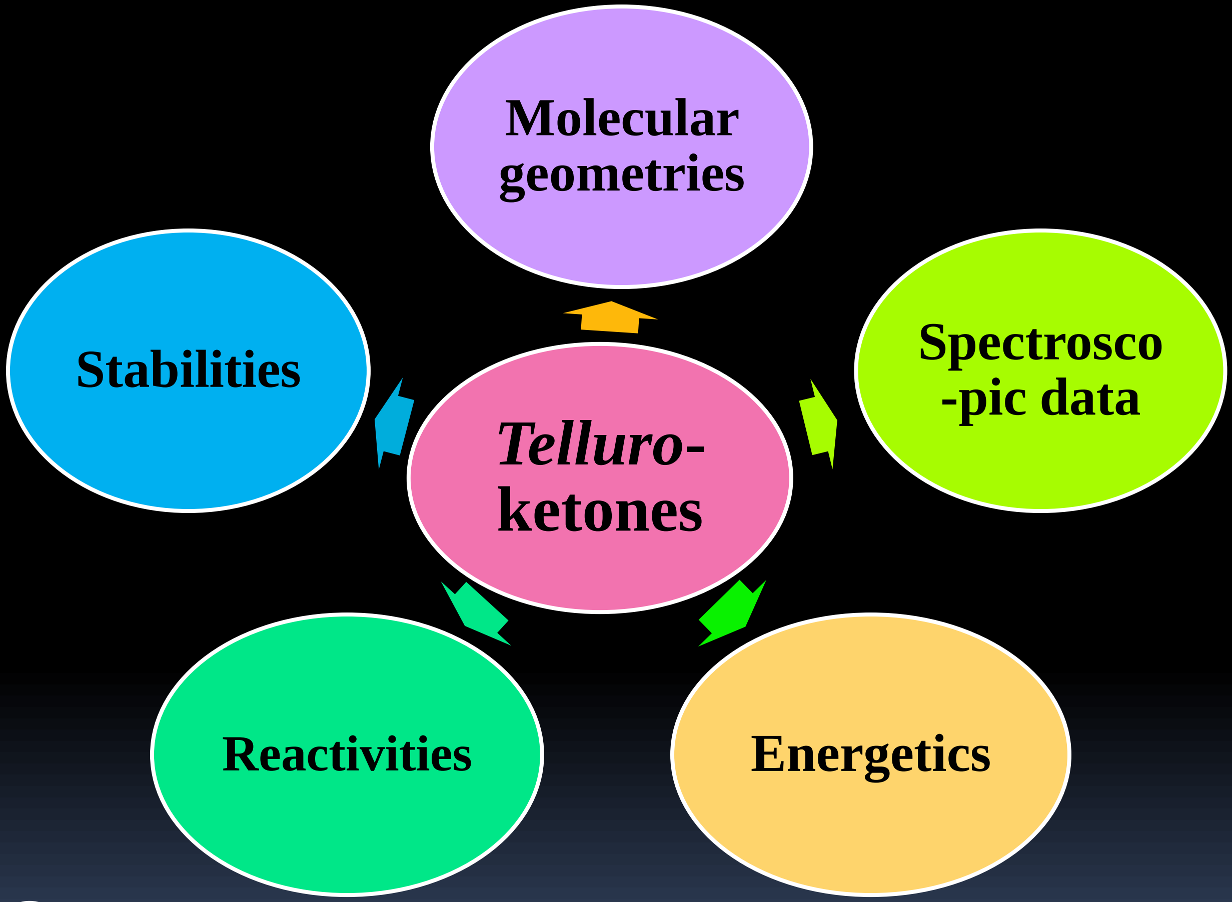
Liangchun Li[1], Tomohide Fukawa[1], Tsukasa Matsuo[1,2]*, Daisuke Hashizume[3], Hiroyuki Fueno[4],
Kazuyoshi Tanaka[4] and Kohei Tamao[1]*

The carbon–oxygen double bond of ketones ($R_2C{=}O$) makes them among the most important organic compounds, but their homologues, heavy ketones with an E=O double bond (E = Si, Ge, Sn or Pb), had not been isolated as stable compounds. Their unavailability as monomeric molecules is ascribed to their high tendency for intermolecular oligomerization or polymerization via opening of the E=O double bond. Can such an intermolecular process be inhibited by bulky protecting groups? We now report that it can, with the first isolation of a monomeric germanium ketone analogue $(\mathrm{Eind})_2Ge{=}O$ (Eind = 1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl), stabilized by appropriately designed bulky Eind groups, with a planar tricoordinate germanium atom. Computational studies and chemical reactions suggest the Ge=O double bond is highly polarized with a contribution of a charge-separated form $(\mathrm{Eind})_2Ge^{+}{-}O^{-}$. The germanone thus exhibits unique reactivities that are not observed with ordinary ketones, including the spontaneous trapping of CO_2 gas to provide a cyclic addition product.

Objectives of My Research



X=C, Si and Ge



Molecular geometries

Stabilities

***Telluro-*ketones**

Spectrosco-pic data

Reactivities

Energetics

Publications

- N.B. Jaufeerally, H.H. Abdallah, P. Ramasami, H.F Schaefer. III, *Theor. Chem. Acc.* 2012, ***131***, 1127. http://www.springerlink.com/content/h3836wk860m6tw2p

- N.B. Jaufeerally, H.H. Abdallah, P. Ramasami, **“Novel Silanetellones: Structures, Ionization Potentials, Electron Affinities, Singlet-Triplet Splittings and Kohn-Sham HOMO-LUMO Gaps of the X_2Si=Te and XYSi=Te (X, Y=H, F, Cl, Br, I and CN) molecules”** *New J . Chem.*, 2012, *submitted*.

- N.B. Jaufeerally, H.H. Abdallah, P. Ramasami, H.F Schaefer. III, **“Novel Germatellones: Structures and Energetics of the X_2Ge=Te and XYGe=Te (X, Y=H, F, Cl, Br, I and CN) molecules”** *In preparation*.

