

from ref 23. Hydrogen positions were computed and refined by using a riding model with C-H distances constrained with an overall isotropic temperature factor and anisotropically the remaining atoms. The final R was 0.053 ($R_w = 0.054$) for all observed reflections. **Complex 10.** Crystal data: $C_{13}H_8N_2ClO_5Rh$, fw 410.58; triclinic; space group $P\bar{1}$; $a = 6.555$ (2) Å, $b = 8.868$ (2) Å, $c = 13.236$ (3) Å, $\alpha = 104.82$ (2)°, $\beta = 104.51$ (2)°, $\gamma = 83.88$ (2)°; $V = 719.3$ (5) Å³; D_{calc} 1.89 g cm⁻³, $Z = 2$; $F(000) = 404$; $\gamma(\text{Mo K}\alpha) = 0.71069$ Å; $\mu(\text{Mo K}\alpha) = 13.63$ cm⁻¹; room temperature; crystal dimensions $0.1 \times 0.1 \times 0.15$ mm; Enraf-Nonius CAD-4 diffractometer; monochromatized Mo K_c radiation; $\theta-2\theta$ technique; 2664 reflections in the range $2 \leq \theta \leq 25^\circ$, 2140 observed [$I \geq 2.5\sigma(I)$]. Lorentz-polarization and absorption corrections were applied. The structure was solved by direct methods (MULTAN²⁴). The structure was refined by treating nonhydrogen atoms anisotropically by full-matrix least-squares methods, using SHELX 76,²² to a final R value of 0.037 ($R_w = 0.036$). The function

minimized was $w\{|F_o| - |F_c|\}^2$, where $w = \{\sigma^2|F_o| + 0.0037|F_o|^2\}^{-1}$ and f, f' , and f'' values were taken from ref 23. Hydrogen atoms were not located.

Tables III and IV give the atomic coordinates for non-hydrogen atoms of complexes 4 and 10, respectively.

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Supplementary Material Available: Tables of anisotropic thermal coefficients of compounds 4 and 10 and computed H atoms of compound 4 (3 pages); listings of observed and calculated structure factors for compounds 4 and 10 (15 pages). Ordering information is given on any current masthead page.

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Synthesis and Molecular Structure of EtGe(SePh)₃: An Unusual Example of Alkylation by LiEt₃BH

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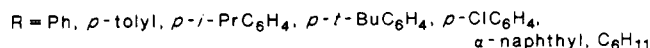
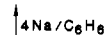
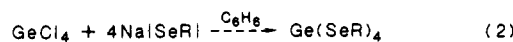
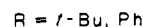
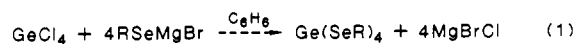
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The reaction of GeCl₄ with 4 equiv of Li[SePh], generated by the reductive cleavage of Ph₂Se₂ with LiEt₃BH in tetrahydrofuran, gave a mixture of Ge(SePh)₄ and EtGe(SePh)₃. These products were separated by fractional crystallization from a hexane solution and characterized by ¹H and ⁷⁷Se NMR spectroscopy and single-crystal X-ray diffraction. The latter compound is the first well-characterized example of ethylation of a metal halide via LiEt₃BH. Crystals of Ge(SePh)₄ are orthorhombic, *Pbca*, with $a = 17.111$ (2) Å, $b = 8.513$ (1) Å, $c = 8.455$ (3) Å, and $Z = 2$. The structure was solved by direct methods and refined by the full-matrix least-squares method to $R = 0.023$. Crystals of EtGe(SePh)₃ are triclinic, *P1*, with $a = 10.631$ (1) Å, $b = 11.022$ (2) Å, $c = 10.166$ (1) Å, $\alpha = 115.048$ (9)°, $\beta = 99.908$ (8)°, $\gamma = 90.864$ (9)°, and $Z = 2$. The structure was solved by the heavy-atom method and refined to $R = 0.025$. The geometry about the Ge in both compounds is approximately tetrahedral. The Ge-Se bond distances are in the range 2.344-2.356 Å, and the Ge-C distance in EtGe(SePh)₃ is 1.952 Å.

Introduction

Although selenium ligand chemistry involving transition metals has been the subject of considerable work,¹ relatively little has been reported concerning analogous materials with main group elements such as germanium.² An early paper³ described the synthesis of several derivatives of the type Ge(SeR)₄, their characterization being limited to elemental analyses and melting points:

Subsequently several other organogermanium compounds incorporating Ge-Se bonds were described ($\{\text{Me}_2\text{GeSe}\}_3$,⁴ $\text{Se}(\text{GeR}_3)_2$ ($\text{R} = \text{Me},^5 \text{Et},^6 \text{Ph},^7 \text{C}_6\text{F}_5^8$), Et_3GeSeH ,^{6b} $\text{Et}_3\text{GeSeSnEt}_3$,^{6b} $\text{Ph}_3\text{GeSeSeGePh}_3$,⁹ $\text{R}_3\text{GeSeHgGeR}_3$ ($\text{R} = \text{Et}, i\text{-Pr}$),¹⁰ and $(t\text{-Bu})_2\text{Ge}(\mu\text{-Se})_2\text{Ge}(t\text{-Bu})_2$).¹¹ In addition, crystal structures have been reported for the cyclic polygermanes $\{(\text{Ph}_2\text{Ge})_4\text{Se}\}^{12}$ and



