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, α = 104.82 (2)°, β = 104.51 (2)°, γ = 83.88 (2)°; V = 719.3 (5) Å^3; D_{calcd} 1.89 g cm^{-3}, Z = 2; $F(000)$ = 404; γ(Mo Kα) = 0.71069 Å; μ(Mo K$_\alpha$) = 13.63 cm^{-1}; room temperature; crystal dimensions 0.1 × 0.1 × 0.15 mm; Enraf-Nonius CAD-4 diffractometer; monocromatized Mo K$_\alpha$ radiation; θ–2θ technique; 2664 reflections in the range $2 \le \theta \le 25°$, 2140 observed [$I \ge 2.5\sigma(I)$]. Lorentz–polarization and absorption corrections were applied. The structure was solved by direct methods (MULTAN[24]). 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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Registry No. 1, 118041-62-6; 2, 118018-68-1; 3, 118018-69-2; 4, 118018-70-5; 5, 118018-71-6; 6, 118018-72-7; 7, 118018-75-0; 8, 118018-77-2; 9, 118018-78-3; 10, 99491-90-4; 11, 118018-79-4; [$Hg(2\text{-}C_6H_4NO_2)_2$], 26953-08-2; [$Pd\{2\text{-}C_6H_4NO_2\}_2$], 118018-80-7; [$Rh(\mu\text{-}Cl)(CO)_2]_2$, 14523-22-9.

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 LiEt$_3$BH

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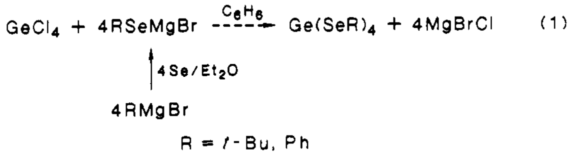
The reaction of $GeCl_4$ with 4 equiv of Li{SePh}, generated by the reductive cleavage of Ph_2Se_2 with $LiEt_3BH$ in tetrahydrofuran, gave a mixture of $Ge(SePh)_4$ and $EtGe(SePh)_3$. These products were separated by fractional crystallization from a hexane solution and characterized by ^1H and ^{77}Se NMR spectroscopy and single-crystal X-ray diffraction. The latter compound is the first well-characterized example of ethylation of a metal halide via $LiEt_3BH$. 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, $P\bar{1}$, with a = 10.631 (1) Å, b = 11.022 (2) Å, c = 10.166 (1) Å, α = 115.048 (9)°, β = 99.908 (8)°, γ = 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.

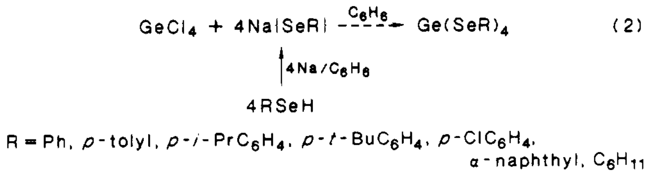
Introduction

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 paper[3] described the synthesis of several derivatives of the type $Ge(SeR)_4$, their characterization being limited to elemental analyses and melting points:



$$GeCl_4 + 4RSeMgBr \xrightarrow{C_6H_6} Ge(SeR)_4 + 4MgBrCl \quad (1)$$
$$4RMgBr \xrightarrow{4Se/Et_2O} 4RSeMgBr$$

R = *t*-Bu, Ph



$$GeCl_4 + 4Na\{SeR\} \xrightarrow{C_6H_6} Ge(SeR)_4 \quad (2)$$
$$4RSeH \xrightarrow{4Na/C_6H_6} 4Na\{SeR\}$$

R = Ph, *p*-tolyl, *p*-*i*-PrC_6H_4, *p*-*t*-BuC_6H_4, *p*-ClC_6H_4, α-naphthyl, C_6H_{11}