The Stability of *Telluro* –ketones always questioned

- N.B. Jaufeerally, H.H. Abdallah, P. Ramasami, H.F. Schaefer III, ***"A Journey Through the Potential Energy Surfaces of the Isomerization and Decomposition Reactions of H_2X=Te and HFX=Te (X=C, Si and Ge)"*** In preparation.

- N.B. Jaufeerally, P. Ramasami, G. Frenking, H.F. Schaefer III, ***"Stabilization of Telluro –ketones using Bulky Substituents"*** In preparation.

Investigating Unimolecular Reactions

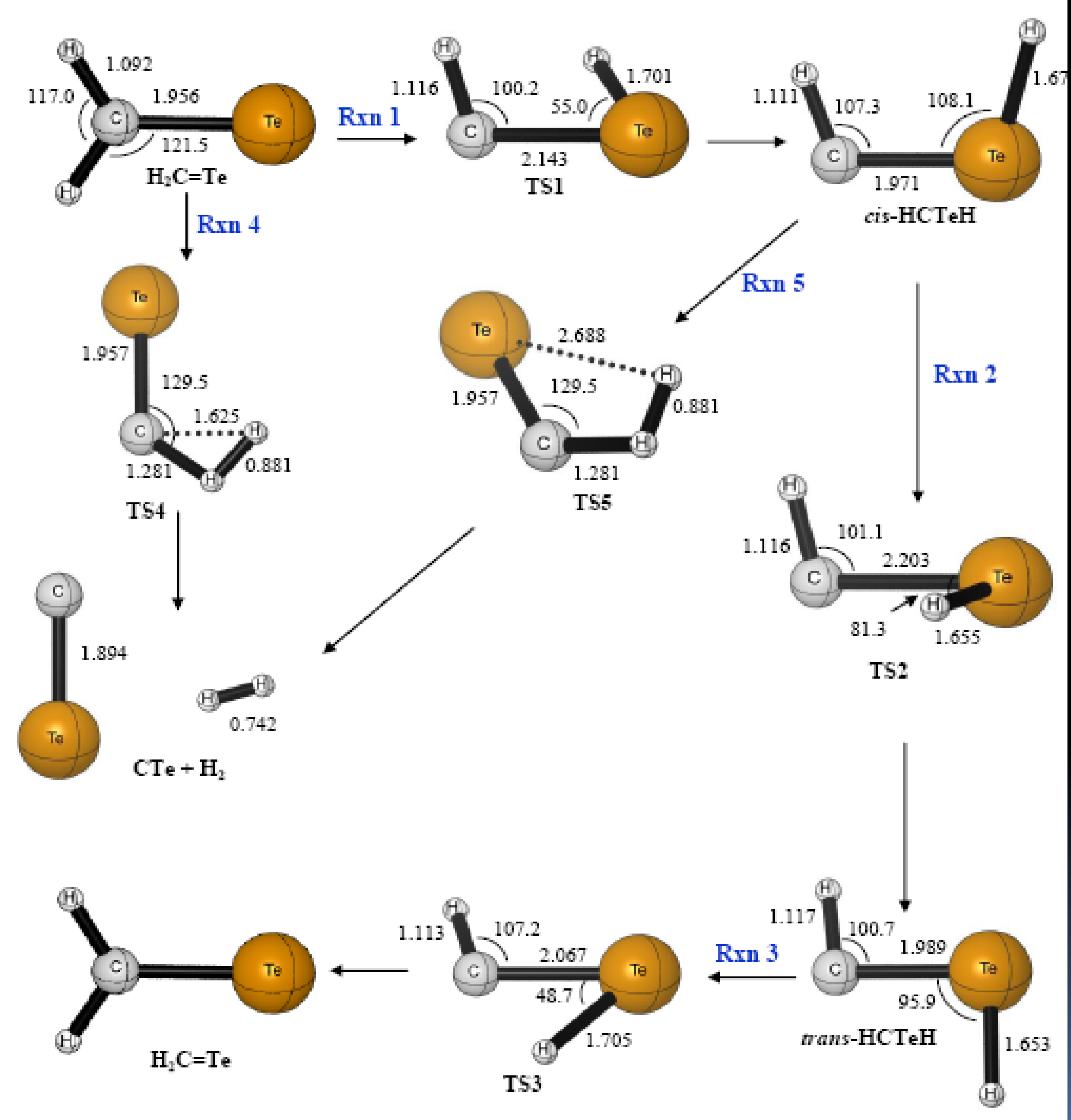