$\{(\text{Ph}_2\text{Ge})_3\text{Se}_2\}$,¹³ 1,3-diselena-2,2-dichlorogermyl-[3]-ferrocenophane ($\text{Fe}(\text{C}_5\text{H}_4\text{Se})_2\text{GeCl}_2$),¹⁴ and GeSe_2 ¹⁵ as well

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Table I. Ge-Se Distances in Some Reported Structures

compound	Ge-Se, Å	ref
GeSe ₂	2.337-2.365	15
Na ₃ Ge ₄ Se ₁₀	2.294-2.335 (terminal)	16a
	2.420-2.456 (bridge)	
Na ₄ [GeSe ₄] ₁₄ H ₂ O	2.350	16d
Tl ₄ [Ge ₄ Se ₁₀]	2.287 (terminal)	16f
	2.380 (bridge)	
(PhGe) ₄ Se	2.373	12b
Ph ₆ Ge ₃ Se ₂	2.37	13
[Fe(C ₅ H ₄ Se) ₂] ₂ GeCl ₂	2.323	14
	2.325	
Ge(SePh) ₄	2.344, 2.347	a
EtGe(SePh) ₃	2.348-2.356	a

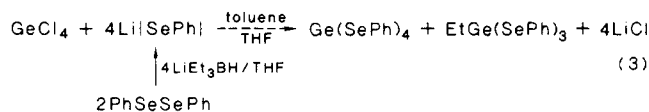
^aThis work.

as a variety of selenogermanate anions¹⁶ (see Table I for some typical Ge-Se bond distances).

We report here the details of the reaction of GeCl₄ with Li[SePh], generated in THF by reductive cleavage of Ph₂Se₂ with LiEt₃BH (Superhydride). This reaction gave, in addition to the expected product Ge(SePh)₄, a product resulting from germanium ethylation, EtGe(SePh)₃.

Results and Discussion

Synthesis and Properties of Ge(SePh)₄ and EtGe(SePh)₃. The reaction of a GeCl₄ solution in toluene with a THF solution of 4 equiv of Li[SePh], generated by the in situ reductive cleavage of Ph₂Se₂ with LiEt₃BH (eq 3),



gave a mixture of Ge(SePh)₄ and EtGe(SePh)₃, the ratio

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Table II. Summary of Crystal Data and Refinement Parameters

	Ge(SePh) ₄	EtGe(SePh) ₃
formula	Se ₄ GeC ₂₄ H ₂₀	Se ₃ GeC ₂₀ H ₂₀
MW	696.86	569.85
space group	<i>Pba</i> 2	<i>P</i> $\bar{1}$
cell constants at 23 (1) °C		
<i>a</i> , Å	17.111 (2)	10.631 (1)
<i>b</i> , Å	8.513 (1)	11.022 (2)
<i>c</i> , Å	8.455 (3)	10.166 (1)
α , deg	90	115.048 (9)
β , deg	90	99.908 (8)
γ , deg	90	90.864 (9)
<i>V</i> , Å ³	1231.6 (7)	1058 (1)
no. of molecules/unit cell (<i>Z</i>)	2	2
<i>D</i> (calcd), g cm ⁻³	1.878	1.789
cryst dimens, mm	0.24 × 0.30 × 0.38	0.28 × 0.33 × 0.38
abs coeff (μ (Mo K α)), cm ⁻¹	70.8	65.4
scan technique	ω -2 θ	ω -2 θ
scan rate, deg 2 θ min ⁻¹	1.7-20	2.4-20
2 θ limit, deg	50	46
<i>hkl</i> range	0 to 10, 0 to 10, 0 to 20	-11 to +11, 0 to 12, -11 to +11
no. of unique data measd	1166	2939
no. of data used in refinement (<i>I</i> > σ (<i>I</i>))	1048	2632
no. of parameters	171	297
<i>R</i> = $\sum F_o - K F_c / \sum F_o $	0.023	0.025
<i>R_w</i> = $(\sum w(F_o - K F_c)^2 / \sum w F_o^2)^{1/2}$	0.032	0.039
<i>S</i> = $(\sum w(F_o - K F_c)^2 / (n_o - n_v))^{1/2}$	0.92	1.03
wtg parameters ($w^{-1} = \sigma^2(F_o) + (pF_o)^2 + q$)		
<i>p</i>	0.03	0.03
<i>q</i>	0	1.0
scale factor, <i>K</i>	2.029 (5)	2.880 (7)
max shift in final cycle (Δ/σ)	0.10 σ	0.15 σ
residual electron density in final diff Fourier synthesis, e/Å ³	-0.25 to +0.38	-0.20 to +0.50

of the products depending on the reaction conditions. The pure products were isolated by concentration of the reaction solution to dryness and extraction/fractional crystallization of the two compounds with hexane. The less soluble product Ge(SePh)₄ can be readily separated from the considerably more soluble EtGe(SePh)₃ by this procedure.

