mechanism I, two different kinetics behaviors are possible according to the magnitudes of k and k_-. When k is not smaller than k_-, [L–M, N]$^+$ will be in the steady state and § is simply expressed as § = $\{kk_+/(k + k_-)\}$[L–M$^+$][N] since the steady state condition will apply to [N–M, L]$^+$. This is the same formulation as that for A$_i$, and the system will depend only on one adimensional parameter, $\lambda = \{kk_+/(k + k_-)\}[\mathrm{N}](RT/\mathcal{F}v)$. $+ k_-)\}[\mathrm{N}](RT/\mathcal{F}v)$. On the other hand, when k is smaller than k_-, eq 25 will be in fast equilibrium and [N–M, L]$^+$ in the steady state, leading to § = k[L–M$^+$]$\{(k_+/k_-)[\mathrm{N}]/[1 + (k_+/k_-)[\mathrm{N}]]\}$ which gives $\Lambda = [k(RT/\mathcal{F}v)]\{(k_+/k_-)[\mathrm{N}]/[1 + (k_+/k_-)[\mathrm{N}]\}b$. This system thus depends on two adimensional parameters, $\lambda = k(RT/\mathcal{F}v)$ and $\kappa = (k_+/k_-)[\mathrm{N}]$, which predict a different effect from variations arising from changes of [N] or v. However, if $(k_+/k_-)[\mathrm{N}] \ll 1$, Λ simplifies to $\Lambda = \{k(k_+/k_-)(RT/\mathcal{F}v)[\mathrm{N}]\}b$, leading to a dependence of the system on one parameter $\lambda' = k(k_+/k_-)(RT/\mathcal{F}v)[\mathrm{N}]$. This last case is indeed included in the above formulation. In other words, the interchange mechanism will appear as two limiting kinetics behaviors—one when $(k_+/k_-)[\mathrm{N}]$ is large or ~1 and the other when it is less than 1. The former will depend on two parameters, $\lambda = k(RT/\mathcal{F}v)$ and $\kappa = (k_+/k_-)[\mathrm{N}]$, and the latter will depend on only one parameter, i.e.,

$$\lambda = k_{\mathrm{ap}}(RT/\mathcal{F}v)[\mathrm{N}]$$

where $k_{\mathrm{ap}} = (k_+k)/(k + k_-)$.

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Registry No. η^5-MeCpMn(CO)$_2$(4-MeOpy)$^+$, 89727-37-7; η^5-MeCpMn(CO)$_2$(4-NO$_2$py)$^+$, 89727-38-8; η^5-MeCpMn(CO)$_2$(4-Mepy)$^+$, 89727-44-6; η^5-MeCpMn(CO)$_2$(py)$^+$, 89727-45-7; η^5-MeCpMn(CO)$_2$(4-CH$_3$COpy)$^+$, 89727-46-8; η^5-MeCpMn(CO)$_2$(3-Mepy)$^+$, 89727-47-9; η^5-MeCpMn(CO)$_2$(3-Fpy)$^+$, 89727-48-0; η^5-MeCpMn(CO)$_2$(3-Clpy)$^+$, 89727-49-1; η^5-MeCpMn(CO)$_2$(4-CH$_3$COpy), 60718-84-5; η^5-MeCpMn(CO)$_2$(py), 60718-82-3; η^5-MeCpMn(CO)$_2$(4-MeOpy), 89727-39-9; η^5-MeCpMn(CO)$_2$(4-NO$_2$py), 89727-40-2; η^5-MeCpMn(CO)$_2$(4-Mepy), 60718-81-2; η^5-MeCpMn(CO)$_2$(3-Mepy), 89727-41-3; η^5-MeCpMn(CO)$_2$(3-Fpy), 89727-42-4; η^5-MeCpMn(CO)$_2$(3-Clpy), 89727-43-5; η^5-MeCpMn(CO)$_2$(PEt$_3$), 65152-86-5; η^5-MeCpMn(CO)$_2$(PPh$_2$Me), 37685-57-7; η^5-MeCpMn(CO)$_2$(PPh$_3$), 12100-95-7; η^5-MeCpMn(CO)$_2$(PPh$_2$Et), 89727-50-4; η^5-MeCpMn(CO)$_2$(PPhEt$_2$), 89727-51-5; η^5-MeCpMn(CO)$_2$(P(OMe)Ph$_2$), 83746-92-3; η^5-MeCpMn(CO)$_2$(P(C$_6$H$_4$CH$_3$-p)$_3$), 83746-90-1; η^5-MeCpMn(CO)$_2$(P(C$_6$H$_4$OCH$_3$-p)$_3$), 89727-52-6; η^5-MeCpMn(CO)$_2$(PPh$_2$(n-Bu)), 89727-53-7; η^5-MeCpMn(CO)$_2$(PPh$_2$(i-Pr)), 89727-54-8; η^5-MeCpMn(CO)$_3$, 12108-13-3; P(OMe)Ph$_2$, 4020-99-9; PPhEt$_2$, 1605-53-4; PPh$_2$Et, 607-01-2; PPh$_3$, 603-35-0; PEt$_3$, 554-70-1; P(p-MePh)$_3$, 1038-95-5; P(p-MeOPh)$_3$, 855-38-9; PPh$_2$Me, 1486-28-8; PPh$_2$(n-Bu), 6372-41-4; PPh$_2$(i-Pr), 6372-40-3.

α-Selenocarbenium Ions: Preparation, X-ray Molecular Structure Determination, and ^{1}H and ^{13}C NMR Spectral Characterization[†]

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Abstract: Bis(methylseleno)carbenium ion salts (I, R = H, Et, PhCH$_2$; Y = BF$_4$, SbCl$_6$) as well as their bis(methylthio) analogues

RC$^+$(SeMe)$_2$ Y$^-$ RC$^+$(SMe)$_2$ Y$^-$
I II

(II, R and Y the same as in I) have been prepared by the reaction of the corresponding orthoseleno- and orthothioesters either with triphenylcarbenium or with appropriate silver salts in dichloromethane. They have been isolated as pure crystalline solids and structurally investigated by NMR and X-ray techniques. Comparison of the results for selenium, sulfur, and oxygen derivatives shows the existence of important mesomeric stabilization of the positive charge in all three types of cations by the unshared electrons of the heteroatomic substituents. The ordering of stabilizing ability of the heteroatoms as obtained from proton chemical shifts (Se > O > S) contrasts with that resulting from ^{13}C and X-ray data (O > S ≃ Se). ^{1}H NMR spectra of bis(methylthio)ethyl-, bis(methylthio)benzyl-, and bis(methylseleno)benzylcarbenium ions were found to be reversibly temperature dependent. This was interpreted as a result of hindered rotation around C$^+$–S and C$^+$–Se bonds having activation energies of 8 ± 2, 14 ± 2, and 13 ± 2 kcal/mol, respectively. The values are comparable to those of the oxocarbenium ions (8–15 kcal/mol), suggesting similar π bonds. X-ray structure determinations carried out on I and II (R = benzyl; Y = SbCl$_6$) reveal substantial shortenings of the C$^+$–Se and C$^+$–S bond distances by 0.15 and 0.14 Å, respectively, as compared to the corresponding single-bond distances in saturated molecules. Estimated π bond orders (~0.50 for both thio- and selenocarbenium ions and 0.66–0.80 for the oxo derivatives) indicate that delocalization of selenium nonbonded electrons is just as strong as that of sulfur lone pairs in these cationic species.

