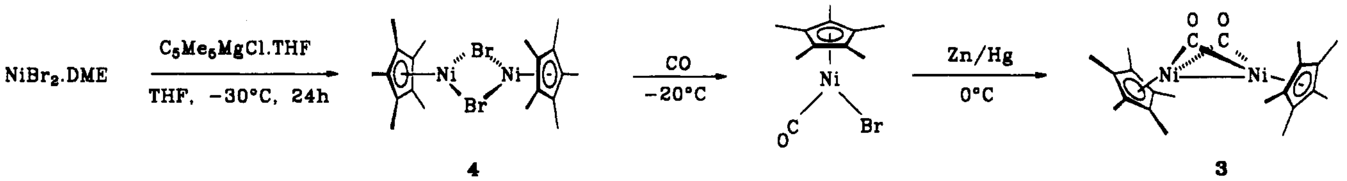
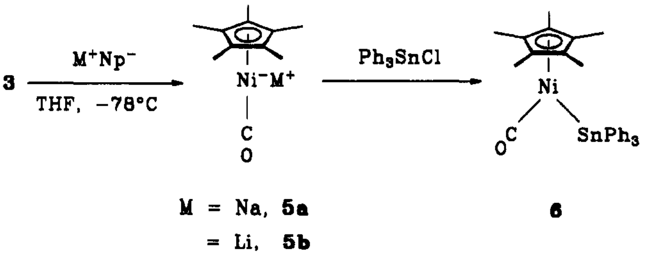
Scheme I



Scheme II



presence of small amounts of adventitious oxygen may lie at the root of the reported differences in the reaction of $Ni(CO)_4$ with $C_5Me_5^-Li^+$.[2,3]

Experimental Section

All manipulations were performed under an atmosphere of dinitrogen using standard Schlenk techniques. Solvents were freshly distilled from sodium/benzophenone (THF), sodium/potassium alloy (hexane), or phosphorus pentoxide (dichloromethane). The naphthalenide anion was prepared by stirring a THF solution of freshly sublimed naphthalene with the appropriate alkali metal overnight and the molarity of the solution determined by the difference in acid titrations of a sample quenched in water and one quenched initially in benzyl chloride. Infrared spectra were measured on a Perkin-Elmer 1710 Fourier transform spectrometer using CaF_2 solution cells fitted with Luer lock taps. NMR spectra were recorded on either a JEOL EX90 or a Bruker AC300 spectrometer. Elemental analyses were by Butterworth Laboratories, London.

$Ni_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (3). A solution of C_5Me_5MgCl[12] (56 cm³ of a 0.32 M solution in THF) was added dropwise with stirring to a suspension of $NiBr_2{\cdot}DME$[4] (5 g, 17.93 mmol) in THF (50 cm³) at −30 °C. The solution was stirred for 24 h at the same temperature. Carbon monoxide was then bubbled through the solution of 10 min at −20 °C, the solution warmed to 0 °C, and amalgamated zinc (5 g) added. The solution was stirred for a further 30 min. The resulting claret solution was reduced to dryness in vacuo at 0 °C and the residue extracted into hexane and stored at −80 °C. Red platelike crystals were produced (2.32 g, 57%). Anal. Calcd for $C_{22}H_{30}O_2Ni_2$ (3): C, 59.52; H, 6.81. Found: C, 58.88; H, 7.05. IR (hexane): 1857, 1816 cm⁻¹. IR (THF): 1853, 1809 cm⁻¹. NMR (toluene-d_8): ^1H (δ 1.70 (s, Me); $^{13}C\{^1H\}$ δ 238.1 (CO), 101.3 (*C*Me), 9.2 (Me).

$Ni(\eta^5\text{-}C_5Me_5)(CO)(SnPh_3)$ (6). A THF solution of sodium naphthalenide (1.36 mmol) was added dropwise with stirring to a solution of $Ni_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (302 mg, 0.68 mmol) in THF (20 cm³) maintained at −78 °C. The solution turned from red to brown. Stirring was continued for 20 min, and Ph_3SnCl was added (581 mg, 1.51 mmol). The solution was warmed to room temperature, and all volatiles were removed in vacuo. The residue was extracted into hexane and column chromatographed on grade IV silica gel at −30 °C. Naphthalene and a small amount of 3 were eluted with hexane. The product, $Ni(\eta^5\text{-}C_5Me_5)(CO)(SnPh_3)$, eluted as a reddish brown band with 10% CH_2Cl_2 in hexane. Crystallization from hexane at −80 °C afforded red-orange crystals of $Ni(\eta^5\text{-}C_5Me_5)(CO)(SnPh_3)$ (400 mg, 51%). Anal. Calcd for $C_{29}H_{30}OSnNi$ (6): C, 60.90; H, 5.29. Found: C, 61.05; H, 5.45. IR (hexane): 2001 cm⁻¹. NMR (benzene-d_6): ^1H δ 7.8–7.1 (m, 15 H, Ph), 1.62 (s, 15 H, Me, J(SnH) = 13.2 Hz); $^{13}C\{^1H\}$ δ 194.6 (CO), 143.8 (C_1, Ph, J(SnC) = 352 Hz), 137.7 ($C_{2,6}$, Ph, J(SnC) = 38 Hz), 128.5 ($C_{3,5}$, Ph, J(SnC) = 43 Hz), 128.4 (C_4, Ph), 102.0 (*C*Me), 10.4 (Me).