If the reaction solution is stirred at room temperature for 36 h and then refluxed for 12 h, EtGe(SePh)₃ is the only product. The ⁷⁷Se NMR spectrum of this reaction solution shows a single resonance at 158.3 ppm (downfield from SeMe₂) assigned to this ethyl derivative. After filtration of the reaction solution, concentration of the filtrate to dryness, extraction of the residue with hot hexane, and crystallization of the yellow product at low temperature a yield of 89.3% EtGe(SePh)₃ was obtained (characterized by elemental analysis, field desorption mass spectroscopy, and ¹H and ⁷⁷Se NMR spectroscopy). The melting point of this new compound is 78 °C. The ¹H NMR spectrum of this product shows aromatic and ethyl resonances in a 3:1 ratio (o-H, δ 7.43 (d, 6, *J* = 8 Hz); m-H, δ 7.13 (t, 6, *J* = 8 Hz); p-H, δ 7.20 (t, 3, *J* = 7 Hz); CH₂, δ 1.34 (q, 2, *J* = 8 Hz); CH₃, δ 0.92 (t, 3, *J* = 8 Hz)). If the initial reaction solution is stirred at room temperature for 4 h and then refluxed for 20 h and worked up as described above, both Ge(SePh)₄ and EtGe(SePh)₃ were isolated in yields of 20.5% and 64.2%, respectively. The ⁷⁷Se NMR spectrum

Table III. Positional Parameters (Esd's in Parentheses) for Ge(SePh)₄^a

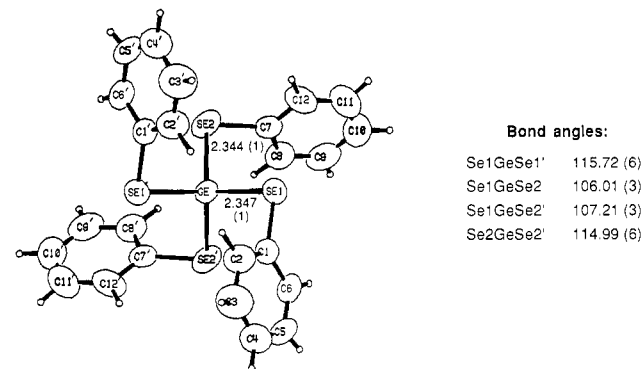
atom	x	y	z	B, Å ²
Se1	0.11442 (3)	-0.03995 (6)	-0.1477 (1)	5.51 (1)
Se2	0.02137 (4)	0.22822 (7)	0.1490 (1)	6.14 (1)
Ge	0.0	0.0	0.0	4.03 (1)
C1	0.1197 (3)	0.1685 (7)	-0.2342 (7)	4.3 (1)
C2	0.0759 (4)	0.2079 (7)	-0.3654 (9)	5.8 (1)
C3	0.0805 (5)	0.354 (1)	-0.4273 (9)	7.6 (2)
C4	0.1277 (4)	0.4679 (7)	-0.359 (1)	6.7 (2)
C5	0.1714 (4)	0.4290 (7)	-0.233 (1)	6.5 (2)
C6	0.1691 (3)	0.2790 (6)	-0.1677 (8)	5.2 (1)
C7	-0.0849 (4)	0.2533 (6)	0.2218 (7)	4.4 (1)
C8	-0.1124 (4)	0.1639 (7)	0.3456 (9)	5.6 (1)
C9	-0.1872 (5)	0.1856 (8)	0.3944 (8)	6.9 (2)
C10	-0.2362 (4)	0.2942 (8)	0.324 (1)	7.6 (2)
C11	-0.2079 (5)	0.3837 (8)	0.204 (1)	7.7 (2)
C12	-0.1319 (4)	0.3634 (7)	0.1508 (9)	6.1 (1)
H2	0.039 (4)	0.129 (7)	-0.426 (9)	8 (2)*
H3	0.058 (4)	0.365 (8)	-0.516 (9)	8 (2)*
H4	0.129	0.571	-0.401	6.7
H5	0.205 (3)	0.479 (5)	-0.206 (7)	4 (1)*
H6	0.201	0.252	-0.080	5.5
H8	-0.075 (5)	0.085 (9)	0.46 (1)	10 (2)*
H9	-0.204 (3)	0.130 (6)	0.468 (7)	5 (1)*
H10	-0.290 (4)	0.314 (9)	0.36 (1)	10 (2)*
H11	-0.240 (4)	0.465 (8)	0.18 (1)	8 (2)*
H12	-0.110 (4)	0.424 (6)	0.05 (1)	8 (2)*

^a Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

of this final reaction solution showed two resonances (158.1 ppm (EtGe(SePh)₃) and 257.8 ppm (Ge(SePh)₄). The melting point of Ge(SePh)₄, 119 °C, is in agreement with that of the previously reported material.³ This compound also showed a molecular ion in its field-desorption mass spectrum. Both compounds exhibit good aerial stability in the solid state. Further work is in progress aimed at the elucidation of the mechanism of the alkylation reaction (i.e., the role of BEt₃ in ethylation of GeCl_n(SePh)_{4-n}, generated by reaction of GeCl₄ with PhSeMgCl).

Superhydride¹⁷ has been widely used as a reductant in both transition-metal chemistry (e.g., reductive cleavage of M-M bonds¹⁸ and reduction of coordinated CO to formyl¹⁹) and main-group chemistry (e.g., reduction of S,²⁰ Se,²¹ and Te²² to various E_n²⁻ species and reductive cleavage of E₂R₂ to ER⁻ (E = S,^{20b} Se,^{21a,b} Te^{21b}).