***Figure 1**: Unimolecular decompositions of Telluroformaldehyde ($H_2C=Te$)*

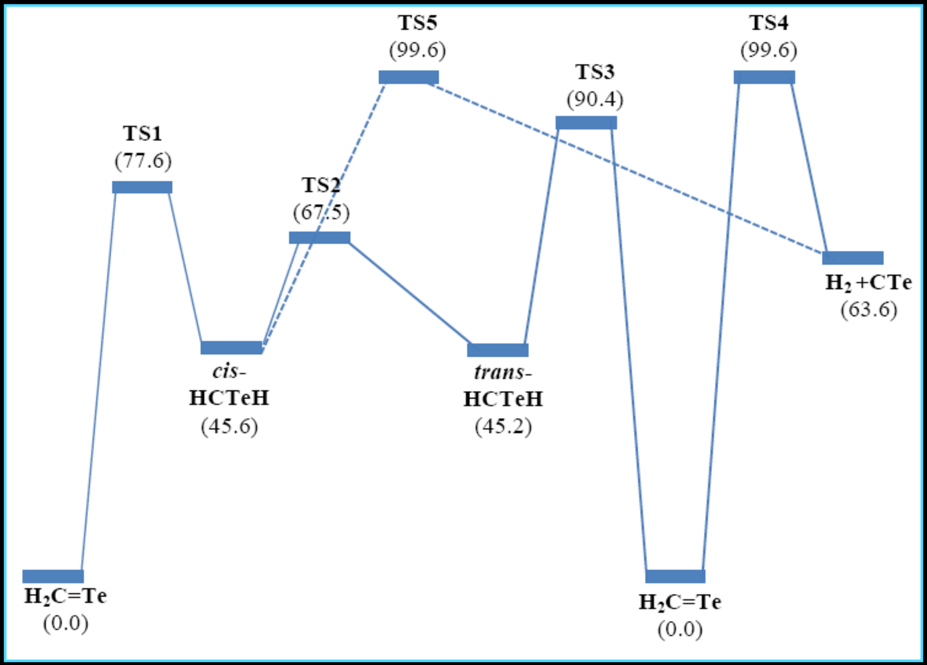


Figure 2

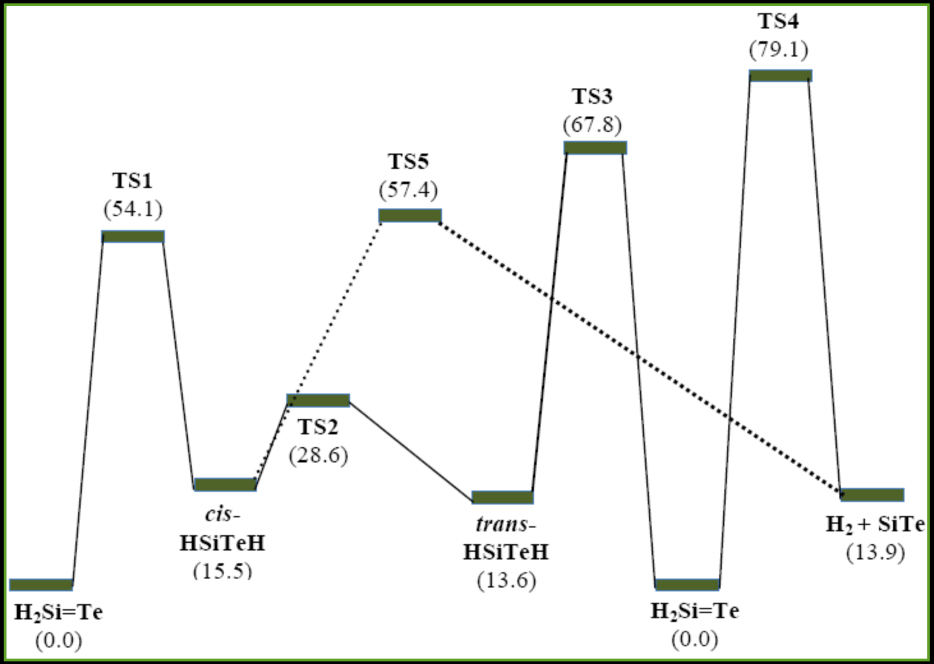


Figure 3

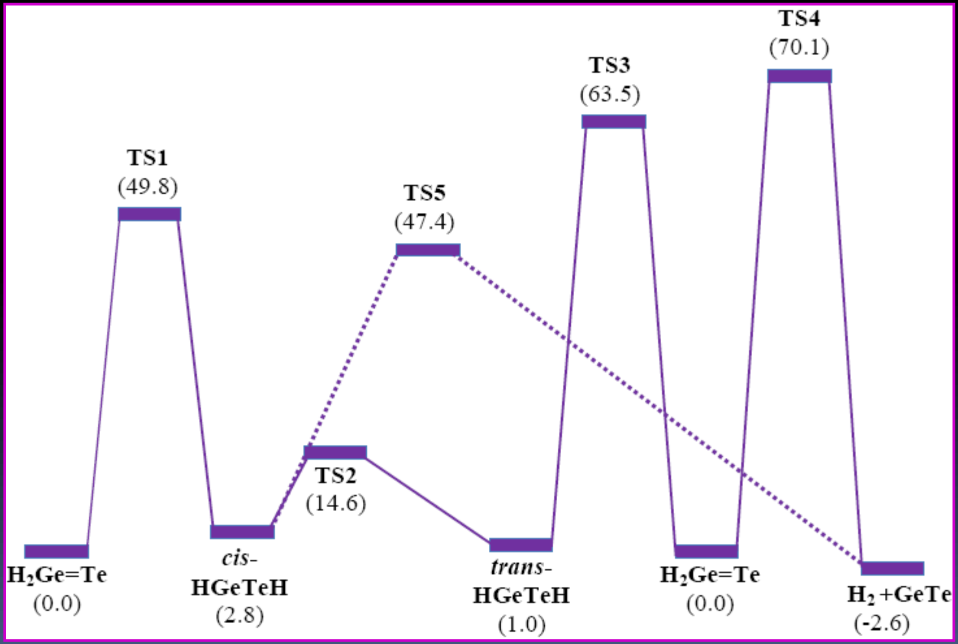


Figure 4

Figures 2-4: Sketch of the PES for the unimolecular reactions of $H_2A=Te$ (A=C, Si and Ge). Relative energies (kcal/mol) are in parentheses.

Isomerization into singly-bonded molecules is more favored in the case of the Ge analogs

