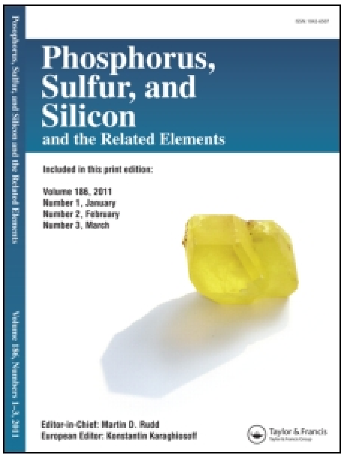

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SELENO- AND TELLUROCARBENIUM IONS

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Abstract: α-Chalcogeno substituted carbenium salts $[(RX)_3C]^+ PF_6^-$ (X = S, Se, Te; R = 2,4,6-$i$$Pr_3C_6H_2$) obtained from reaction of the copper complexes [(bipy)CuXR] with CBr_4 are stabilized to the same extent; but the electronic mechanism is very different.

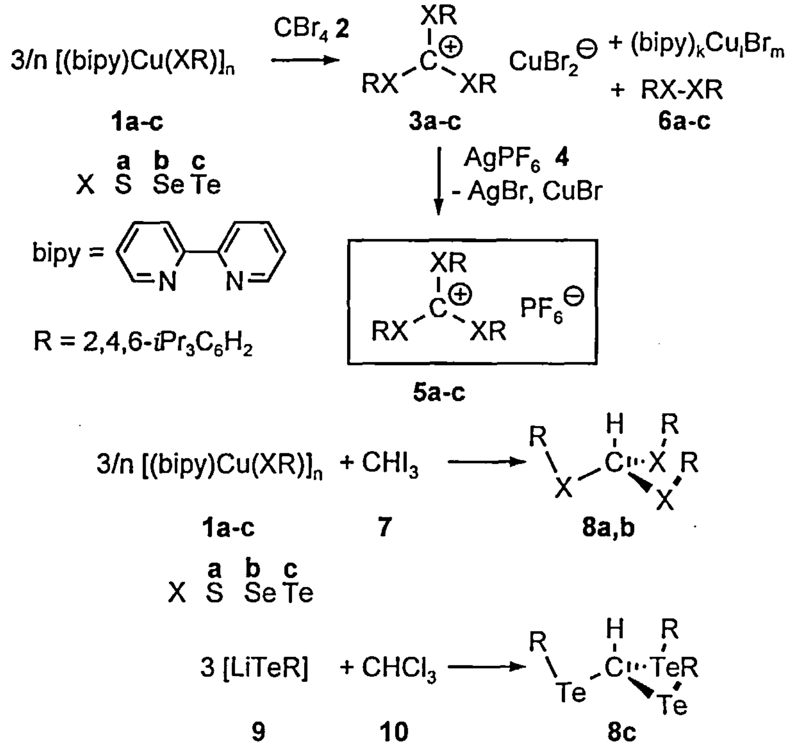
Keywords: Carbenium Ions; Tellurium; Selenium; Stability; Ab initio calculations; Structures

INTRODUCTION

Stabilizing effects of chalcogeno centers are controversially discussed[1]. The notion, that heteroatoms from the higher periods are poorer π-donors than their lighter congeners was repeatedly criticized[2,3]. 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[4].

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)[5].



SCHEME 1

Some selected physical data are given in Table I. The relative C-X bond shortening Δ 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_{exp}/CX_{cal} [Å]	Δ [%]	δ ^{13}C	δ ^{77}Se/ ^{125}Te	λ_{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 seperation energies (BSE) were calculated according to *(1)* and *(2)*, respectively.

$$[(HX)_nCH_{3-n}]^+ + CH_4 \rightarrow (HX)_nCH_{4-n} + [CH_3]^+ \quad (1)$$

$$[(HX)_nCH_{3-n}]^+ + n\,CH_4 \rightarrow n\,(HX)CH_3 + [CH_3]^+ \quad (2)$$

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

TABLE II NBA total charges on carbon in $[(HX)_nCH_{3-n}]^+$

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

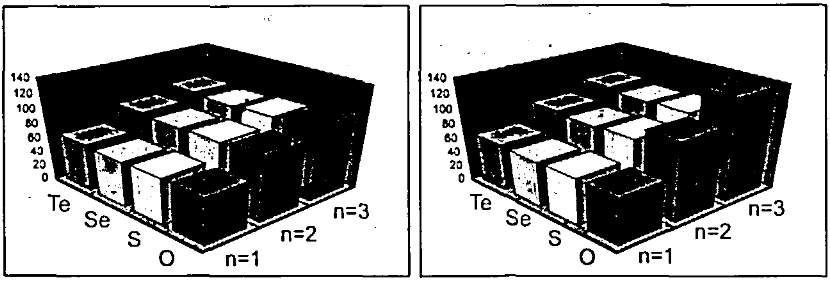


FIGURE 1 Presentation of the HTE's (left) and BSE's (right) of carbenium ions $[(HX)_nCH_{3-n}]^+$ (X = O, S, Se, Te; n = 1-3)

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 α-heteroatom to the carbenium center which leads to negatively charged carbon centers. Clearly, these heteroelements are the better π-donors. Note also that the most positively charged carbon nucleus in $[(HO)_3C]^+$ shows the lowest frequency shifted ^{13}C carbon resonance.

Acknowledgements

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