In spite of this extensive application of Superhydride over the past 10 years few examples of ethyl incorporation in an organometallic product resulting from the use of this

**Figure 1.** Molecular structure of Ge(SePh)₄.**Table IV. Positional Parameters (Esd's in Parentheses) for EtGe(SePh)₃^a**

atom	x	y	z	B, Å ²
Se1	0.19647 (5)	0.01985 (4)	0.12844 (4)	5.17 (1)
Se2	0.19081 (4)	0.37424 (4)	0.33700 (4)	4.720 (9)
Se3	0.42086 (4)	0.17895 (4)	0.50174 (4)	5.10 (1)
Ge	0.21376 (4)	0.17901 (3)	0.37598 (4)	3.564 (8)
C1	0.0814 (4)	0.1418 (4)	0.4690 (4)	4.81 (9)
C2	-0.0524 (4)	0.1518 (5)	0.3984 (5)	6.5 (1)
C3	0.1578 (4)	-0.1362 (3)	0.1593 (4)	4.00 (9)
C4	0.2521 (4)	-0.1912 (4)	0.2183 (5)	5.2 (1)
C5	0.2243 (5)	-0.3051 (4)	0.2373 (5)	6.5 (1)
C6	0.0999 (5)	-0.3634 (4)	0.1951 (5)	6.5 (1)
C7	0.0058 (4)	-0.3084 (4)	0.1368 (5)	6.1 (1)
C8	0.0340 (4)	-0.1954 (4)	0.1190 (5)	5.2 (1)
C9	0.2424 (4)	0.5063 (3)	0.5384 (4)	4.26 (9)
C10	0.3550 (4)	0.5899 (4)	0.5793 (5)	5.5 (1)
C11	0.3899 (5)	0.6889 (5)	0.7228 (5)	6.5 (1)
C12	0.3182 (5)	0.7021 (5)	0.8251 (5)	6.7 (1)
C13	0.2077 (4)	0.6194 (5)	0.7850 (5)	6.3 (1)
C14	0.1678 (4)	0.5233 (4)	0.6418 (4)	5.0 (1)
C15	0.3854 (4)	0.2094 (4)	0.6916 (4)	4.40 (9)
C16	0.3860 (5)	0.3382 (5)	0.7981 (5)	5.9 (1)
C17	0.3648 (6)	0.3534 (7)	0.9365 (6)	9.0 (2)
C18	0.3424 (5)	0.2444 (7)	0.9630 (5)	8.1 (2)
C19	0.3429 (5)	0.1178 (6)	0.8564 (5)	7.8 (1)
C20	0.3631 (4)	0.1011 (4)	0.7215 (4)	5.4 (1)
H1C1	0.094 (3)	0.076 (3)	0.477 (3)	2.6 (6)*
H2C1	0.096 (5)	0.193 (4)	0.553 (5)	7 (1)*
H1C2	-0.115 (4)	0.125 (4)	0.433 (5)	8 (1)*
H2C2	-0.067 (5)	0.241 (5)	0.393 (5)	8 (1)*
H3C2	-0.066 (6)	0.110 (6)	0.306 (6)	11 (2)*
H4	0.324 (4)	-0.153 (4)	0.248 (4)	6 (1)*
H5	0.285 (5)	-0.341 (5)	0.263 (5)	8 (1)*
H6	0.098 (4)	-0.437 (4)	0.203 (4)	7 (1)*
H7	-0.081 (5)	-0.348 (5)	0.116 (5)	9 (1)*
H8	-0.023 (4)	-0.161 (4)	0.097 (4)	4.8 (9)*
H10	0.410 (3)	0.582 (3)	0.511 (3)	3.8 (8)*
H11	0.461 (5)	0.742 (5)	0.746 (5)	8 (1)*
H12	0.361 (7)	0.764 (6)	0.916 (6)	12 (2)*
H13	0.155 (4)	0.630 (3)	0.834 (4)	4.8 (9)*
H14	0.092 (4)	0.460 (4)	0.610 (4)	4.9 (9)*
H16	0.396 (4)	0.405 (4)	0.781 (4)	5.1 (9)*
H17	0.373 (4)	0.427 (4)	0.992 (4)	5.3 (9)*
H18	0.334 (4)	0.238 (4)	1.047 (4)	7 (1)*
H19	0.339 (5)	0.046 (5)	0.885 (5)	9 (1)*
H20	0.377 (4)	0.021 (4)	0.650 (4)	6 (1)*

^a Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

reagent have been reported.