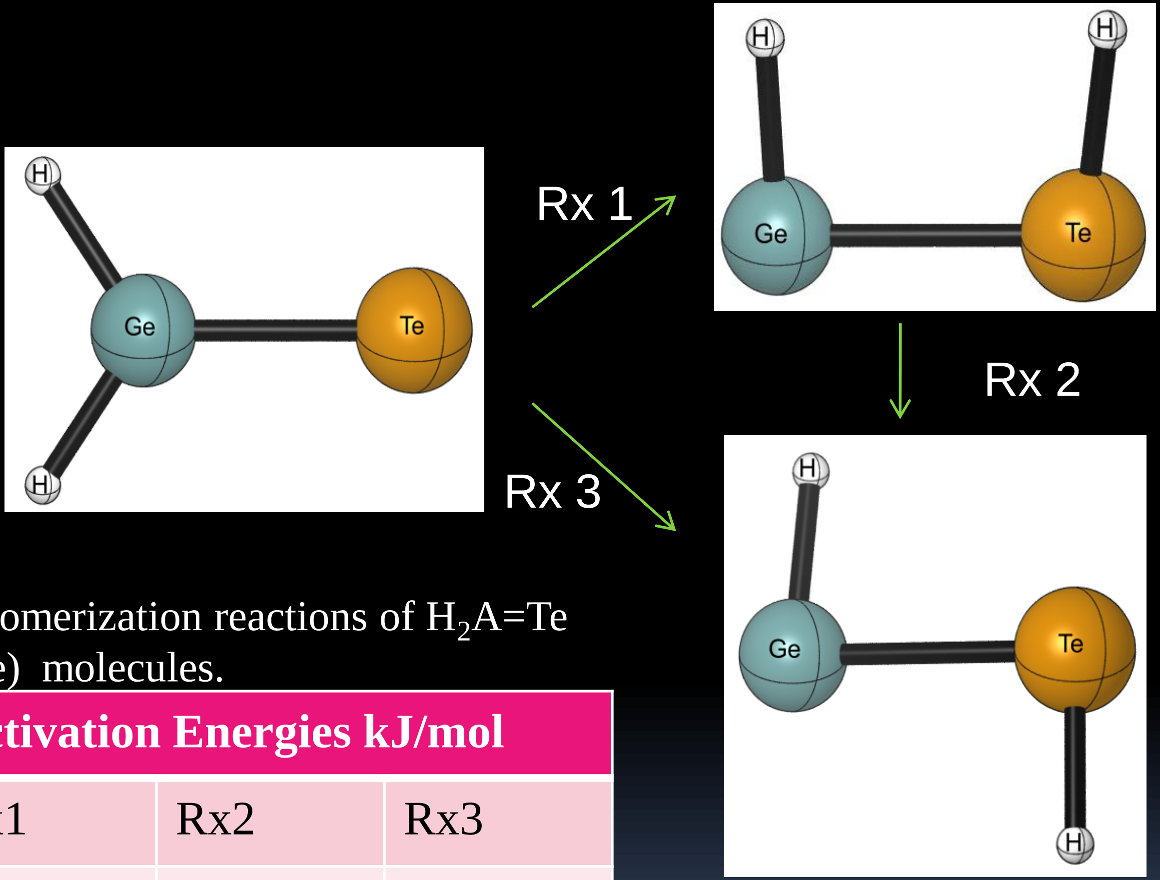


Table 1: E_A of isomerization reactions of $H_2A=Te$ (A=C, Si and Ge) molecules.

	Activation Energies kJ/mol		
	Rx1	Rx2	Rx3
$H_2C=Te$	77.6	22.0	90.4
$H_2Si=Te$	54.1	13.1	97.8