Subsequently several other organogermanium compounds incorporating Ge–Se bonds were described ($\{Me_2GeSe\}_3$,[4] $Se(GeR_3)_2$ (R = Me,[5] Et,[6] Ph,[7] C_6F_5[8]), Et_3GeSeH,[6b] $Et_3GeSeSnEt_3$,[6b] $Ph_3GeSeSeGePh_3$,[9] $R_3GeSeHgGeR_3$ (R = Et, *i*-Pr),[10] and $(t\text{-}Bu)_2Ge(\mu\text{-}Se)_2Ge(t\text{-}Bu)_2$)[11]). In addition, crystal structures have been reported for the cyclic polygermanes $\{(Ph_2Ge)_4Se\}$[12] and $\{(Ph_2Ge)_3Se_2\}$,[13] 1,3-diselena-2,2-dichlorogermyl-[3]-ferrocenophane ($Fe(C_5H_4Se)_2GeCl_2$),[14] and $GeSe_2$[15] as well

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(1) Gysling, H. J. Ligand Properties of Organic Selenium and Tellurium Compounds. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Wiley: New York, 1986; Vol. 1, pp 679–855.

Table I. Ge–Se Distances in Some Reported Structures

compound	Ge–Se, Å	ref
$GeSe_2$	2.337–2.365	15
$Na_8Ge_4Se_{10}$	2.294–2.335 (terminal) 2.420–2.456 (bridge)	16a
$Na_4[GeSe_4]\cdot 14H_2O$	2.350	16d
$Tl_4[Ge_4Se_{10}]$	2.287 (terminal) 2.380 (bridge)	16f
$(PhGe)_4Se$	2.373	12b
$Ph_6Ge_3Se_2$	2.37	13
$[Fe(C_5H_4Se)_2]_2GeCl_2$	2.323 2.325	14
$Ge(SePh)_4$	2.344, 2.347	*a*
$EtGe(SePh)_3$	2.348–2.356	*a*

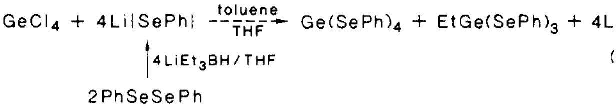
[a] This work.

as a variety of selenogermanate anions[16] (see Table I for some typical Ge–Se bond distances).

We report here the details of the reaction of $GeCl_4$ with Li{SePh}, generated in THF by reductive cleavage of Ph_2Se_2 with $LiEt_3BH$ (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 $GeCl_4$ solution in toluene with a THF solution of 4 equiv of Li{SePh}, generated by the in situ reductive cleavage of Ph_2Se_2 with $LiEt_3BH$ (eq 3),



$$GeCl_4 + 4Li\{SePh\} \xrightarrow[THF]{toluene} Ge(SePh)_4 + EtGe(SePh)_3 + 4LiCl \qquad (3)$$
$$2PhSeSePh \xrightarrow{4LiEt_3BH/THF} 4Li\{SePh\}$$

gave a mixture of $Ge(SePh)_4$ and $EtGe(SePh)_3$, the ratio 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.

Table II. Summary of Crystal Data and Refinement Parameters

	$Ge(SePh)_4$	$EtGe(SePh)_3$
formula	$Se_4GeC_{24}H_{20}$	$Se_3GeC_{20}H_{20}$
MW	696.86	569.85
space group	*Pba*2	$P\bar{1}$
cell constants at 23 (1) °C		
a, Å	17.111 (2)	10.631 (1)
b, Å	8.513 (1)	11.022 (2)
c, 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)
V, Å^3	1231.6 (7)	1058 (1)
no. of molecules/unit cell (*Z*)	2	2
D(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 Kα)), cm^{-1}	70.8	65.4
scan technique	ω–2θ	ω–2θ
scan rate, deg 2θ min^{-1}	1.7–20	2.4–20
2θ limit, deg	50	46
hkl 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 ($I > \sigma(I)$)	1048	2632
no. of parameters	171	297
$R = \sum\|\|F_o\| - K\|F_c\|\|/\sum\|F_o\|$	0.023	0.025
$R_w = (\sum w(\|F_o\| - K\|F_c\|)^2/\sum wF_o^2)^{1/2}$	0.032	0.039
$S = [(\sum w(\|F_o\| - K\|F_c\|)^2/(n_o - n_v)]^{1/2}$	0.92	1.03
wtg parameters ($w^{-1} = \sigma^2(F_o) + (pF_o)^2 + q$)		
p	0.03	0.03
q	0	1.0
scale factor, *K*	2.029 (5)	2.880 (7)
max shift in final cycle (Δ/σ)	0.10σ	0.15σ
residual electron density in final diff Fourier synthesis, e/Å^3	−0.25 to +0.38	−0.20 to +0.50