Seyferth et al.²³ have reported that reactions of organomercury chlorides with $[Fe_2(\mu-S)_2(CO)_6]^{2-}$, generated by the LiEt₃BH reductive cleavage of the μ_2, η^2-S_2 ligand in

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Table V. Bond Distances (Å) for Ge(SePh)₄^a

atom 1	atom 2	dist	atom 1	atom 2	dist
Se1	Ge	2.347 (1)	C5	H5	0.75 (8)
Se1	C1	1.921 (7)	C6	H6	0.95
Se2	Ge	2.344 (1)	C7	C8	1.376 (10)
Se2	C7	1.931 (8)	C7	C12	1.373 (10)
C1	C2	1.380 (12)	C8	C9	1.358 (12)
C1	C6	1.385 (9)	C9	C10	1.38 (2)
C2	C3	1.355 (14)	C9	H9	0.83 (8)
C2	H2	1.05 (9)	C10	C11	1.36 (2)
C3	C4	1.385 (15)	C10	H10	0.99 (11)
C3	H3	0.85 (11)	C11	C12	1.386 (14)
C4	C5	1.342 (15)	C11	H11	0.90 (10)
C4	H4	0.95	C12	H12	1.10 (11)
C5	C6	1.392 (11)			

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

Table VI. Bond Angles (deg) for Ge(SePh)₄^a

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Ge	Se1	C	96.2 (2)	C6	C5	H5	115 (6)
Ge	Se2	C7	96.7 (2)	C1	C6	C5	118.6 (8)
Se1	Ge	Se1'	115.72 (6)	C1	C6	H6	120
Se1	Ge	Se2	106.01 (3)	C5	C6	H6	121
Se1	Ge	Se2'	107.21 (3)	Se2	C7	C8	120.2 (5)
Se2	Ge	Se2'	114.99 (6)	Se2	C7	C12	119.2 (6)
Se1	C1	C2	120.3 (5)	C8	C7	C12	120.6 (7)
Se1	C1	C6	120.1 (5)	C7	C8	C9	118.6 (8)
C2	C1	C6	119.5 (7)	C8	C9	C10	122 (1)
C1	C2	C3	120.2 (8)	C8	C9	H9	118 (5)
C1	C2	H2	124 (5)	C10	C9	H9	120 (5)
C3	C2	H2	116 (5)	C9	C10	C11	118.8 (9)
C2	C3	C4	121 (1)	C9	C10	H10	122 (7)
C2	C3	H3	115 (8)	C11	C10	H10	119 (6)
C4	C3	H3	124 (8)	C10	C11	C12	120 (1)
C3	C4	C5	118.9 (8)	C10	C11	H11	111 (7)
C3	C4	H4	121	C12	C11	H11	127 (7)
C5	C4	H4	121	C7	C12	C11	119.5 (9)
C4	C5	C6	121.7 (9)	C7	C12	H12	118 (5)
C4	C5	H5	122 (6)	C11	C12	H12	122 (5)

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

Fe₂(CO)₆(S₂), gave mixed products (i.e., Fe₂(μ-SEt)(μ-SHgR)(CO)₆, R = Me, Et) in addition to the expected products Fe₂(μ-SHgR)₂(CO)₆. It was shown in this work that LiEt₃BH was the source of the ethyl group directly bonded to the sulfur.

Weatherill²⁴ has found that the reactions of 3 equiv of Li₂E (E = S, Se, Te) with 2 equiv of Fe₂(μ-I)₂(NO)₄ gave, in addition to the reported products ((Fe₂(μ-E)₂(NO)₄)₂)^{2b}, the neutral ethyl esters Fe₂(μ-EEt)₂(NO)₄ (E = S, negligible yield; E = Se and Te, 14% yields). These products were shown to form via ethylation by BEt₃ present in the Li₂E solutions which were generated by LiEt₃BH reduction of the elemental chalcogens in THF solution.

Jones²⁵ recently isolated and structurally characterized the compound (Me₅C₅)Rh(PMe₃)(Ph)(Et) which formed in an attempt to convert (Me₅C₅)Rh(PMe₃)(Ph)Br to the corresponding hydride by reaction with Superhydride.

Molecular Structures of Ge(SePh)₄ and EtGe(SePh)₃. Figures 1 and 2 show the structures of both compounds with atomic labeling. Hydrogen atom labels were omitted for clarity but were given the number of the parent carbon atom. Complete tables of bond distances and angles and positional and thermal parameters are

Table VII. Bond Distances (Å) for EtGe(SePh)₃^a

atom 1	atom 2	dist	atom 1	atom 2	dist
Se1	Ge	2.353 (1)	C8	H8	0.78 (5)
Se1	C3	1.925 (4)	C9	C10	1.388 (6)
Se2	Ge	2.356 (1)	C9	C14	1.377 (6)
Se2	C9	1.917 (4)	C10	C11	1.382 (8)
Se3	Ge	2.348 (1)	C10	H10	0.96 (4)
Se3	C15	1.920 (4)	C11	C12	1.353 (8)
Ge	C1	1.952 (4)	C11	H11	0.88 (6)
C1	C2	1.507 (8)	C12	C13	1.365 (8)
C1	H1C1	0.78 (4)	C12	H12	0.91 (8)
C1	H2C1	0.79 (6)	C13	C14	1.375 (7)
C2	H1C2	0.90 (6)	C13	H13	0.79 (5)
C2	H2C2	1.02 (7)	C14	H14	0.97 (5)
C2	H3C2	0.83 (8)	C15	C16	1.372 (7)
C3	C4	1.361 (6)	C15	C20	1.377 (7)
C3	C8	1.374 (7)	C16	C17	1.403 (10)
C4	C5	1.384 (7)	C16	H16	0.84 (5)
C4	H4	0.81 (5)	C17	C18	1.364 (12)
C5	C6	1.375 (8)	C17	H17	0.76 (6)
C5	H5	0.82 (6)	C18	C19	1.357 (11)
C6	C7	1.356 (8)	C18	H18	0.91 (7)
C6	H6	0.85 (6)	C19	C20	1.359 (8)
C7	C8	1.368 (7)	C19	H19	0.95 (8)
C7	H7	0.96 (6)	C20	H20	0.91 (6)

