

## SELENO- AND TELLUROCARBENIUM IONS

HANSJÖRG GRÜTZMACHER<sup>a</sup>, GRACE SHIAHUY CHEN<sup>a</sup>,  
DIETMAR OHLMANN<sup>a</sup>, CHRISTINA M. MARCHAND, RAINER  
GLASER<sup>b</sup>

<sup>a</sup>ETH-Zentrum, Universitätsstrasse 6, CH-8092 Zürich, e-mail:gruetz@inorg.chem.ethz.ch; <sup>b</sup>University of Missouri-Columbia, Department of Chemistry, 209 Chemistry Building, Columbia, Missouri 65211

**Abstract:**  $\alpha$ -Chalcogeno substituted carbenium salts  $[(RX)_3C]^+ PF_6^-$  (X = S, Se, Te; R = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) obtained from reaction of the copper complexes [(bipy)CuXR] with CBr<sub>4</sub> are stabilized to the same extent; but the electronic mechanism is very different.

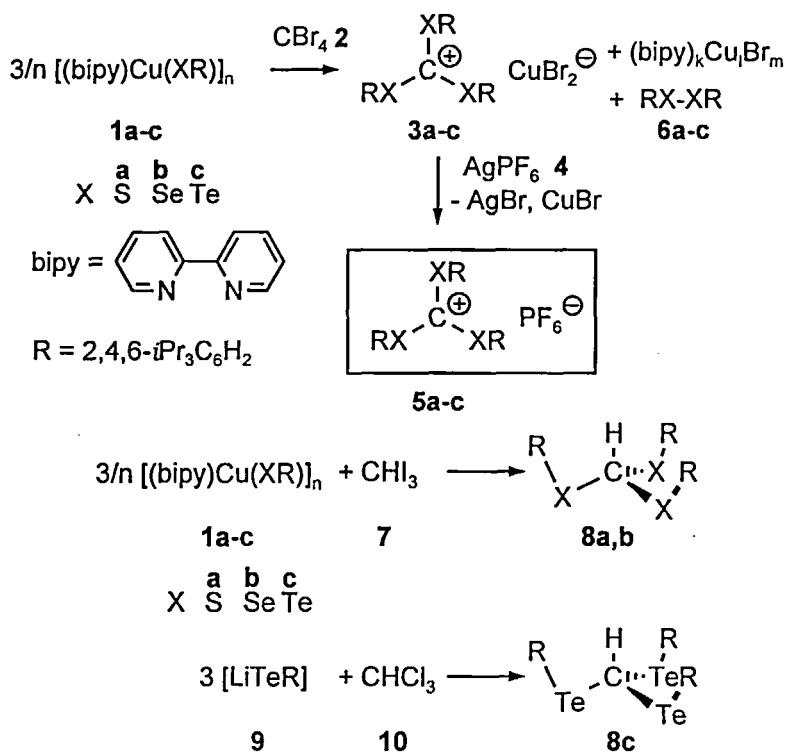
**Keywords:** Carbenium Ions; Tellurium; Selenium; Stability; Ab initio calculations; Structures

### INTRODUCTION

Stabilizing effects of chalcogeno centers are controversially discussed<sup>[1]</sup>. The notion, that heteroatoms from the higher periods are poorer  $\pi$ -donors than their lighter congeners was repeatedly criticized<sup>[2,3]</sup>. The influence of multiple substitution ( $n > 1$ ) on the stability of ions  $[(HX)_nCH_{3-n}]^+$  (X = O, S, Se;  $n = 1-3$ ) is little investigated<sup>[4]</sup>.

### EXPERIMENTAL AND QUANTUM CHEMICAL RESULTS

We studied systematically chalcogeno carbenium ions  $[(RX)_3C]^+$  as  $CuBr_2^-$  (3a-c) or  $PF_6^-$  (5a-c) salts and their corresponding methanes  $(RX)_3CH$  (X = S, Se, Te) (8a-c) (Scheme 1)<sup>[5]</sup>.



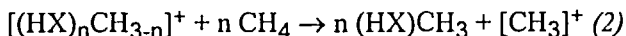
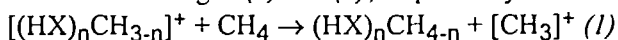
SCHEME 1

Some selected physical data are given in Table I. The relative C-X bond shortening  $\Delta$  in the ions, when compared to the methanes, slightly decreases S = Se > Te.