A large variety of heterosubstituted carbenium ion salts has been described[1] in which the positive charge is stabilized by second-row elements such as nitrogen and oxygen.

The subject of dithiolium ions[2,3] and that of other mono- and dithiocarbenium ions[1,4,5] are now also well documented. However, virtually nothing is known about the possibility and extent of stabilization of carbocations by the fourth-row element selenium.[6] We wish to report here on the easy preparation and some structural

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investigations of bis(methylseleno)carbenium ions where R is

$$\underset{\mathbf{1}}{\mathrm{RC^+(SeCH_3)_2}}$$

hydrogen or an alkyl group. Taking into account the rather spectacular development in recent years of the synthetic applications of organoselenium chemistry,[7] it is clear that having general access to cations of type **1** in a stable form is of great potential interest. A priori, they can be used as electrophilic reagents for the introduction of selenyl moieties into organic molecules and then as versatile functional group generators.

Vinyl selenides[8] and ketene selenoacetals[9] in acidic media undergo protonation at their β-carbon atoms as do their thio analogues.[10] Therefore, this reaction should in principle be a valuable approach to the preparation and isolation of mono- and bis(alkylseleno)carbenium ion salts. We found, however, that the reaction of orthoselenoesters **2** with triphenylcarbenium salts or with appropriate silver salts (hexafluoroantimonate or tetrafluoroborate), as featured by eq 1, is much easier to carry out experimentally and usually leads to the desired salt **1** in high yield.

$$\underset{\mathbf{2}}{\mathrm{RC(SeCH_3)_3}} + \mathrm{M^+Y^-} \rightarrow \underset{\mathbf{1}}{\mathrm{RC^+(SeCH_3)_2Y^-}} + \mathrm{MSeCH_3} \qquad (1)$$

$$\mathrm{R = H, CH_3, C_2H_5, C_6H_5CH_2;}$$
$$\mathrm{M^+ = (C_6H_5)_3C^+, Ag^+; Y^- = BF_4^-, SbCl_6^-, SbF_6^-}$$

Experimental Section

Reagents and Instruments. All organic and inorganic reagents and solvents including the deuterated ones were purchased from Aldrich Europe (Beerse, Belgium) or from Merck (Belgolabo, Overijse, Belgium). Triethyl orthoformate was used as received, tetrahydrofuran (THF) and ether were distilled before use from sodium benzophenone ketyl in a recycling still, and dichloromethane, acetonitrile, and nitromethane were distilled from phosphorus pentoxide and stored on 4-Å molecular sieves. Commercial diisopropylamine was distilled from calcium hydride and stored on 4-Å molecular sieves.

Methaneselenol was prepared by hypophosphorus acid reduction of dimethyl diselenide according to Günther[11] and methanethiol was purchased from Matheson.

Deuterated solvents were dried on 4-Å molecular sieves.

^{1}H and ^{13}C NMR spectra were recorded on a JEOL MH-100 (100 MHz) or on a JEOL FX90Q (90 MHz for proton) instrument mounted with a tunable multinuclear probe and provided with variable-temperature accessories.

Preparation of Trimethyl Orthoselenoesters (2). One of the easiest ways to achieve this consists of the alkylation of (tris(methylseleno)methyl)lithium[12] by various alkyl halides. The reaction is analogous to that described by Seebach for the alkylation of trimethyl and triphenyl orthothioformate[13] and triphenyl orthoselenoformate,[14] based on the quantitative metalation of the orthoformates by *n*-butyllithium and LDA for the thio and seleno derivatives, respectively.[12]

A typical experimental procedure is the following. Diisopropyl amine (1.05 equiv) is dissolved in dry THF (3 mL for 1 mM) and cooled under argon to −78 °C. *n*-Butyllithium (1.05 equiv) is added (1.6 M hexane solution, Aldrich) and followed after 10 min by a solution of 1 equiv of trimethyl orthoselenoformate in THF (1 mL for 1 mM). A yellow precipitate of (tris(methylseleno)methyl)lithium appears after 30 min of stirring. To this, the alkyl halide (iodide or bromide) is added, and the temperature is raised progressively to room temperature. Water is added and the mixture is extracted with ether. The organic layer is washed with a saturated sodium chloride solution, dried over magnesium sulfate, and freed from solvents under vacuum. The crude orthoselenoesters **2** can be purified by vacuum distillation (for R = H, CH_3, C_2H_5) or by column chromatography (R = higher alkyl, benzyl) on silica gel using pentane/ether (99/1, v/v) as eluant.

Trimethyl orthoselenoformate itself was prepared by mixing under argon and without solvent 1 equiv of triethyl orthoformate, 3 equiv of methaneselenol, and 0.02 equiv of $BF_3.O(C_2H_5)_2$. After 16 h of stirring, the reaction mixture was poured into a saturated solution of sodium bicarbonate and extracted with ether. The etheral solution was washed with water and with saturated sodium chloride, dried, concentrated on a rotary evaporator, and distilled under reduced pressure ($bp_{15\,\mathrm{torr}}$ = 128 °C, pale yellow liquid, 81% yield). ^{1}H NMR (CCl_4) δ 2.10 (s, 9 H), 4.82 (s, 1 H). Anal. Calcd: C, 16.29; H, 3.42. Found: C, 16.67; H, 3.50.

Analytical data for other, yet undescribed, orthothio- and orthoselenoesters are as follows:

Trimethyl orthothiopropionate: ^{1}H NMR (CCl_4) δ 1.08 (t, 3 H), 1.94 (q, 2 H), 2.04 (s, 9 H). Anal. Calcd: C, 39.52; H, 7.74. Found: C, 39.73; H, 7.52.

Trimethyl orthothiophenylacetate: ^{1}H NMR (CCl_4) δ 1.96 (s, 9 H), 3.18 (s, 2 H), 7.26 (m, 5 H). Anal. Calcd: C, 54.05; H, 6.60. Found: C, 54.21; H, 6.52.