$H_2Ge=Te$	49.8	11.8	63.5

Why Isomerization of $H_2Ge=Te$ is more favored?

- Accommodation of lone pair of electrons from Te atom
- Polarity of A-Te bond

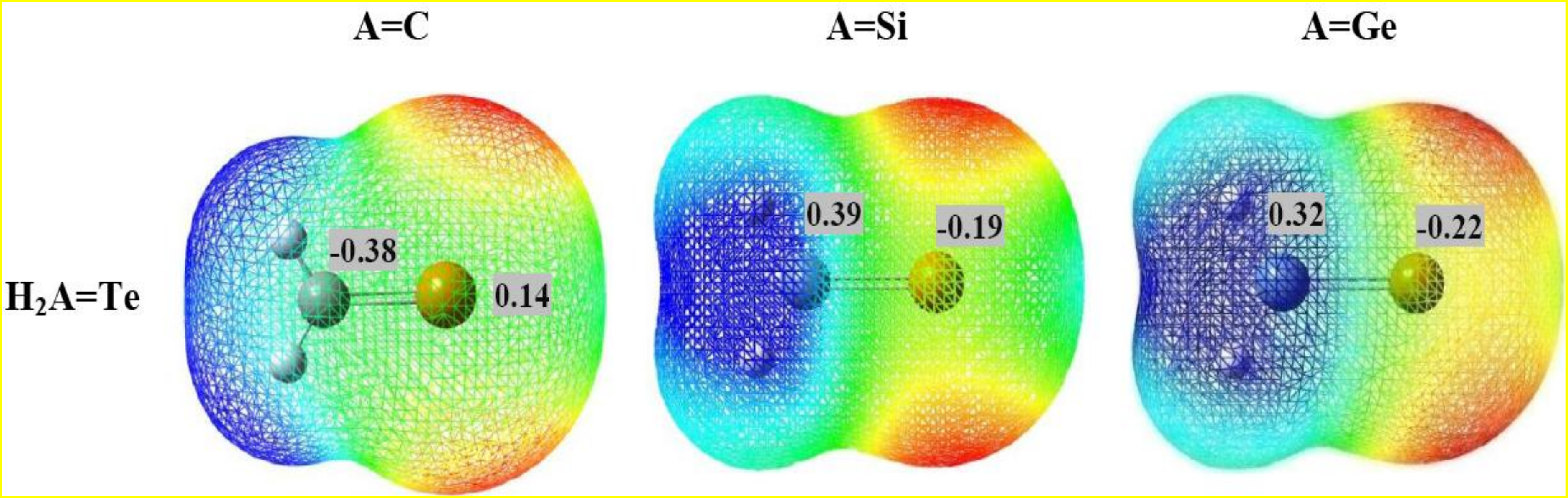
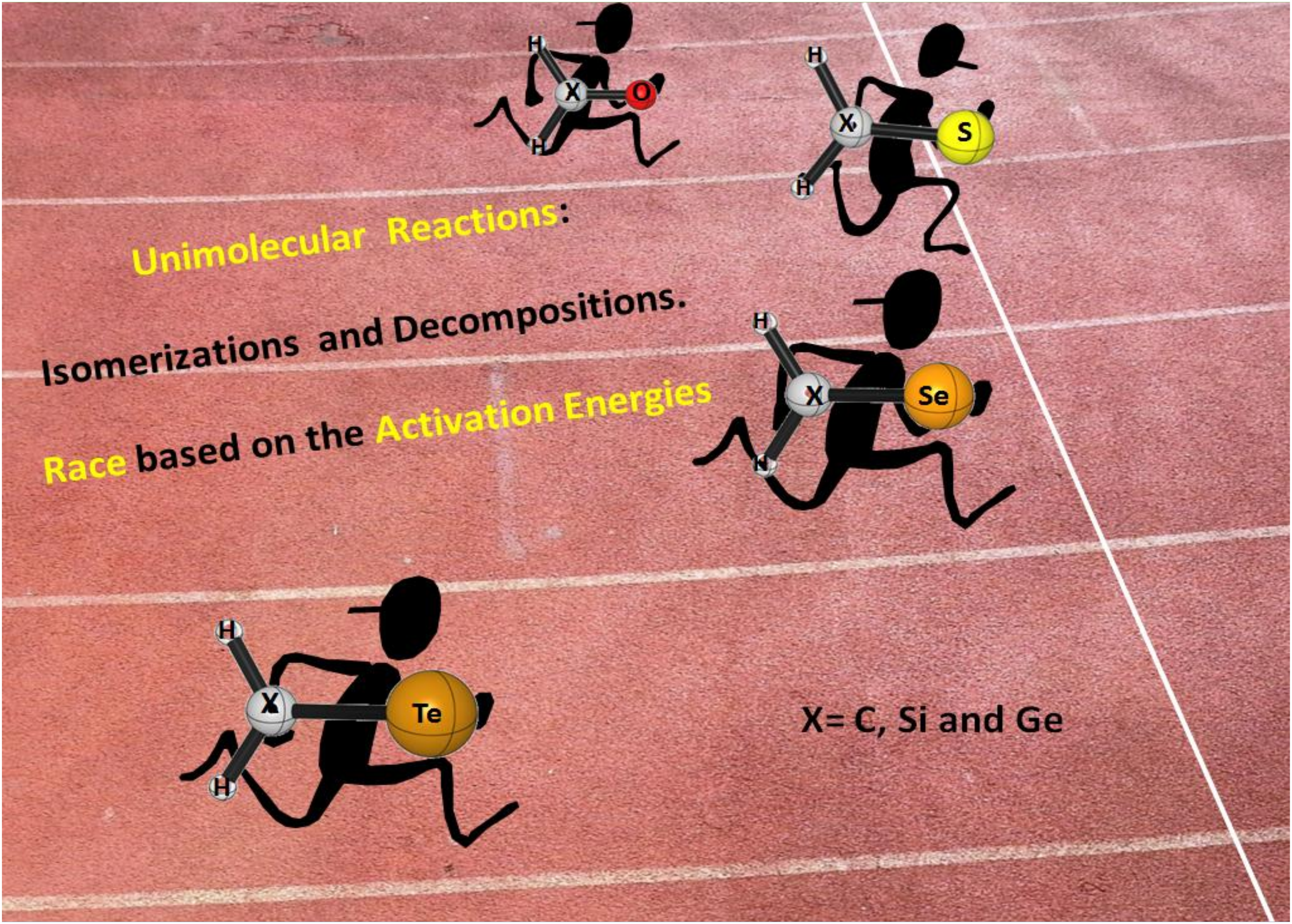