TABLE I. Selected physical data for 3a-c and 8a-c

	$CX_{\text{exp}}/CX_{\text{cal}}$ [Å]	$\Delta$ [%]	$\delta^{13}\text{C}$	$\delta^{77}\text{Se}/^{125}\text{Te}$	$\lambda_{\text{max}}$ [nm]
3a X=S	1.706 / 1.710	6.5	239.5		309
3b X=Se	1.839 / 1.860	6.5	253.7	770	388
3c X=Te	2.060 / 2.056	4.7	230.6	/ 1279	500
8a X=S	1.817 / 1.821		73.06		275
8b X=Se	1.960 / 1.973		39.77	280	300
8c X=Te	2.156 / 2.169		-64.24	/ 562	379

Hydride transfer energies (HTE) and bond separation energies (BSE) were calculated according to (1) and (2), respectively.



In Table II, total charges on carbon (NBA; MP2/LANL1DZ+P') are listed. Multiple substitution increasingly stabilizes all carbenium ions  $[(\text{HX})_n\text{CH}_{3-n}]^+$  to the same extent (see HTE's).

 TABLE II NBA total charges on carbon in  $[(\text{HX})_n\text{CH}_{3-n}]^+$ 

n	1	2	3
X = O	0.476	0.823	1.212
X = S	-0.326	-0.493	-0.553
X = Se	-0.446	-0.700	-0.853
X = Te	-0.666	-1.065	-1.339

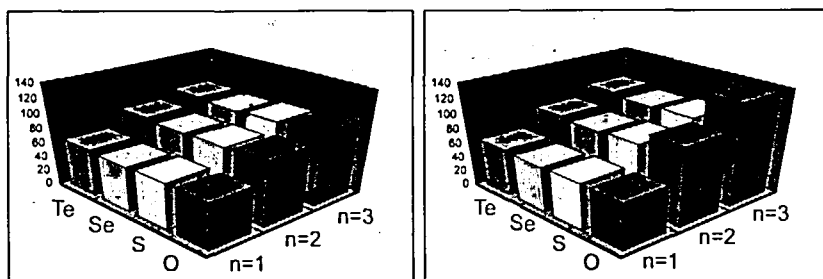


FIGURE 1 Presentation of the HTE's (left) and BSE's (right) of carbenium ions  $[(\text{HX})_n\text{CH}_{3-n}]^+$  (X = O, S, Se, Te; n = 1-3)

The electronic mechanism causing this phenomena is very different for  $X = O$  versus  $X = S, Se, Te$ . Instead of charge dispersal, an increased charge separation is seen in  $[(HO)_nCH_3-n]^+$  leading to increasingly polar and increasingly stronger  $C^{\delta+}-O^{\delta-}$  bonds (manifested by the strong increase of BSE with increasing  $n$ ). On the contrary, the heavier homologues are indeed stabilized by increasing  $\sigma+\pi$  donation from the  $\alpha$ -heteroatom to the carbenium center which leads to negatively charged carbon centers. Clearly, these heteroelements are the better  $\pi$ -donors. Note also that the most positively charged carbon nucleus in  $[(HO)_3C]^+$  shows the lowest frequency shifted  $^{13}C$  carbon resonance.

### Acknowledgements

We thank the Swiss National Science Foundation and the NATO (CRG 940399) for financial support.

### References

- [1.] Review: H. Grützmacher, Ch.M. Marchand, *Coord. Chem. Rev.*, 163, 287 (1997).
- [2.] G. Frenking, S. Fau, Ch. M. Marchand, H. Grützmacher, *J. Am. Chem. Soc.*, 119, 6648 (1997).
- [3.] J. Kapp, C. Schade, A. M. El-Nahas, and P. v. R. Schleyer, *Angew. Chem.*, 108 (1996) 2373.
- [4.] K. Ösapay, J. Delhalle, K. M. Nsunda, E. Rolli, R. Houriet, and L. Hevesi, *J. Am. Chem. Soc.*, 111 (1989) 5028.
- [5.] H. Grützmacher, D. Ohlmann, C. M. Marchand, G. S. Chen, D. Farmer, R. Glaser, A. Currao, R. Nesper, and H. Pritzkow, *Angew. Chem. Int. Ed. Engl.*, 35 (1996) 300.