Trimethyl orthoselenopropionate: ^{1}H NMR (CCl_4) δ 1.10 (t, 3 H); 2.00 (q, 2 H); 2.10 (s, 9 H). Anal. Calcd: C, 22.31; H, 4.37. Found: C, 22.69; H, 4.64.

Trimethyl orthoselenophenylacetate: ^{1}H NMR (CCl_4) δ 1.94 (s, 9 H), 3.40 (s, 2 H), 7.14 (m, 5 H). Anal. Calcd: C, 34.31; H, 4.19. Found: C, 34.43; H, 4.28.

All the thio analogues were prepared according to known procedures.[13-15]

Preparation of Bis(methylthio)- and Bis(methylseleno)carbenium Ion Salts. Bis(methylseleno)ethyl carbenium hexachloroantimonate (1, R = C_2H_5; Y = $SbCl_6$) was prepared by slow (~30 min) addition of 320 mg (1 mM in 2 mL of CH_2Cl_2) of trimethyl orthoselenopropionate to 580 mg (~1 mM) of triphenylcarbenium hexachloroantimonate (Aldrich) dissolved under argon in 8 mL of dry dichloromethane and precooled to -20 °C. No crystals were observed at this temperature. Further cooling to -78 °C resulted in the formation of fine needles. The mother liquor was filtered off by suction, and the crystals were washed 3 times with 5 mL of precooled ether. Drying under vacuum at -20 °C yielded 440 mg (75%) of pale yellow needles, which melted around 80 °C with decomposition.[16] The title structure was attributed to this material on the basis of its NMR spectral data (CD_3CN): ^{1}H NMR ($SiMe_4$) δ 1.47 (t, *J* = 7.5 Hz, 3 H, $\mathit{CH}_3\mathrm{CH}_2$), 3.04 (brs, 6 H), CH_3Se), 3.27 (q, *J* = 7.5 Hz, 2 H, $\mathrm{CH}_3\mathit{CH}_2$); ^{13}C NM ($SiMe_4$) δ 265.3 ($C^+$), 42.8 ($\mathrm{CH}_3\mathit{CH}_2$), 18.4 ($\mathit{CH}_3\mathrm{Se}$), 13.7 ($\mathit{CH}_3\mathrm{CH}_2$).

The main byproduct methyl triphenylmethyl selenide (eq 1, M = $(C_6H_5)_3C$) was also isolated and purified by PLC (SiO_2, ether/pentane 5/95 v/v, R_f 0.7). The colorless crystalline solid melted at 131 °C (Koffler apparatus) and presented the following analytical data: ^{1}H NMR ($CDCl_3$) δ 1.70 (s, 3 H), 7.15 (m, 15 H); mass spectrum, *m/e* 243 ($M^+ - SeCH_3$) 165 ($(C_6H_5)_3C^+ - C_6H_6$). Anal. Calcd: C, 71.21; H, 5.38. Found: C, 71.51; H, 5.64.

Bis(methylthio)ethylcarbenium Hexachloroantimonate (1, R = C_2H_5; Y = $SbCl_6$, Thio Analogue). 182 mg (1 mM) of trimethyl orthothiopropionate dissolved in 1 mL of dichloromethane was added by a syringe to a solution of triphenylcarbenium hexachloroantimonate (580 mg, 1 mM in 6 mL or dry dichloromethane) maintained at 0 °C under argon. Rapid formation of colorless needles was observed. The supernatant solution was filtered and the crystals were washed twice with 3-mL portions of dichloromethane and twice with 3-mL portions of dry ether. Drying with an argon stream yielded 450 mg (95%) of the desired salt as a colorless crystalline material: mp (instantaneous) 151 °C; ^{1}H NMR (CD_3CN, $SiMe_4$) δ 1.46 (t, *J* = 7.5 Hz, 3 H, $\mathit{CH}_3\mathrm{CH}_2$), 3.08 (brs, 6 H, CH_3S), 3.40 (q, *J* = 7.5 Hz, 2 H, $\mathrm{CH}_3\mathit{CH}_2$); ^{13}C NMR ($CD_3CN$, $SiMe_4$) δ 246.8 (C^+), 38.3 ($\mathrm{CH}_3\mathrm{CH}_2$), 21.6 ($CH_3S$), 12.2 ($\mathit{CH}_3\mathrm{CH}_2$).

Bis(methylseleno)benzylcarbenium Hexachloroantimonate (1, R = $C_6H_5CH_2$; Y = $SbCl_6$). Slow addition (10 min) of a dichloromethane solution (1 mL) of 388 mg (1 mM) of trimethyl orthoselenophenylacetate

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(6) To out knowledge, the only stable diselenocarbenium ion salts reported to date are (a) 2-amino-1,3-diselenolan-2-ylium salts (Tanaka, K.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 489) and (b) 1,3-diselenolium salts (Timm, U.; Plücken, U.; Petersen, H.; Meier, H. *J. Heterocycl. Chem.* **1979**, *16*, 1303). Both of these gain considerable additional stabilization from specific structural features: the 2-amino group in the first case and the conjugated six π-electron ring system in the second.

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(16) In fact, even an instantaneous melting point can hardly be determined because the material decomposes within a few minutes already at room temperature.

Table I. Crystal Data and Experimental Settings for Structure Determination of Bis(methylthio)- and Bis(methylseleno)carbenium Ion Salts

	$C_6H_5CH_2C(SeMe)_2SbCl_6$	$C_6H_5CH_2C(SMe)_2SbCl_6$	$C_2H_5C(SMe)_2SbF_6$
formula weight	625.6	533.0	371.0
space group	*Pbca*	*Pbca*	R_3C
unit cell			
a, Å	16.372 (1)	16.276 (1)	8.520 (2)
b, Å	17.918 (1)	17.581 (8)	8.520 (2)
c, Å	13.093 (1)	13.012 (2)	8.520 (2)
$\alpha = \beta = \gamma$, deg	90	90	78.42 (2)
V, Å^3	3840.9	3723.4	585.2
Z	8	8	2
D_X	2.16	1.90	2.1
λ, Å; graphite monochromator	Mo Kα 0.71069	Mo Kα 0.71069	Cu Kα 1.54178
μ, cm^{-1}	26.9	23.7	200.4
F(000)	2352	2072	346
T, K	173 (2)	163 (2)	163 (2)
$R = \sum(\|F_o\| - \|F_c\|)/\sum\|F_o\|$	0.06	0.05	0.06
crystal shape and size, mm	nearly spherical $\bar{\phi} = 0.25$	plate, 0.40 × 0.31 × 0.08	plate, 0.35 × 0.30 × 0.10
diffractometer	Philips PW 1100	Nonius CAD-4	Nonius CAD-4
scan	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan width, deg	1.2 + 0.5 tan θ	0.9 + 0.35 tan θ	0.7 + 0.3 tan θ
ω range, deg	$3 < \omega < 22.5$	$2 < \omega < 26$	$2 < \omega < 72$
no. measured reflexions	3387	3644	1477 measured, 409 unique, *R* = 0.05
no. obsd reflexions	2813, $I > \sigma(I)$	2060, $I > 2.5\sigma(I)$	303, $I > 2.5\sigma(I)$