Figure 5: Electrostatic potential maps of $H_2A=Te$ (A=C, Si and Ge). Blue and red regions represent positive and negative potentials, respectively. Mulliken Charges on atoms A and Te are reported.

Comparison with literature



Unimolecular Reactions:

Isomerizations and Decompositions.

Race based on the Activation Energies

X= C, Si and Ge

Optimized Complexes of Monomeric *Telluro* -ketones

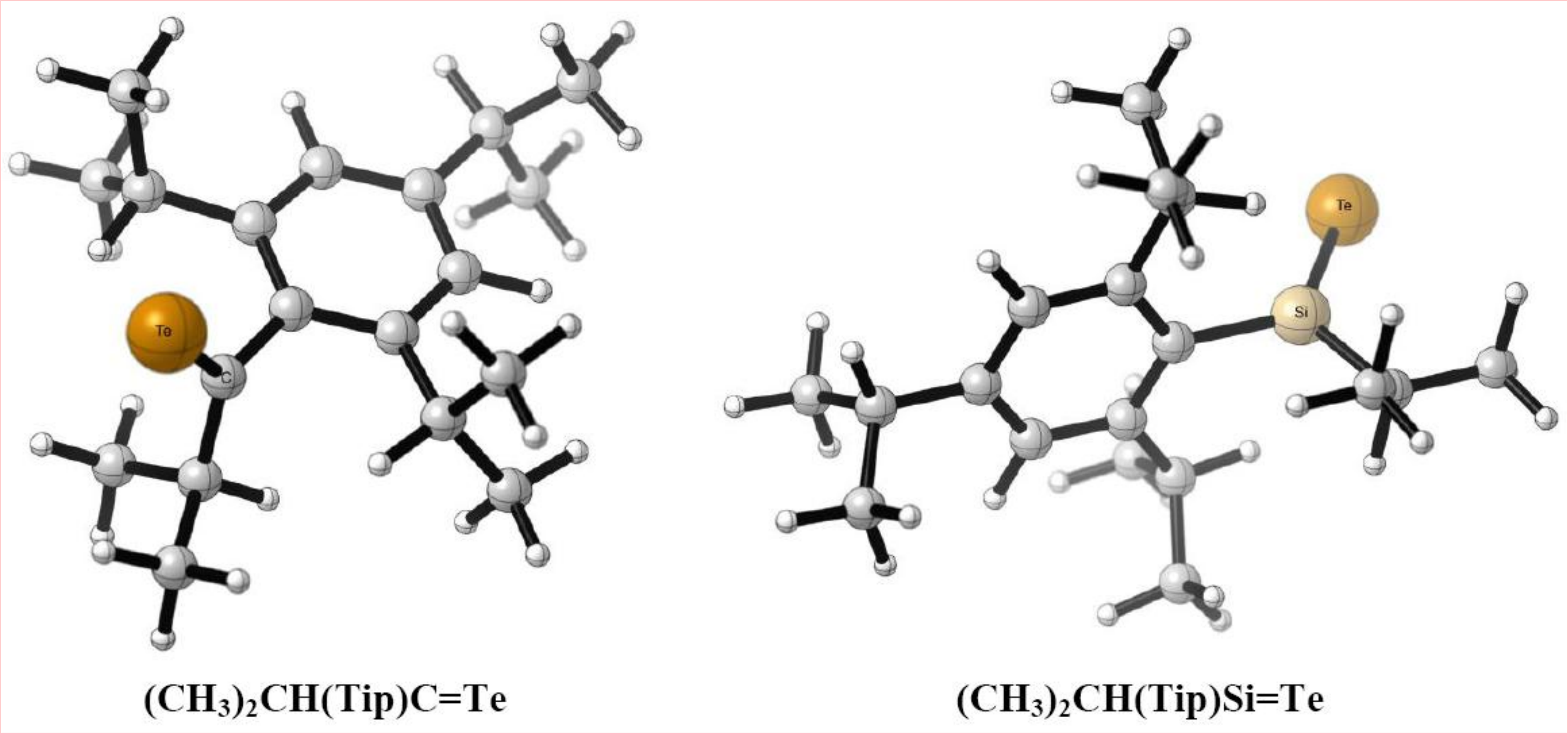


Figure 6: Optimized structures of $(CH_3)_2CH(Tip)A{=}Te$, A=(C and Si).

Optimized Complexes of Monomeric *Telluro* -ketones

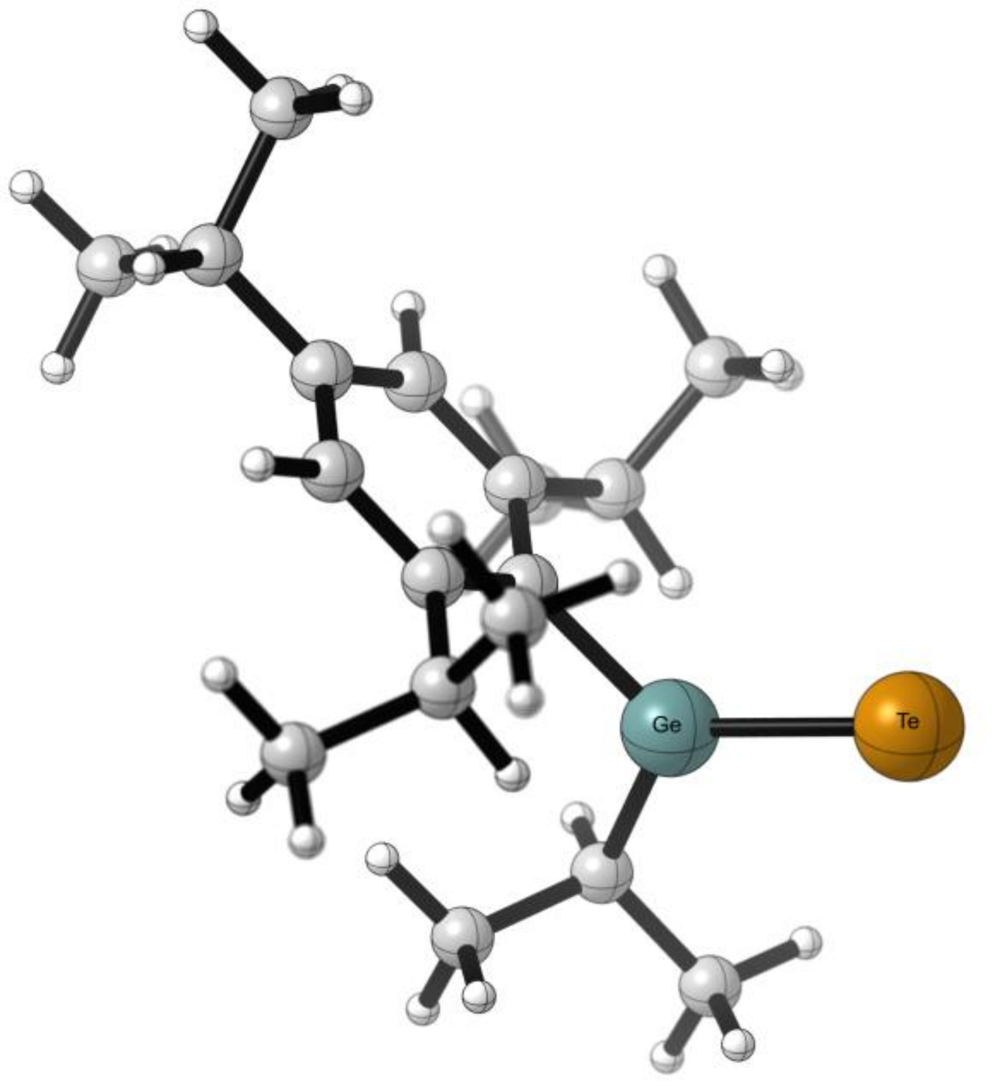


Figure 7: Optimized structures of $(CH_3)_2CH(Tip)Ge{=}Te$.