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 ^{77}Se NMR spectrum of this reaction solution shows a single resonance at 158.3 ppm (downfield from $SeMe_2$) 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 ^{77}Se 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); CH_2, δ 1.34 (q, 2, J = 8 Hz); CH_3, 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 ^{77}Se NMR spectrum

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Table III. Positional Parameters (Esd's in Parentheses) for $Ge(SePh)_4$[a]

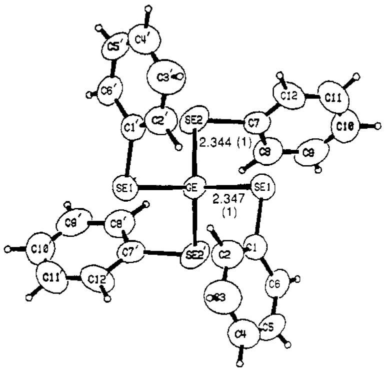
atom	*x*	*y*	*z*	*B*, Å^2
Se1	0.11442 (3)	−0.03995 (6)	−0.1477 (1)	5.51 (1)
Se2	0.02137 (4)	0.22822 (7)	0.1490 (1)	6.14 (1)
Ge	0.0	0.0	0.0	4.03 (1)
C1	0.1197 (3)	0.1685 (7)	−0.2342 (7)	4.3 (1)
C2	0.0759 (4)	0.2079 (7)	−0.3654 (9)	5.8 (1)
C3	0.0805 (5)	0.354 (1)	−0.4273 (9)	7.6 (2)
C4	0.1277 (4)	0.4679 (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 BEt_3 in ethylation of $GeCl_n(SePh)_{4-n}$, generated by reaction of $GeCl_4$ with PhSeMgCl).

Superhydride[17] has been widely used as a reductant in both transition-metal chemistry (e.g., reductive cleavage of M–M bonds[18] and reduction of coordinated CO to formyl[19]) and main-group chemistry (e.g., reduction of S,[20] Se,[21] and Te[22] to various E_n^{2-} species and reductive cleavage of E_2R_2 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 reagent have been reported.



Bond angles:

Se1GeSe1'	115.72 (6)
Se1GeSe2	106.01 (3)
Se1GeSe2'	107.21 (3)
Se2GeSe2'	114.99 (6)

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 $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Seyferth et al.[23] have reported that reactions of organomercury chlorides with $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$, generated by the $LiEt_3BH$ reductive cleavage of the $\mu_2,\eta^2\text{-}S_2$ 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)			

[a] Numbers 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)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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)

[a] Numbers 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)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

$Fe_2(CO)_6(S_2)$, gave mixed products (i.e., $Fe_2(\mu\text{-SEt})(\mu\text{-SHgR})(CO)_6$, R = Me, Et) in addition to the expected products $Fe_2(\mu\text{-SHgR})_2(CO)_6$. It was shown in this work that $LiEt_3BH$ was the source of the ethyl group directly bonded to the sulfur.

Weatherill[24] has found that the reactions of 3 equiv of Li_2E (E = S, Se, Te) with 2 equiv of $Fe_2(\mu\text{-I})_2(NO)_4$ gave, in addition to the reported products $(\{Fe_2(\mu\text{-E})_2(NO)_4\}^{2-})$,[21b] the neutral ethyl esters $Fe_2(\mu\text{-EEt})_2(NO)_4$ (E = S, negligible yield; E = Se and Te, 14% yields). These products were shown to form via ethylation by BEt_3 present in the Li_2E solutions which were generated by $LiEt_3BH$ reduction of the elemental chalcogens in THF solution.

Jones[25] recently isolated and structurally characterized the compound $(Me_5C_5)Rh(PMe_3)(Ph)(Et)$ which formed in an attempt to convert $(Me_5C_5)Rh(PMe_3)(Ph)Br$ 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 included in Tables III–VIII.

The geometry about Ge is approximately tetrahedral with some distortion due to steric effects. $Ge(SePh)_4$ has C_2 symmetry occupying a crystallographic twofold axis. The Ge–Se bond distances are comparable to values re-

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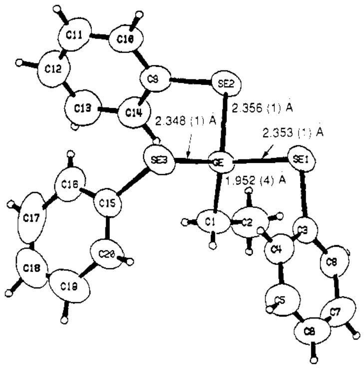
(24) Weatherill, T. D. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1985, pp 11–13, 21–22.