to a cooled (-20 °C) solution of triphenylcarbenium hexachloroantimonate in 6 mL of dry dichloromethane under argon resulted in the rapid formation of an abundant crystalline precipitate. After 30 min, the yellow mother liquor was filtered off; the crystals were washed once with 2 mL of dichloromethane and twice with ether and dried in an argon stream. During all these operations the sample was kept at -20 °C. The title compound, 550 mg (97%) (shiny pale yellow plates), was obtained: ^{1}H NMR (CD_3CN, $SiMe_4$) δ 3.12 (brs, 6 H, CH_3Se), 4.43 (s, 2 H, CH_2), 7.45 (m, 5 H, C_6H_5); ^{13}C NMR (CD_3CN, -20 °C, $SiMe_4$) δ 263.4 (C^+), 132.9, 129.9, 129, 128.9 (C_6H_5), 53.7 (CH_2), 18.5 ($SeCH_3$).

Bis(methylthio)benzylcarbenium Hexachloroantimonate (Thio Analogue of 1, R = $C_6H_5CH_2$; Y = $SbCl_6$). Addition by a syringe of 244 mg (1 mM) of triethyl orthothiophenylacetate in dichloromethane (1 mL) to a solution of 580 mg (1 mM) of triphenylcarbenium hexachloroantimonate in 6 mL of dry dichloromethane under argon and at 0 °C was immediately followed by the tumultuous formation of the title salt as colorless needles. Washing with ether and drying as above yielded 425 mg (90%) of the compound: mp (instantaneous) 143 °C; ^{1}H NMR (CD_3CN, $SiMe_4$) δ 3.08 (brs, 6 H, CH_3S), 4.50 (s, 2 H CH_2), 7.32 (m, 5 H, C_6H_5); ^{13}C NMR (CD_3CN, $SiMe_4$) δ 244.5 (C^+), 131.2, 130.2, 129.3, 129.0 (C_6H_5), 49.1 (CH_2), 21.8 (SCH_3).

It is interesting to note that all the bis(methylthio) carbenium ion salts can be prepared at room temperature (instead of 0 °C) and stored in the refrigerator (−18 °C) for several weeks. However, storage at room temperature leads to decomposition within 1 day. For the selenium analogue the optimal operating temperature is around −20 °C, even at this temperature they cannot be stored longer than 1–2 days. For this reason, elemental analyses of the carbenium ion salts could not be obtained. All the hexachloroantimonate salts are insoluble in chloroform, very slightly soluble in dichloromethane, and quite soluble (more than 100 mg/mL) in acetonitrile or nitromethane. The latter solvents were used for recrystallization for X-ray purposes. Typically, one batch of about 550 mg of bis(methylseleno)benzylcarbenium hexachloroantimonate was quickly dissolved under argon in 1.5 mL of dry nitromethane at room temperature so that a nearly saturated pale yellow solution resulted. This was immediately placed in the refrigerator (-18 °C), and on standing for 4–5 h it deposited 20–30 crystals, which were suitable for X-ray diffraction.

Diethoxyethylcarbenium tetrafluoroborate was prepared in high yield from triethyl orthopropionate and boron trifluoride–ether complex according to literature procedure.[17]

As indicated in eq 1, some complex silver salts also generate bis(methylthio)- and bis(methylseleno)carbenium ions on reaction with the corresponding orthothio- or orthoselenoesters. However, since silver methyl sulfide and silver methyl selenide are very insoluble compounds, this method requires careful choice of the reaction solvent and the counter anion (Y^-), so that the carbenium ion salt formed be completely soluble even at lower temperatures. We noticed that fluorinated anion-containing salts are markedly more soluble (in dichloromethane, for example) than those containing chlorinated anions, and tetrafluoroborates are more soluble than hexafluoroantimonates. Also, (methylseleno)carbenium ion salts are somewhat more soluble than the thio analogues. Altogether, preparation of bis(methylseleno)carbenium salts according to this method is more tedious because, due to their greater instability, low-temperature evaporation of relatively larger amounts of solvent is required. We have used the silver salt method for the preparation of the lower homologues (**1**, R = H, CH_3). These experiments were primarily devoted to testing the possibility of using these cation salts as reagents, so that the latters were not isolated.

Temperature-dependent ^{1}H NMR experiments have been carried out for the hexachloroantimonate salts of bis(methylthio)benzyl-, bis(methylseleno)benzyl-, and bis(methylthio)ethylcarbenium ions in deuterioacetonitrile solution at ca. 5% (w/w) concentration and in the temperature range of -45 to 50 °C and 25.5 °C, respectively.

Exchange rate constants have been determined by the line-shape simulation method. Computations have been performed using an interactive graphic program based on classical two-sites exchange theory.[18] The mean lifetimes have been varied until the best visual fit with the experimental spectra was reached. In this way, the rate constants could be calculated with an accuracy of ±5%. Activation energies (E_a) were determined by linear regression analysis of Arrhenius plots.

X-ray Structure Determinations. Crystal data and experimental conditions for structure determination of bis(methylseleno)benzylcarbenium hexachloroantimonate, bis(methylthio)benzylcarbenium hexachloroantimonate, and bis(methylthio)ethylcarbenium hexafluoroantimonate are collected in Table I.

Scattering factors were taken from *International Tables for X-ray Crystallography*. For both benzylcarbenium salts, the structure was solved by direct methods;[19] *E* maps based on the most probable set of phases revealed the inorganic moiety. Subsequent difference-Fourier maps disclosed all the remaining atoms (H atoms excepted).

In the case of bis(methylthio)ethylcarbenium hexafluoroantimonate, space group symmetry considerations and unit cell content as reported in Table I allowed formulation of the following starting hypothesis for the structure. Central atoms of both anionic (Sb) and cationic (C^+) moieties should lie on special positions. Accordingly, Sb and C^+ atoms were assigned the coordinates (000) and ($^1/_4{}^1/_4{}^1/_4$), respectively, and the subsequent Fourier map revealed the remaining atoms (H atoms excepted). It follows that the cationic moiety must mimic a threefold symmetry around the central C^+ atom, and, therefore, proportionally adopted form factors ($^2/_3$S, $^1/_3$C) were used during the refinement.