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

Table VIII. Bond Angles (deg) for EtGe(SePh)₃^a

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Ge	Se1	C3	96.6 (1)	C3	C4	H4	119 (4)
Ge	Se2	C9	98.6 (1)	C5	C4	H4	120 (4)
Ge	Se3	C15	100.2 (1)	C4	C5	C6	119.4 (5)
Se1	Ge	Se2	98.85 (2)	C4	C5	H5	118 (5)
Se1	Ge	Se3	107.05 (2)	C6	C5	H5	122 (4)
Se1	Ge	C1	112.4 (2)	C5	C6	C7	120.0 (5)
Se2	Ge	Se3	112.06 (2)	C5	C6	H6	110 (4)
Se2	Ge	C1	113.8 (2)	C7	C6	H6	130 (4)
Se3	Ge	C1	111.8 (2)	C6	C7	C8	120.3 (5)
Ge	C1	C2	113.3 (4)	C6	C7	H7	117 (4)
Ge	C1	H1C1	108 (3)	C8	C7	H7	122 (4)
Ge	C1	H2C1	108 (5)	C3	C8	C7	120.7 (5)
C2	C1	H1C1	117 (3)	C3	C8	H8	122 (4)
C2	C1	H2C1	110 (5)	C7	C8	H8	117 (4)
H1C1	C1	H2C1	100 (5)	Se2	C9	C10	119.2 (3)
C1	C2	H1C2	114 (4)	Se2	C9	C14	121.4 (3)
C1	C2	H2C2	115 (3)	C9	C10	C11	119.5 (5)
H1C2	C2	H2C2	112 (5)	C9	C10	H10	122 (2)
H1C2	C2	H3C2	109 (7)	C11	C10	H10	118 (2)
H2C2	C2	H3C2	92 (6)	C10	C11	C12	120.9 (6)
Se1	C3	C4	120.9 (3)	C10	C11	H11	118 (4)
Se1	C3	C8	120.1 (3)	C12	C11	H11	121 (4)
C4	C3	C8	119.0 (4)	C11	C12	C13	119.6 (6)
C3	C4	C5	120.7 (5)	C11	C12	H12	109 (5)
C13	C12	H12	131 (5)	C16	C17	C18	121.2 (7)
C12	C13	C14	120.9 (5)	C16	C17	H17	112 (4)
C12	C13	H13	125 (4)	C18	C17	H17	127 (4)
C14	C13	H13	113 (4)	C17	C18	C19	120.5 (7)
C9	C14	C13	119.7 (5)	C17	C18	H18	131 (4)
C9	C14	H14	117 (3)	C19	C18	H18	108 (3)
C13	C14	H14	124 (3)	C18	C19	C20	119.0 (7)
Se3	C15	C16	120.2 (4)	C18	C19	H19	117 (4)
Se3	C15	C20	119.5 (4)	C20	C19	H19	123 (4)
C16	C15	C20	120.3 (5)	C15	C20	C19	121.6 (6)
C15	C16	C17	117.3 (7)	C15	C20	H20	114 (3)
C15	C16	H16	122 (3)	C19	C20	H20	124 (3)
C17	C16	H16	121 (3)				

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

included in Tables III–VIII.

The geometry about Ge is approximately tetrahedral with some distortion due to steric effects. Ge(SePh)₄ has C₂ symmetry occupying a crystallographic twofold axis. The Ge–Se bond distances are comparable to values re-

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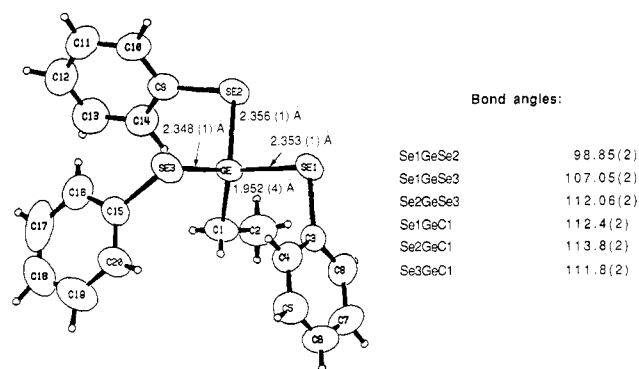


Figure 2. Molecular structure of EtGe(SePh)₃.

ported for a variety of selenogermanate anions and organometallic derivatives (Table I). The Ge-C bond in EtGe(SePh)₃ (1.952 Å) is in the range of Ge-C(aryl and alkyl) (1.94–1.99 Å) given in ref 26. The Se-C(phenyl) bonds (1.917–1.931 Å) in the two compounds are normal values comparable with those found in structures such as triphenylselenonium chloride (1.924–1.941 Å in ref 27) and in perfluoroselenanthrene (average = 1.910 Å, in ref 28).