Optimized Complexes of Monomeric *Telluro*-ketones

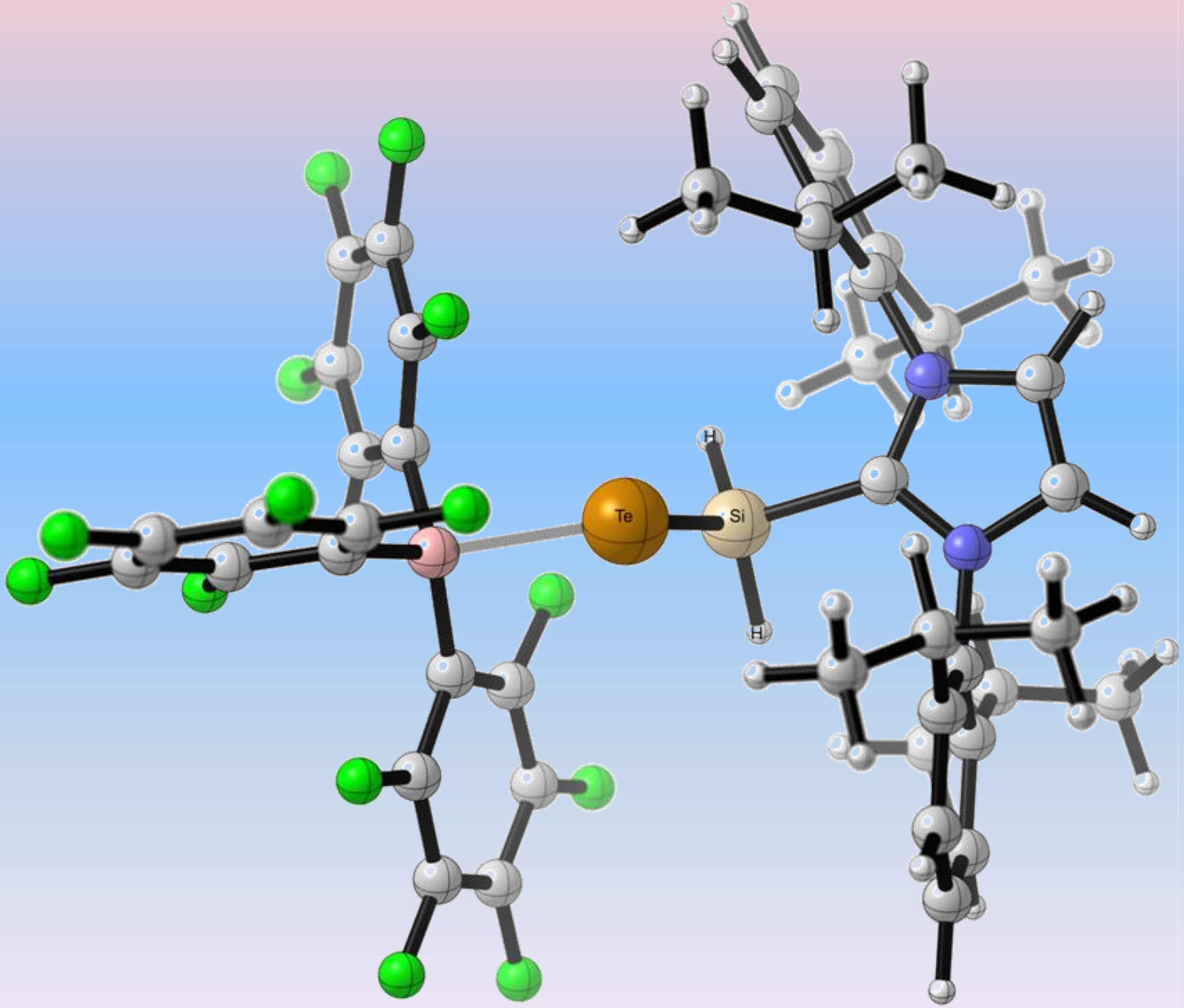


Figure 7: Optimized structures of IPr.Si(H_2)=Te.B(C_6F_5)$_3$.