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Table II. ^1H Chemical Shifts (δ, $SiMe_4$) of (a) Carbenium Ions[a] $C_\gamma H_3C_\beta H_2C^+_\alpha(XCH_3)_2$ and of (b) the Corresponding Acetals[b] $C_\gamma H_3C_\beta H_2C_\alpha H(XCH_3)_2$

	X								
	O			S			Se		
	a[c]	b	Δδ	a	b	Δδ	a	b	Δδ
H_α		4.26			3.44			3.75	
H_β	2.98	1.56	1.42	3.40	1.74	1.66	3.27	1.92	1.35
H_γ	1.21	0.86	0.35	1.46	1.04	0.42	1.47	1.04	0.43
XCH_3	4.95[d]	3.24	1.71[d]	3.08	1.98	1.10	3.04	1.90	1.14

[a] $SbCl_6^-$ salts in CD_3CN solution and at room temperature. [b] All in CCl_4 solution. [c] These are chemical shifts of the diethoxyethylcarbenium ion. [d] Methyldimethoxycarbenium ion in 30% $SO_3 \cdot H_2SO_4$, from ref 26.

Refinement of positional and thermal parameters was carried out by full-matrix least-squares calculations.[20] Positional and thermal parameters of the non-hydrogen atoms for the three compounds are given in the supplementary material.

Results and Discussion

Two bis(methylseleno)carbenium ion salts (**1**, R = C_2H_5, $C_6H_5CH_2$; Y = $SbCl_6$) as well as their thio analogues have been prepared according to eq 1 and investigated in some detail from the structural point of view by ^1H and ^{13}C NMR and by X-ray diffraction. For comparison purposes, we have also prepared the oxo, thio, and seleno acetals of propionaldehyde.

^1H NMR Spectra. Proton chemical shifts have long been used to characterize the structure and to quantify the amount of positive charge at various positions of carbenium ions.[21,22] The most valuable information has been obtained concerning neutralization of the charge by inductive or mesomeric effects in homologous series of cations, such as 2-alkyl- or 2-aryl-1, 3-dioxolanylium ions.[22] However, when trying to compare the influences of charge delocalization and stabilization in species bearing heteroatomic substituents, it is necessary to take into account factors affecting the chemical shifts other than charge density.[23] An attractive way of doing this is to consider difference chemical shifts, Δδ, rather than chemical shifts themselves.[24] The data for the cations $CH_3CH_2C(XCH_3)_2^+$ (X = O, S, Se) and the corresponding acetals chosen as reference compounds are summarized in Table II. It is probably the most interesting to examine the resonances due to the β-hydrogens of the different compounds. In the cationic species, they all occur in the same region, around 3 ppm. We can therefore draw as a major conclusion that sulfur and selenium are very similar to oxygen in their ability to disperse the positive charge of the central carbon atom. The same conclusion is arrived at on the basis of the Δδ values. However, both sets of values fail to produce the expected order O >S >Se (which is probably the correct one), since δ gives O >Se >S and Δδ gives Se >O >S. This can be due to the fact that either the choice of the reference compounds is wrong or more likely that in the cations we are faced with new diamagnetic anisotropy, permanent electric field, and polarizability effects that are not the same in any reference compound. The same comments pertain to the resonances of nearly all other hydrogens. The only exception would be the γ position, but the differences are too small. Although independent of the present problem, it is interesting to note the regular downfield shift of the β-methylene protons in the acetals on going from oxygen to sulphur to selenium. The same type of variation was observed[25] for the methyl groups in ketals of methyl ketones.

Table III. Rate Constants (s^{-1})[a] of Hindered Rotation in Bis(methylthio)- and Bis(methylseleno)carbenium Ions

T, °C	$C_6H_5CH_2C^+$-$(SeCH_3)_2$	$C_2H_5C^+$-$(SCH_3)_2$	$C_2H_5CH_2^+$-$(SCH_3)_2$
−45	0.7		
−39		1.0	
−27		1.7	
−25	10		
−18	25		0.7
−17		2.5	
−9		2.8	
−7.5	66.7		1.7
3.5	166.7		5
4.5		5	
10.5		11	
14.5	333		12.5
18.5		12.5	
25.5	500		35.7
26.5		20	
30			45.4
39		71.4	
40			125
50			250
51		100	

[a] As obtained by the line-shape simulation method with an accuracy of ±5%.

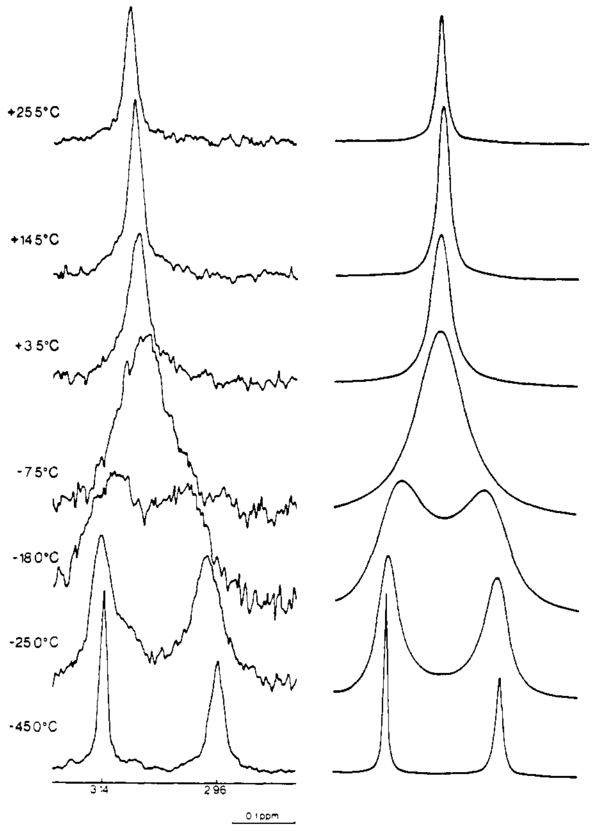

Figure 1. Effect of temperature on the $SeCH_3$ signal of $C_6H_4CH_2(SeCH_3)_2SbCl_6$ in CD_3CN.