Experimental Section

General Techniques, Reagents, and Physical Measurements. Manipulations were carried out under an argon atmosphere by using Schlenk techniques.²⁹

GeCl₄ was purchased from Strem Chemicals. A stock solution of this material was prepared by adding a weighed amount to a Schlenk flask fitted with a burette side arm and adding dry toluene to a known volume. This solution (0.58 M) was added to the Schlenk reaction vessels via a Teflon stopcock at the bottom of the burette under a heavy flush of Ar. Se₂Ph₂ and LiEt₃BH were purchased from Aldrich Chemical Co.

Field desorption mass spectra were measured for CH₂Cl₂ solutions with a Finnegan MAT 731 spectrometer. Proton NMR spectra were recorded on an IBM-WP270SY spectrometer at 270 MHz. ⁷⁷Se NMR spectra were recorded on a Nicolet 200 spectrometer. Elemental analyses were performed by the Analytical Technology Division of the Kodak Research Laboratories (C and H, Control Equipment Corp. Model 240XA automatic analyzer; Ge and Se, neutron activation analysis).

EtGe(SePh)₃. A solution of Li[SePh] was prepared by adding 70 mL of 1 M LiEt₃BH via syringe to a solution of Ph₂Se₂ (10.9 g, 35 mmol) in 200 mL of anhydrous THF. After the mixture was stirred for 10 h at room temperature, 30 mL of a 0.58 M solution of GeCl₄ in toluene was added. The resulting clear orange solution was stirred at room temperature for 36 h with no visible change. When this solution was refluxed for 15 min, a heavy white precipitate deposited, but on further refluxing overnight most of this precipitate redissolved (total reflux time = 12 h). Removal of the reaction solvent under vacuum gave an oil that was extracted with 500 mL of warm hexane, and a peach colored insoluble residue was removed by filtration. The clear yellow filtrate was concentrated under vacuum to ca. 50 mL resulting in the deposition of a heavy crop of pale yellow powder. The precipitate was then redissolved by warming the flask with a heat gun and cooling the resulting solution overnight in a refrigerator gave a crop of bright yellow crystals. The yellow supernatant was decanted off by cannula, and the residue was vacuum dried (8.9 g,

89.3%; mp 78 °C (clear yellow melt); mol wt 569.85 (FDMS (CHCl₃) 574) (⁷⁴Ge, ⁸⁰Se). Anal. Calcd (Found) for C₂₀H₂₀GeSe₃: C, 42.16 (42.3); H, 3.54 (3.5); Ge, 12.74 (12.7); Se, 41.57 (41.0).

Ge(SePh)₄. This compound was obtained by the reaction of GeCl₄ with 4 equiv of Li[SePh] in THF as described above but with a modification of the reaction conditions and fractional crystallization of the products.

A solution of Li[SePh] (70 mmol) in THF was prepared by adding 70 mL of a 1 M THF solution of LiEt₃BH to a solution of Se₂Ph₂ (10.9 g, 35 mmol) in 200 mL of THF and stirring at room temperature overnight. To this solution was added a solution of GeCl₄ in toluene (17.5 mmol, 30 mL of 0.58 M solution). The resulting solution was stirred at room temperature for 4 h and then refluxed for 20 h to give a clear yellow solution. The THF was then removed under vacuum, and the oily yellow residue was extracted with 450 mL of hot hexane, and the extract was filtered, via a metal cannula, through a medium porosity Schlenk filter, a layer of off-white solid being removed in the filter. On standing overnight at room temperature, a crop of bright yellow crystals deposited from the yellow filtrate, and, after this solution was cooled overnight in a freezer compartment (with a negligible increase in the amount of crystals deposited), the supernatant was removed via a cannula. The remaining bright yellow crystals were vacuum dried at room temperature to give 2.5 g (20.5%) of product which was identified by elemental analysis, field-desorption mass spectroscopy, and ⁷⁷Se NMR as pure Ge(SePh)₄ (C₂₀H₂₀GeSe₄; mol wt 696.85 (FDMS = 702) (⁷⁴Ge, ⁸⁰Se). Anal. Calcd (Found): C, 41.37 (42.2); H, 2.89 (3.0); Se, 45.32 (46.3); Ge, 10.42 (10.7).

Concentration under vacuum at room temperature of the yellow supernatant from the above transfer to 50 mL gave a heavy yellow precipitate. This was redissolved by heating and allowed to stand overnight at room temperature to give a crop of bright yellow crystals. After the solution was cooled in a freezer compartment for 24 h, the supernatant was decanted off via a cannula and the yellow crystals were vacuum dried to give 6.4 g (64.3%) of product. This product was identified by field-desorption mass spectroscopy and ⁷⁷Se NMR as a EtGe(SePh)₃.

Crystallography. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo K α radiation. Table II summarizes the unit-cell data and refinement parameters. Unit-cell dimensions were determined by least-squares refinement of 25 reflections [19.2 < 2 θ < 35.0° for Ge(SePh)₄ and 16.6 < 2 θ < 26.6° for EtGe(SePh)₃]. Three standard reflections were remeasured every hour of X-ray exposure. The data for EtGe(SePh)₃ were corrected for a small decrease in intensity (maximum correction = 1.045 on I) over time. An empirical absorption correction³⁰ was applied to both data sets. The correction factor (on *F*) ranged from 0.875 to 1.0 for Ge(SePh)₄ and 0.835 to 1.0 for EtGe(SePh)₃.