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Registry No. 3, 69239-93-6; 4, 101163-02-4; 5a, 142781-14-4; 5b, 81230-31-1; 6, 142781-15-5; $NiBr_2{\cdot}DME$, 28923-39-9; C_5Me_5MgCl, 74430-27-6; Ph_3SnCl, 639-58-7; Ni, 7440-02-0.

OM9202175

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Neopentyl- or *tert*-Butylzinc Complexes with Diethylthio- or Diethylselenocarbamates: Precursors for Zinc Chalcogens

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Summary: A series of compounds with the general formula $RZnE_2CNEt_2$ ($R = Me_3CCH_2$, Me_3C; $E = S$, Se) have been synthesized, characterized, and used to grow thin films of ZnS or ZnSe by MOCVD. An X-ray crystal structure for $Me_3CCH_2ZnSe_2CNEt_2$ has been determined and shows the compound to be dimeric. The compound crystallizes in space group $P\bar{1}$, with a = 12.993 (3) Å, b = 12.631 (3) Å, c = 10.179 (2) Å, α = 94.96 (2)°, β = 109.75°, and γ = 106.48 (2)°.

Recently a substantial interest has developed in single-molecule precursors for the deposition of compound semiconductors by metalloorganic chemical vapor deposition (MOCVD). Suitable molecules for the deposition of III/V materials, such as InP and GaAs, have been developed by Bradley and Faktor[1] and Cowley and Jones.[2,3] A number of reports have also appeared concerning single-molecule precursors for the deposition of II/VI materials, and systems studied have included thio-

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phosphinates,[4,5] thiocarbamates,[6,7] selenocarbamates,[8] thiolates,[9-11] 2,4,6-tri-*tert*-butylphenyl chalcogenides,[10,11] silicon-based systems (e.g. $MESi(SiCH_3)_3$: M = Zn, Cd, Hg; E = Se, Te),[12] and alkylmetal thio- and selenocarbamates.[13,14] Alkylmetal thio- and selenocarbamates have been found to be dimers of empirical formula $[RME_2CNR'_2]_2$, and a wide range of derivatives of dimethyl- and diethylzinc and dimethylcadmium have been prepared (e.g. R = Me, R′ = Me, Et, M = Cd, Zn, $Cd_{0.5}Zn_{0.5}$, E = S and R = Et, E = Se).[13,14] X-ray crystal structures of $[MeZnS_2CNEt_2]_2$,[13] $[MeZnSe_2CNEt_2]_2$, $[EtZnSe_2CNEt_2]_2$, and $[MeCd_{0.5}Zn_{0.5}Se_2CNEt_2]_2$[15] have established a common dimeric structure in which each carbamate chelates one metal atom and bridges to the next one. In the present paper we have extended our studies to compounds derived from the more bulky *tert*-butyl- and neopentylzinc species. Four new compounds, the thio- and selenocarbamato derivatives for each alkyl, have been prepared and used to deposit thin films of metal chalcogen by MOCVD. The X-ray crystal structure of one of the precursors, $[MeCCH_2ZnSe_2CNEt_2]_2$, is reported.

Experimental Section

Chemicals. (Diethyldithiocarbamato)zinc(II), 1-Bromo-2,2-dimethylpropane, and 2-Bromo-2-methylpropane were purchased from Aldrich Chemical Co. Ltd. Solvents were obtained from BDH and were dried and degassed before use.

Physical Measurements. NMR spectra were recorded using a Bruker AM250 pulsed Fourier transform instrument, infrared spectra were recorded on a Mattson Polaris FT-IR spectrometer as Nujol mulls between KBr plates, and electronic spectra were recorded with a Perkin-Elmer 330 spectrophotometer. Melting points were measured in sealed tubes with an Electrothermal melting point apparatus and are uncorrected. Microanalyses were performed by the University College London service. Electron microscopy and elemental detection by analytical X-ray methods (EDAX) were carried out with a JEOL JSM35CF scanning electron microscope.