In addition to chemical shift similarities between alkoxyalkyl, bis(methylthio)alkyl, and bis(methylseleno)alkyl cations, their proton NMR spectra also resemble each other in that they all appear to be temperature dependent. Thus, the XCH_3 (X = S or Se) groups of all the carbenium ion salts reported here appear (δ 3.04–3.12) at room temperature as broad singlets, which can reversibly be sharpened by slightly raising the temperature and resolved into two separate relatively sharp signals at moderately low temperatures (-20 to -40 °C). This cycle can be repeated several times, but then more and more decomposition can be detected especially in the case of the selenocarbenium salts. As

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Table IV. Arrhenius Activation Energies for Hindered Rotation for Carbenium Ions

derivatives	E_a, kcal/mol	solvent	ref
$CH_3C(OH)_2^+$	13.5 ± 0.6	$HF-BF_3$	28
	12.6 ± 0.6	$HFSO_3-SbF_5-SO_2$	
	11.2 ± 0.2	$HF-SbF_6$	
$HC(OH)_2^+$	15.3 ± 0.9	$HF-SbF_5$	28
$CH_3C(OCH_3)_2^+$	11 ± 4	CF_3COOH	26
$HOC(OCH_3)_2^+$	8 ± 2	$HFSO_3-SbF_5-SO_2$	27
$C_2H_5C(SCH_3)_2^+$	8 ± 2	CD_3CN	
$C_6H_5CH_2C(SCH_3)_2^+$	14 ± 2	CD_3CN	
$C_6H_5CH_2C(SeCH_3)_2^+$	13 ± 2	CD_3CN	

Table V. ^{13}C Chemical Shifts (δ, $SiMe_4$)[a] of Carbenium Ions $R_{1\,\gamma}C_\beta H_2C^+{}_\alpha(XCH_3)_2$

R_1	X	C_α	C_β	C_γ	XCH_3
CH_3	O[b]	191.6	26.7	6.3	
CH_3	S	246.9	38.3	12.2	21.6
C_6H_5	S	244.5	49.1	131.2[c] (130.2, 129.3, 129.0)	21.8
CH_3	Se	265.3	42.8	13.7	18.4
C_6H_5	Se	263.4	53.7	132.9[c] (129.9, 129.0, 128.9)	18.5

[a] $SbCl_6^-$ salts in CD_3CN solution and at room temperature, except for the selenium derivative recorded at -20 °C. [b] Chemical shifts of diethoxyethylcarbenium ion (BF_4^- salts). [c] Ipso carbon atom; other aromatic carbons in parentheses.

Table VI. ^{13}C Chemical Shifts (δ, $SiMe_4$)[a] of the Acetals $C_\gamma H_3C_\beta H_2C_\alpha H(XCH_3)_2$

X	C_α	C_β	C_γ	XCH_3
O	105.8 (85.8)	25.6 (1.1)	9.4 (−3.1)	52.7
S	56.6 (190.3)	28.3 (10.0)	12.1 (0.1)	12.6 (9.0)
Se	39.4 (225.4)	30.1 (12.7)	13.4 (0.3)	4.9 (13.5)

[a] In CD_3Cl at room temperature. Difference chemical shifts ($\Delta\delta$) with the corresponding carbenium ions (from Table V) are given in parentheses.

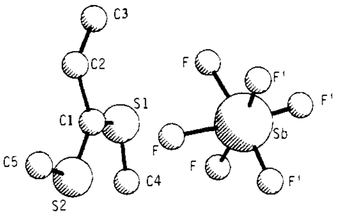
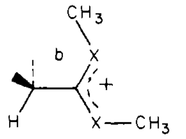


Figure 2. Molecular structure of $C_2H_5C(SCH_3)_2SbF_6$.

in the case of oxocarbenium ions,[26-28] we attribute the above behavior to conformational changes in the cations through hindered rotation around the $C-XCH_3$ bonds. Rate constants for two sulfur and one selenium derivatives as obtained from line-shape simulation calculations[18] are given in Table III, and experimental vs. theoretical spectra for bis(methylseleno)benzylcarbenium ion are shown in Figure 1. Arrhenius activation energies together with literature data[26-28] for some oxocarbenium ions are listed in Table IV. Line-shape simulation was based on the two-site exchange model with equal populations. In all three cases the higher field components of the low-temperature doublets showed some fine structure most likely arising from an incompletely resolved long-range coupling with the β-CH_2 protons. We did not attempt to reproduce this fine structure on the simulated spectra.

Presumably the preferred conformation of these ions in solution is



a

similar to that suggested for dimethoxymethyl cation[26] with methyl group a resonating at higher field. Table IV indicates that the barrier to rotation has comparable values in all cases (8–15 kcal/mol) regardless the nature of the heteroatomic substituents. This points to similar percentages of double-bond character for the three types of cations, in agreement with the high π bond orders as estimated from X-ray structure data (vide infra, Table VIII).

^{13}C NMR Spectra. Considerable effort has been devoted in recent years to work out suitable correlations between carbon chemical shifts and calculated charge densities.[27,29-32] Olah and White found an excellent linear relationship with a slope of 306 ppm per electron between ^{13}C chemical shifts of mono, di- and trioxocarbenium ions and their π charges as determined by the simple Hückel method.[27] This relationship has been applied and confirmed in the case of 1,3-dioxolan-2-ylium ions[33] and successfully extended to cyclic oxonium ions even though more elaborate methods were used in the calculation.[32] Therefore, we expect ^{13}C chemical shifts to reflect better π charge delocalization than do ^1H chemical shifts also in the case of our heterosubstituted cations. This is borne out qualitatively by the data gathered in Tables V and VI. Especially striking are the $\Delta\delta$ values (parentheses in Table VI) observed for the α-carbon atoms of oxygen, sulfur, and selenium-substituted ions (86, 190, and 225 ppm, respectively). Due to the heavy atom effect (upfield carbon chemical shift) clearly present in selenium derivatives, we feel the picture given by $\Delta\delta$ more reliable than that given by δ itself. Indeed the latter would indicate only a moderate change in charge density on the α-carbon atom of the order of 0.18 unit charge difference between O and S and 0.06 unit charge difference between S and Se stabilized cations, as calculated from Table VI and by Olah's equation.[27] If, however, $\Delta\delta$ is used for the same calculation, the charge differences one obtains are ~0.35 and ~0.12, respectively. Although the correlation of Olah and White includes very different substitution pattern it is by no means established that it applies without any slope adjustment to the carbenium ions discussed here. Therefore, in the absence of thorough verification by appropriate theoretical calculations, the above figures only represent rough estimates rather than real values. In spite of this limitation, it appears quite clear that there is much smaller difference between sulfur and selenium than between oxygen and sulfur in their ability to stabilize the positive charge of carbenium ions. This finding is in qualitative agreement with rate differences found in the hydrolysis of vinyl ethers, vinyl sulfides, and vinyl selenides.[8] On a smaller scale, a similar but sharper trend is found when $\Delta\delta$'s of the β-carbon atoms are examined (Table VI, note again the downfield shift for $C\beta$ of the O, S, and Se acetals). As already observed in other cases,[1] the effect of the positive charge on the C_γ chemical shifts drops nearly to zero (Table VI); the small negative $\Delta\delta$ for the oxo derivative might be due to solvent effect. Finally, Table V shows that a change in the nature of the alkyl substituent modifies only slightly the chemical shift of the positively charged carbon atom.