(25) Jones, W. A., private communication.



Bond angles:

Se1GeSe2	98.85(2)
Se1GeSe3	107.05(2)
Se2GeSe3	112.06(2)
Se1GeC1	112.4(2)
Se2GeC1	113.8(2)
Se3GeC1	111.8(2)

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]

GeCl$_4$ 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. Se$_2$Ph$_2$ and LiEt$_3$BH were purchased from Aldrich Chemical Co.

Field desorption mass spectra were measured for CH$_2$Cl$_2$ solutions with a Finnegan MAT 731 spectrometer. Proton NMR spectra were recorded on an IBM-WP270SY spectrometer at 270 MHz. ^{77}Se 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 LiEt$_3$BH via syringe to a solution of Ph$_2$Se$_2$ (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 GeCl$_4$ 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 (CHCl$_3$) 574) (^{74}Ge, ^{80}Se). Anal. Calcd (Found) for C$_{20}$H$_{20}$GeSe$_3$: 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 GeCl$_4$ 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 LiEt$_3$BH to a solution of Se$_2$Ph$_2$ (10.9 g, 35 mmol) in 200 mL of THF and stirring at room temperature overnight. To this solution was added a solution of GeCl$_4$ 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 ^{77}Se NMR as pure Ge(SePh)$_4$ (C$_{24}$H$_{20}$GeSe$_4$; mol wt 696.85 (FDMS = 702) (^{74}Ge, ^{80}Se). 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 ^{77}Se NMR as a EtGe(SePh)$_3$.

Crystallography. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Table II summarizes the unit-cell data and refinement parameters. Unit-cell dimensions were determined by least-squares refinement of 25 reflections [$19.2 < 2\theta < 35.0°$ for Ge(SePh)$_4$ and $16.6 < 2\theta < 26.6°$ 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 correction[30] 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 H$_4$ and H$_6$ 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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(31) Programs used in this package were from the Structure Determination Package, SDP-PLUS, V 1.1 (1983) Enraf-Nonius Corp., Delft, Holland.

excellent indication that the absolute structure assignment was correct.

Registry No. $EtGe(SePh)_3$, 118112-64-4; $LiEt_3BH$, 22560-16-3; Ph_2Se_2, 1666-13-3; $GeCl_4$, 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 $Fe(\eta^3{:}\eta^1\text{-allylacyl})(CO)_2L$ (**6**, L = CO; **7**, L = PPh_3; **8**, L = PPh_2Me; **9**, L = $PPhMe_2$) in good to excellent yields; the insertion of a carbon monoxide into the carbene–iron bond readily occurs. Complex **7** crystallizes in space group $P2_1/c$ with $a = 13.926$ (2) Å, $b = 10.227$ (2) Å, $c = 35.835$ (7) Å, $\beta = 101.81$ (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 $PPhMe_2$ to give a ferracyclopent-2-en-5-one derivative, **12**, in 19% yield. $Fe(\eta^3{:}\eta^1\text{-allylacyl})(CO)_2L$ (**8**, L = PPh_2Me; **9**, L = $PPhMe_2$) further reacts with carbon monoxide, PPh_2Me, or $PPhMe_2$ to give a ferracyclopent-2-en-5-one derivatives (**10**, L = L′ = PPh_2Me; **11**, L = $PPhMe_2$ L′ = CO; **12**, L = L′ = $PPhMe_2$). Complex **11** crystallizes in space group $P2_1/n$ with $a = 13.393$ (4) Å, $b = 16.906$ (3) Å, $c = 8.774$ (2) Å, $\beta = 93.10$ (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 PPh_3 at 50 °C to afford the phosphine-substituted η^3-vinylcarbene complex **19**. Complex **3b** reacts with PPh_2Me or $PPhMe_2$ to give the corresponding $Fe(\eta^3{:}\eta^1\text{-allylacyl})(CO)_2L$ (**14** and **15**) which further react with carbon monoxide or $PPhMe_2$ 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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