Synthesis. (Diethyldiselenocarbamato)zinc(II). CSe_2 was prepared by the method of Henrikson[16] and incorporated into (diethyldiselenocarbamato)zinc(II) as described previously.[14]

Metal Alkyls. All reactions were performed under an inert atmosphere using Schlenk techniques and a vacuum line. Dineopentylzinc and di-*tert*-butylzinc were prepared from Grignard reagents.[17,18]

Alkylzinc Diethyldiselenocarbamates. In a typical preparation a solution of (diethyldiselenocarbamato)zinc(II) (3.5 g, 6.4 mmol) in toluene (35 cm^3) was stirred with dineopentylzinc (1.32 g, 6.4 mmol) at room temperature for 0.5 h. The colorless solution, on concentration under vacuum, gave transparent crystals of neopentylzinc diethyldiselenocarbamate (**2**; 4.30 g, 11.4 mmol, 89%), mp 135 °C. Other compounds were prepared by the same method using the required carbamate and alkyl compounds. All the compounds have been characterized by satisfactory elemental analysis and NMR and infrared spectroscopy.

Table I. Crystal Data, Intensity Measurement, and Structure Refinement

formula	$C_{20}H_{42}N_2Se_4Zn_2$
M_r	757.187
cryst syst	triclinic
space group	$P1$
a, Å	12.993 (3)
b, Å	12.631 (3)
c, Å	10.179 (2)
α, deg	94.96 (2)
β, deg	109.75 (2)
γ, deg	106.48 (2)
V, Å^3	1476.58 (65)
z	2
D_c, g cm^{-3}	1.703
$F(000)$	744
radiation	Mo Kα
λ, Å	0.71069
μ, cm^{-1}	65.571
$\theta_{min/max}$, deg	1.5/25
total no. of rflns	4378
no. of unique rflns	4099
no. of obsd rflns ($F_o > 3\sigma(F_o)$)	1953
no. of refined params	295
weighting scheme param g in $w = 1[\sigma^2(F) + gF^2]$	0.000021
final R	0.0587
final R_G	0.0402

$Me_3CCH_2ZnS_2CNEt_2$ (1): 92% yield; mp 158–160 °C; ^1H NMR ($[^2H_6]C_6H_6$, 250.1 MHz) δ 3.41 (4 H, q, $^3J_{H-H}$ = 7.2 Hz, $(CH_3CH_2)_2N$), 0.91 (6 H, t, $^3J_{H-H}$ = 7.2 Hz, $(CH_3CH_2)_2N$), 1.37 (9 H, s, $(CH_3)_3C$), 1.06 (2 H, s, CH_2Zn); ^{13}C NMR ($[^2H_6]C_6H_6$, 62.9 MHz) δ 201.39 (CS_2), 49.61 (NCH_2), 36.20 ($C(\mathit{C}H_3)_3$), 33.16 (CH_2Zn), 32.22 (($\mathit{C}(CH_3)_3$), 12.65 (($\mathit{C}H_3CH_2)_2N$); IR (major bands and tenative assignments, cm^{-1}) 423 (ν(Zn–S)), 506, 563 (ν(Zn–C)), 994 (ν(C–S)), 1493 (ν(C–N)). Anal. Calcd for $C_{10}H_{21}NS_2Zn$: C, 42.18; H, 7.43; N, 4.29. Found: C, 41.97; H, 7.38; N, 5.04.

$Me_3CCH_2ZnSe_2CNEt_2$ (2): 89% yield; mp 135 °C; ^1H NMR ($[^2H_6]C_6H_6$, 250.1 MHz) δ 3.50 (4 H, q, $^3J_{H-H}$ = 7.1 Hz, $(CH_3CH_2)_2N$), 0.95 (6 H, t, $^3J_{H-H}$ = 7.1 Hz, $(CH_3CH_2)_2N$), 1.35 (9 H, s, (($CH_3)_3C$), 1.03 (2 H, s, CH_2Zn); ^{13}C NMR ($[^2H_6]C_6H_6$, 62.9 MHz) δ 188.26 (CSe_2), 51.62 (CH_2N), 36.24 (($\mathit{C}H_3)_3C$), 33.41 (CH_2Zn), 32.25 (($\mathit{C}(CH_3)_3$), 12.42 (($\mathit{C}H_3CH_2)_2N$); IR (major bands and tentative assignments, cm^{-1}) 457 (ν(Zn–Se)), 510, 604 (ν(Zn–C)), 854 (ν(C–Se)), 1499 (ν(C–N)). Anal. Calcd for $C_{10}H_{21}NSe_2Zn$: C, 31.72; H, 5.59; N, 3.70. Found: C, 31.66; H, 5.55; N, 3.74.