X-ray Diffraction. Despite the fact that stable oxonium salts have been known for several decades, X-ray structure determination of some 1,3-dioxolan-2-ylium salts have been reported only recently.[34,35] Such data are even scarcer for sulfur-substituted

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Table VII. Bond Distances (Å) and Selected Bond Angles (deg) and Torsion Angles (deg) for Bis(methylthio)- and Bis(methylseleno)carbenium Ion Salts

	$C_2H_5C(SCH_3)_2SbF_6$		
	Bond Distances		
Sb–F	2.00 (3)	C_1–S_1	1.67 (1)[a]
Sb–F′	1.75 (2)	C_4–S_1	1.64 (5)[a]
	Bond Angles[b]		
C_1–S_1–C_4	110 (2)	S_1–C_1–S_2	120 (1)
	$C_6H_5CH_2(SMe)_2SbCl_6$		
	Bond Distances		
Sb_1–Cl_1	2.378 (3)	C_1–C_4	1.50 (2)
Sb_1–Cl_2	2.375 (3)	C_4–C_5	1.51 (2)
Sb_1–Cl_3	2.354 (3)	C_5–C_6	1.38 (2)
Sb_1–Cl_4	2.365 (3)	C_5–C_{10}	1.41 (2)
Sb_1–Cl_5	2.329 (4)	C_6–C_7	1.37 (2)
Sb_1–Cl_6	2.381 (3)	C_7–C_8	1.40 (2)
S_1–C_1	1.68 (1)	C_8–C_9	1.36 (2)
S_1–C_3	1.79 (2)	C_9–C_{10}	1.38 (2)
S_2–C_1	1.67 (1)		
S_2–C_2	1.80 (1)		
	Bond Angles[c]		
C_1–S_1–C_3	103.4 (7)	S_1–C_1–S_2	120.3 (8)
C_1–S_2–C_2	104.9 (6)	S_1–C_1–C_4	117 (1)
C_1–C_4–C_5	116 (1)	S_2–C_1–C_4	123 (1)
	Torsion Angles		
C_3–S_1–C_1–S_2	−179.4 (10)	S_1–C_1–C_4–C_5	173.3 (14)
C_3–S_1–C_1–C_4	0.4 (10)	S_2–C_1–C_4–C_5	−6.4 (9)
C_2–S_2–C_1–S_1	−0.6 (8)	C_1–C_4–C_5–C_6	−93.1 (14)
C_2–S_2–C_1–C_4	179.2 (12)	C_1–C_4–C_5–C_{10}	85.5 (14)
	$C_6H_5CH_2C(SeMe)_2SbCl_6$		
	Bond Distances		
Sb_1–Cl_1	2.383 (3)	C_1–C_4	1.49 (1)
Sb_1–Cl_2	2.378 (3)	C_4–C_5	1.51 (1)
Sb_1–Cl_3	2.358 (3)	C_5–C_6	1.40 (2)
Sb_1–Cl_4	2.363 (3)	C_5–C_{10}	1.41 (1)
Sb_1–Cl_5	2.338 (3)	C_6–C_7	1.36 (2)
Sb_1–Cl_6	2.389 (3)	C_7–C_8	1.40 (2)
Se_1–C_1	1.83 (1)	C_8–C_9	1.37 (2)
Se_1–C_3	1.96 (1)	C_9–C_{10}	1.43 (2)
Se_2–C_1	1.84 (1)		
Se_2–C_2	1.96 (1)		
	Bond Angles[c]		
C_1–Se_1–C_3	100.8 (5)	Se_1–C_1–Se_2	119.3 (6)
C_1–Se_2–C_2	100.1 (5)	Se_1–C_1–C_4	122.1 (9)
C_1–C_4–C_5	113 (1)	Se_2–C_1–C_4	118.6 (9)
	Torsion Angles		
C_3–Se_1–C_1–Se_2	−179.2 (5)	Se_1–C_1–C_4–C_5	173.9 (6)
C_3–Se_1–C_1–C_4	0.8 (8)	Se_2–C_1–C_4–C_5	−6.2 (8)
C_2–Se_2–C_1–Se_1	−0.3 (5)	C_1–C_4–C_5–C_6	−95.3 (9)
C_2–Se_2–C_1–C_4	179.8 (6)	C_1–C_4–C_5–C_{10}	86.5 (9)

[a] As a result of the apparent threefold symmetry, all other distances are the same. [b] All F–Sb–F′ angles are close to 90° or 180°. [c] All Cl–Sb–Cl angles are close to 90° or 180°.

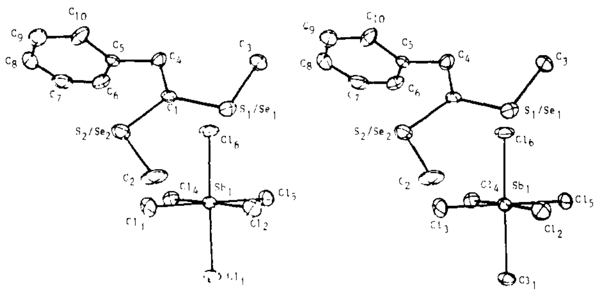

Figure 3. Molecular structure of $C_6H_5CH_2C(SeCH_3)_2SbCl_6$ and of $C_6H_5CH_2C(SCH_3)_2SbCl_6$.

Table VIII. Bond Lengths and Bond Orders in Oxo-, Thio-, and Selenocarbenium Ions

bond	single	double	cation	π bond order[a]
C–O	1.41[b]	1.22[c]	1.26[d] 1.29[d]	0.7–0.8
C–S	1.81[c]	1.54[c]	1.68[e]	0.5
C–Se	1.98[c]	1.67[c]	1.84[e]	0.5

[a] Estimated by graphic interpolation on linear plots of bond length vs. bond order. [b] Bond distance in 1,3-dioxolane, ref 33. [c] Taken from: Sutton, L. E., Ed. "Tables of Interatomic Distances and Configuration in Molecules and Ions"; The Chemical Society: London, 1965. [d] Reference 33. [e] Taken from Table VII.

carbenium ions since the only structure reported is that of tris(methylthio)carbenium tetrachloroferrate,[36] and of course no selenium derivatives have been studied. For this reason, we decided to investigate the X-ray crystal structure of one of our bis(methylseleno)carbenium ion salts as well as the corresponding sulfur derivative and to compare them with existing data on 1,3-dioxolan-2-ylium salts.