Optimized Complexes of Monomeric *Telluro*-ketones

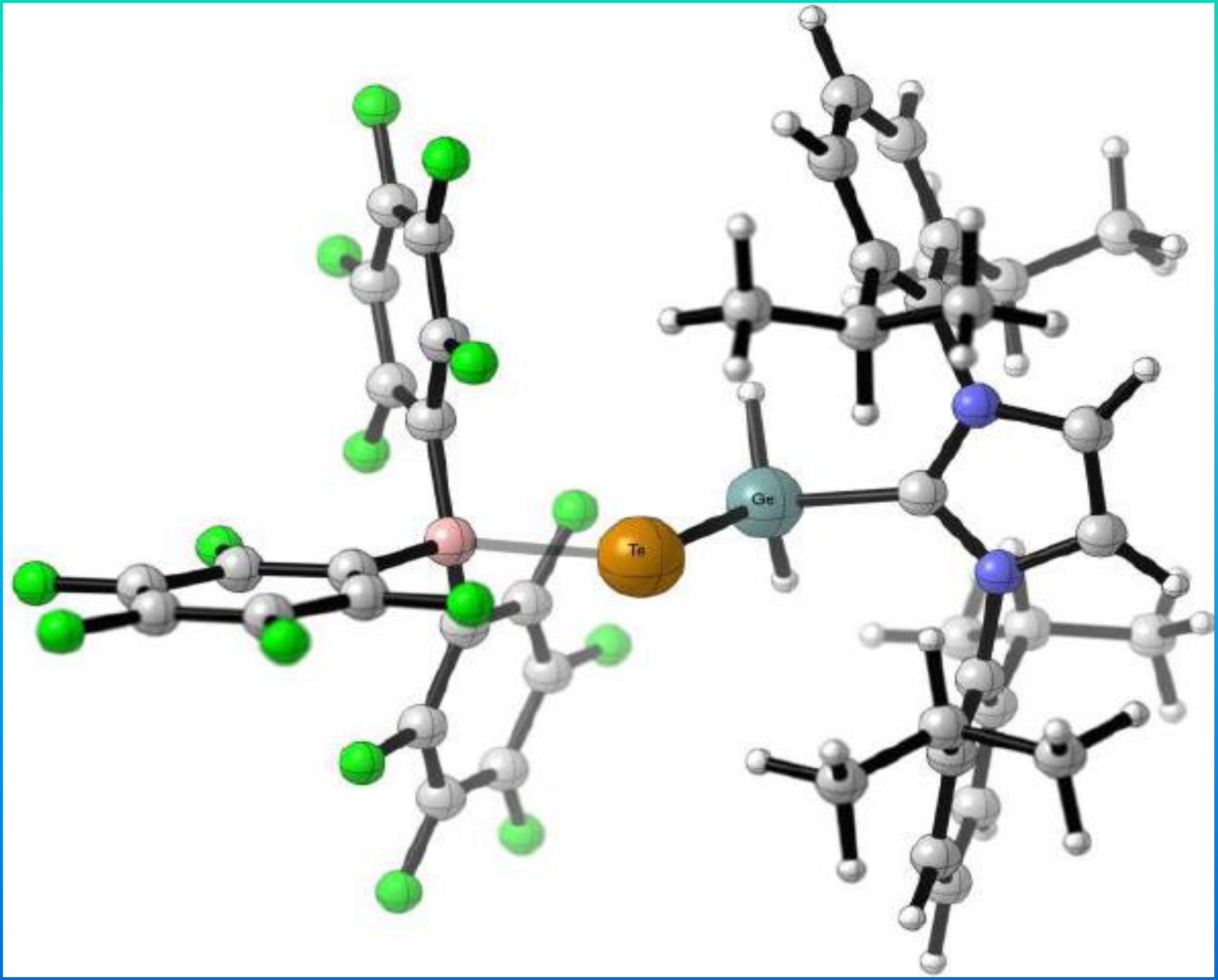
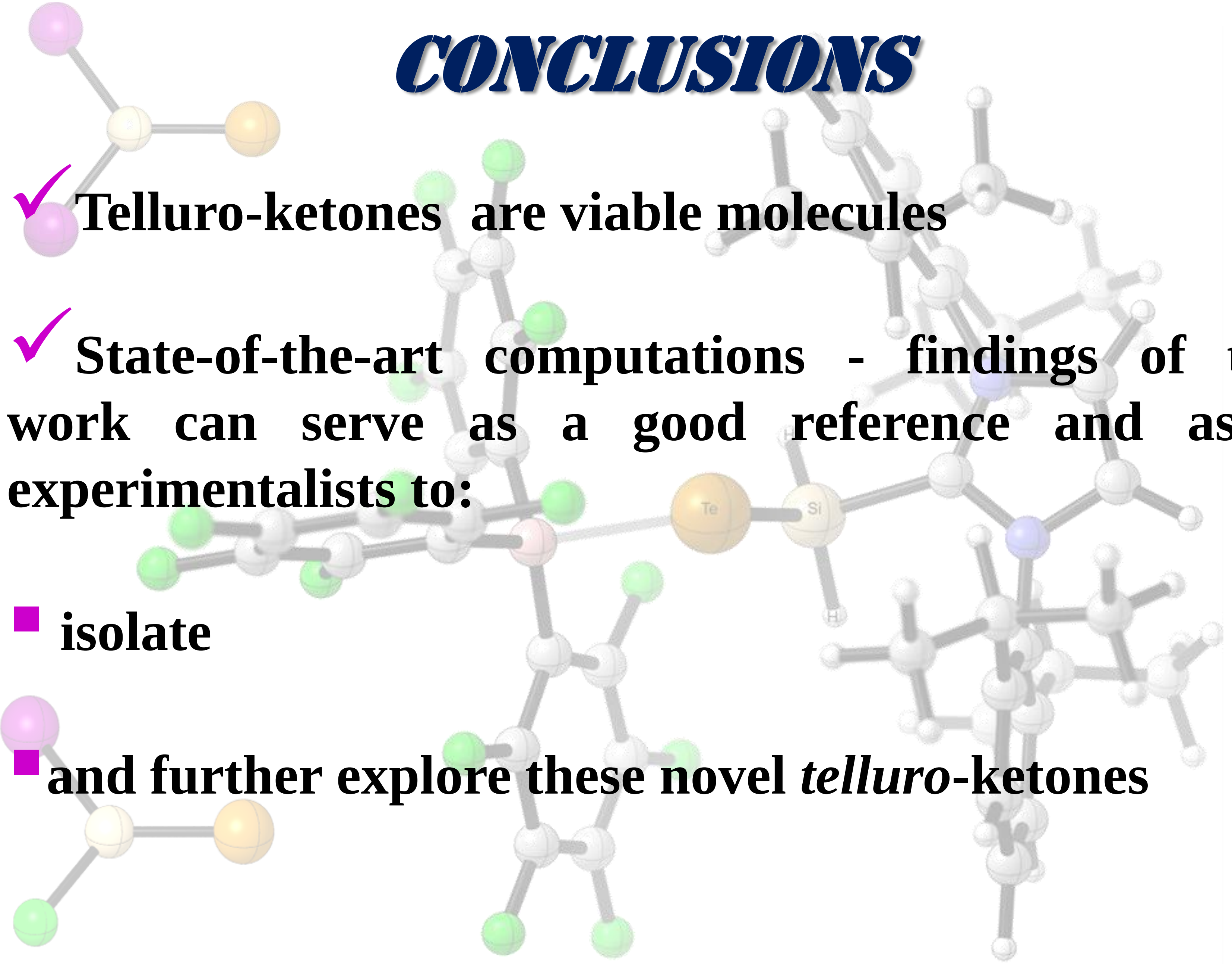


Figure 8: Optimized structures of IPr.Ge(H_2)=Te.B(C_6F_5)$_3$.

CONCLUSIONS



✓Telluro-ketones are viable molecules

✓State-of-the-art computations - findings of this work can serve as a good reference and assist experimentalists to:

- isolate
- and further explore these novel *telluro*-ketones

Future Work

- Calculating bond dissociation energies to assess the stabilities of $(CH_3)_2CH(Tip)A=Te$, $Pr.A(H_2)=Te.B(C_6F_5)_3$, (A=C and Si) molecules.

- Analyzing structural and spectroscopic data.

- Performing NBO analysis.

- Analyzing of the Kohn-Sham frontier orbitals.

- Hence predicting the stabilities of A-Te double-bond.

Acknowledgements

I gratefully acknowledge:

- ✓ the organizing committee of the 16th ECSOC
- ✓ my supervisor Prof. P Ramasami
- ✓ the University of Mauritius and University of Sains Malaysia.
- ✓ the Tertiary Education Commision (TEC)

Thank you
for your attention

For any query, contact me:

naziah0512@gmail.com