The structure of Ge(SePh)₄ was solved by direct methods using MULTAN 11/82.³¹ The structure of EtGe(SePh)₃ was deduced from a Patterson map. Both structures were refined by the full-matrix least-squares method with anisotropic thermal parameters applied to all non-hydrogen atoms. Hydrogen atom positions were obtained from difference electron density maps and included in the refinement. Hydrogens H₄ and H₆ of Ge(SePh)₄ were eventually fixed at calculated positions, given isotropic thermal parameters equivalent to the parent carbons, and allowed to ride on these atoms.

The absolute structure of Ge(SePh)₄ was determined in the following manner. The structure was refined with isotropic thermal parameters, unit weighting and all *f''* = 0. The *f''* values were then included in the structure factor calculations both with positive signs to give *R_w⁺* = 0.1125 and with negative signs (representing the inverse structure) to give *R_w⁻* = 0.1126. This difference is not significant, so the Friedel pairs of the 184 reflections most sensitive to anomalous scattering effects were remeasured. The signs of Δ_o and Δ_c were compared ($\Delta = |F_{hkl}| - |F_{\bar{h}\bar{k}\bar{l}}|$), and agreement in the signs for 177 reflections was an

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excellent indication that the absolute structure assignment was correct.

Registry No. EtGe(SePh)₃, 118112-64-4; LiEt₃BH, 22560-16-3; Ph₂Se₂, 1666-13-3; GeCl₄, 10038-98-9; Ge(SePh)₄, 118141-54-1.

Supplementary Material Available: Tables of general temperature expressions for Ge(SePh)₄ and EtGe(SePh)₃ (2 pages); listings of structure factors for Ge(SePh)₄ and EtGe(SePh)₃ (42 pages). Ordering information is given on any current masthead page.

Reactions of (1-3- η -Vinylcarbene)tricarbonyliron Complexes with Carbon Monoxide or Tertiary Phosphines. "Insertion" of Carbon Monoxide into a Carbon-Metal Double Bond and Reactivities of the Formed Tricarbonyl(η^3 : η^1 -allylacyl)irons

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A (η^3 -vinylcarbene)iron complex, tricarbonyl(1-3- η -1-methoxy-2-(methoxycarbonyl)prop-2-en-1-ylidene)iron (**3a**), reacts with carbon monoxide (1 atm) or tertiary phosphines (L) at 30–35 °C to give Fe(η^3 : η^1 -allylacyl)(CO)₂L (**6**, L = CO; **7**, L = PPh₃; **8**, L = PPh₂Me; **9**, L = PPhMe₂) in good to excellent yields; the insertion of a carbon monoxide into the carbene-iron bond readily occurs. Complex **7** crystallizes in space group *P2₁/c* with *a* = 13.926 (2) Å, *b* = 10.227 (2) Å, *c* = 35.835 (7) Å, β = 101.81 (2)°, and *Z* = 8. Pertinent bond distances are C(2)–Fe = 1.899 (7) Å, C(2)–C(3) = 1.484 (11) Å, C(3)–C(4) = 1.403 (10) Å, and C(4)–C(5) = 1.416 (11) Å. These data show that for the description of **7**, (η^3 : η^1 -allylacyl)tricarbonyliron, is preferable to (η^4 -vinylketene)tricarbonyliron. Complex **3a** reacts with 2 mol equiv of PPhMe₂ to give a ferracyclopent-2-en-5-one derivative, **12**, in 19% yield. Fe(η^3 : η^1 -allylacyl)(CO)₂L (**8**, L = PPh₂Me; **9**, L = PPhMe₂) further reacts with carbon monoxide, PPh₂Me, or PPhMe₂ to give a ferracyclopent-2-en-5-one derivatives (**10**, L = L' = PPh₂Me; **11**, L = PPhMe₂, L' = CO; **12**, L = L' = PPhMe₂). Complex **11** crystallizes in space group *P2₁/n* with *a* = 13.393 (4) Å, *b* = 16.906 (3) Å, *c* = 8.774 (2) Å, β = 93.10 (2)°, and *Z* = 4. Tricarbonyl(1-3- η -1-methoxy-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene)iron (**3b**) reacts with carbon monoxide to give tricarbonyl(3-6- η -4-(methoxycarbonyl)-5,6-dimethoxy-2-pyrone)iron (**13**). Complex **13** belongs to the orthorhombic space group *Pbca* with *a* = 13.104 (1) Å, *b* = 19.646 (2) Å, *c* = 11.346 (2) Å, and *Z* = 8. Complex **3b** reacts with PPh₃ at 50 °C to afford the phosphine-substituted η^3 -vinylcarbene complex **19**. Complex **3b** reacts with PPh₂Me or PPhMe₂ to give the corresponding Fe(η^3 : η^1 -allylacyl)(CO)₂L (**14** and **15**) which further react with carbon monoxide or PPhMe₂ to give ferracyclopent-3-en-2-ones (**16**, **17**, and **18**).

Introduction

The chemistry of transition-metal vinylcarbene or allylidene complexes have recently attracted considerable attention.¹⁻²⁵ Two kinds of vinylcarbene complexes are

known; one is a η^1 -vinylcarbene or 1-metalla-1,3-butadiene complex, **1**,^{17,18,24} and the other is a η^3 -vinylcarbene or

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