For reasons of availability X-ray diffraction study was started with bis(methylthio)ethylcarbenium hexafluoroantimonate (Figure 2 and Table VII). The cation of this compound appears to be planar with bond angles of nearly 120°. As stated before (Experimental Section), space group symmetry and density considerations impose special positions for both antimony and positive carbon atoms ((000) and ($^1/_4{}^1/_4{}^1/_4$) coordinates, respectively). Therefore the organic moiety should possess in the crystal an average threefold symmetry, which makes this cation crystallographically identical with tris(methylthio)carbenium ion. We think the nearly isosteric nature of a methylene group with a sulfur atom is at the origin of this identity. Due to be threefold positional degeneracy of ligands around the central carbon atom, all three bonds appear as averages of the two C–S and C–C bonds. It is therefore impossible in this particular case to determine correct bond distances for the cationic part. However, inspection of the antimony–fluorine distances (Table VII) unveils an interesting consequence of the above-mentioned arrangement following the threefold symmetry axis running through the C^+ and antimony atoms. Three of the six fluorine atoms lie in closer proximity to the plane of the cation than do the other three. Therefore, the stronger cation–anion interaction gives rise to considerable lengthening of the former three Sb–F bonds. Similar, though less spectacular, differentiation of bond distances in SbF_6^- anion has been observed earlier.[37]

In order to break up the apparent threefold symmetry of the cation, we next studied bis(methylthio)benzylcarbenium hexachloroantimonate and its seleno analogue. Figure 3 shows the three-dimensional structures of these species, and bond lengths and bond angles as well as main torsional angles are displayed in Table VII. In both derivatives the antimony–chlorine distances of the $SbCl_6^-$ anions appear much more homogeneous than the corresponding ones in the previous case. The slight dispersion in these bond lengths has been explained in terms of ionic contacts between cation and anion in the crystal.[38]

Both cations show trigonal geometry around the positively charged carbon atom with mean bond angles of 120°. They exhibit very similar molecular conformations as can be judged from the torsional angles listed in Table VII.

As to the problem of positive charge dispersion and stabilization by the heterostaomic substituents, the most relevant information

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stems from the C–heteroatom distances. In order to appreciate the effect of the presence of a positively charged carbon atom, we listed in Table VIII the C–heteroatom bond lengths of oxo-, thio-, and selenocarbenium ions together with typical single- and double-bond lengths of carbon with each heteroatom. Obviously, we see very significant bond shortening in all three types of carbenium ions. These bond shortenings can be converted into bond–order changes, at least on an approximate level, by means of interpolation on bond length vs. bond order plots, taken as straight lines for simplicity. The results of this procedure are also listed in Table VIII. It is to be noted, however, that because of the small negative slopes in the bond length vs. bond order plots a small variation in bond length gives rise to a large change in bond order, so that the error on the estimated bond orders in Table VIII may be quite important. The following example illustrates this point. In the case of bis(methylthio)benzylcarbenium ion, we determined $C_1^+{-}S_1$ and $C_1^+{-}S_2$ distances of 1.68 (1) and 1.67 (1) Å, respectively (Table VII). On the other hand, crystal structures of 1,2-dithiolylium ions have also been determined,[39,40] and the reported C–S bond length in bis(3,5-dimethyl-1,2-dithiolylium) tetrachloroferrate(II)[40] is 1.69 (2) Å, which is nearly identical with the values we found. Yet, the π bond orders are quite different, $\sim$0.50 in our case and 0.67 in 1,2-dithiolylium ion.[39] This difference most certainly arises from the $C{=}S$ bond length used to assess π bond orders, 1.61 Å in the case of 1,2-dithiolylium ion and 1.54 Å in ours.

Regardless the precise numerical values, inspection of Table VIII leads to the conclusion that the positive charge of the species we examined is efficiently delocalized and nearly to the same extent by both methylthio and methylseleno substituents.

A priori it may seem difficult to admit extensive overlap between the large 4p orbitals of selenium and the 2p orbital of the adjacent positive carbon atom. However, a plausible mechanism for making this overlap operational might be the valence-shell contraction of selenium under the influence of the strong ligand field due to the neighboring positive charge. Such phenomena have often been invoked in the past for the description of bonding in molecules containing third- and fourth-row elements.

Finally, the results we report here have bearing on the question of charge delocalization in species like 1,3-dithiol-2-ylium and 1,3-diselenol-2-ylium ions, which have been the subject of some controversy in recent years. It was indeed suggested[6b,41] for both ions that the whole positive charge resides on the C2 carbon atom with essentially no delocalization into the rest of the systems, the latters having therefore no aromatic character. Our results point to the opposite in accordance with the conclusion arrived at from ^{13}C chemical shift measurements.[42]

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Supplementary Material Available: Tables of amplitudes of thermal vibrations, fractional atomic coordinates, equivalent isotropic thermal parameters, and observed and calculated structure factors for **1**, R = $C_6H_5CH_2$, $Y^- = SbCl_6^-$, and its thio analogue (14 pages). Ordering information is given on any current masthead page.

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Affinities of Crown Ethers, Glymes, and Polyamines for Alkali Picrates in Toluene. Application of Polymer-Supported Linear Polyethers

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Abstract: A scale of relative ligand affinities of crown ethers, linear polyethers (glymes), polyamines, and other cation-binding ligands for lithium and sodium picrate in toluene at 25 °C was obtained. The experimental procedure utilizes solvent-swollen microporous polystyrene resins to which crown ethers or linear polyethers are anchored. The immobilized ligands, N*, are allowed to compete with a soluble ligand, L, for the ionic solute, A^-M^+, according to the reaction $A^-M^+N^* + L \rightleftarrows A^-M^+L + N^*$. The equilibrium constant, *K*, is calculated from the spectrophotometric determination of the soluble ligand–picrate salt complex A^-M^+L. For glymes the *K* values for lithium and sodium picrate rapidly increase up to glyme 5 (tetraethylene glycol dimethyl ether). For longer glymes the increase in *K* is chiefly due to a statistical factor as the number of binding sites increases. On a molar basis long-chain linear polyethers such as carbowax 6000 (134 oxygen atoms) have affinities comparable to those of crown ethers. Measurements of *K* for the same soluble ligand but with different resins afford a comparison of the affinities of immobilized ligands for picrate salts as a function of ligand structure and ligand content of the network. For example, the affinity of a benzo-18-crown-6 containing resin for sodium picrate in toluene exceeds that of a glyme-7 resin with the same ligand content by a factor 265. An increase in ligand content of the resin enhances the *K* for that resin. Measurements were also performed with a transparent, flexible, cross-linked polyacrylate film containing immobilized glyme chains. The implications of our results for phase transfer catalysis reactions are briefly discussed.

We recently demonstrated that crown ethers immobilized on cross-linked polystyrene resins can be used to determine formation constants of complexes between ionic solutes and ion binding ligands in solvents such as tetrahydrofuran or dioxane.[1,2] In the procedure the soluble ligand, L, and the immobilized crown, Cr*, are allowed to compete for the ionic solute according to the reaction

$$A^-M^+Cr^* + L \rightleftarrows A^-M^+L + Cr^* \qquad (1)$$

By using a picrate salt the release of A^-M^+L can be monitored

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