$Me_3CZnS_2CNEt_2$ (3): 94% yield; mp 177–179 °C; ^1H NMR ($[^2H_6]C_6H_6$, 250.1 MHz) δ 3.43 (4 H, q, $^3J_{H-H}$ = 7.2 Hz, $(CH_3CH_2)_2N$), 0.91 (6 H, t, $^3J_{H-H}$ = 7.2 Hz, $(CH_3CH_2)_2N$), 1.60 (9 H, s, (($CH_3)_3C$); ^{13}C NMR ($[^2H_6]C_6H_6$, 62.9 MHz) δ 201.12 (CS_2), 49.56 (CH_2N), 34.17 (($\mathit{C}H_3)_3C$), 26.33 ($\mathit{C}(CH_3)_3$), 12.63 (($\mathit{C}H_3CH_2)_2N$); IR (major bands and tentative assignments, cm^{-1}) 420 (ν(Zn–S)), 506, 559 (ν(Zn–C)), 989 (ν(C–S)), 1502 (ν(C–N)). Anal. Calcd for $C_9H_{19}NS_2Zn$: C, 39.92; H, 7.07; N, 5.17. Found: C, 40.04; H, 7.11; N, 5.21.

$Me_3CZnSe_2CNEt_2$ (4): 92% yield; mp 163 °C; ^1H NMR ($[^2H_6]C_6H_6$, 250.1 MHz) δ 3.51 (4 H, q, $^3J_{H-H}$ = 7.1 Hz, $(CH_3CH_2)_2N$), 0.96 (6 H, t, $^3J_{H-H}$ = 7.1 Hz, $(CH_3CH_2)_2N$), 1.59 (($CH_3)_3C$); ^{13}C NMR ($[^2H_6]C_6H_6$, 62.9 MHz) δ 188.09 (CSe_2), 52.01 (CH_2N), 34.13 ($C(\mathit{C}H_3)_3$), 25.70 ($\mathit{C}(CH_3)_3$), 12.35 (($\mathit{C}H_3CH_2)_2N$); IR (major bands and tenative assignments, cm^{-1}) 466 (ν(Zn–Se)), 509, 590 (ν(Zn–C)), 853 (ν(C–Se)), 1504 (ν(C–N)). Anal. Calcd for $C_9H_{19}NSe_2Zn$: C, 29.65; H, 5.25; N, 3.84. Found: C, 29.72; H, 5.23; N, 3.88.

Crystallography. Measurements were made on a sample mounted in a glass capillary with an Enraf-Nonius CAD4 diffractometer operating in the $\omega/2\theta$ scan mode with graphite-monochromated Mo Kα radiation as described previously.[19] The

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Table II. Fractional Atomic Coordinates ($\times 10^4$) for $[Me_3CCH_2ZnSe_2CNEt_2]_2$ (2)

	x	*y*	*z*
Zn(1)	4771 (1)	8667 (2)	4064 (2)
Zn(2)	1174 (2)	9501 (2)	5914 (2)
Se(1)	3407 (1)	9826 (1)	3923 (2)
Se(2)	4947 (1)	9672 (2)	2114 (2)
Se(3)	113 (1)	10677 (1)	6804 (2)
Se(4)	2463 (1)	11459 (1)	6283 (2)
N(1)	3511 (8)	10967 (10)	1719 (11)
N(2)	1496 (9)	12925 (9)	7246 (14)
C(1)	3941 (10)	10279 (11)	2454 (14)
C(2)	4552 (11)	7137 (11)	4284 (17)
C(3)	3484 (12)	6206 (13)	3567 (17)
C(4)	1403 (10)	11833 (11)	6861 (14)
C(5)	1528 (12)	8159 (11)	6430 (17)
C(6)	1125 (11)	7546 (11)	7419 (15)
C(11)	3850 (11)	11346 (12)	574 (15)
C(12)	4877 (11)	12397 (12)	1060 (15)
C(13)	2715 (10)	11535 (12)	2013 (15)
C(14)	1557 (10)	10934 (13)	1166 (15)
C(21)	589 (12)	13257 (12)	7592 (16)
C(22)	820 (13)	13407 (14)	9122 (17)
C(23)	2440 (11)	13912 (13)	7088 (18)
C(24)	3342 (13)	14210 (16)	8367 (19)
C(31)	3381 (14)	5003 (12)	3531 (20)
C(32)	3348 (15)	6231 (16)	2054 (20)
C(33)	2487 (13)	6339 (15)	3438 (26)
C(61)	1473 (14)	6515 (12)	7692 (17)
C(62)	−171 (12)	7180 (15)	6826 (17)
C(63)	1558 (14)	8341 (14)	8828 (16)

structures were solved via standard heavy-atom procedures and refined by using full-matrix least-squares methods[20] with scattering factors calculated by using the data from ref 21. All non-hydrogen atoms were refined with anisotropic displacement factors; hydrogen atoms were identified in difference maps and included with isotropic displacement factors. Crystal data and details of the intensity measurements and refinement are given in Table I. Positional parameters are given in Table II. Tables of H atom coordinates, all bond lengths and angles, and anisotropic displacement factor coefficients are included in the supplementary material.

Deposition of Thin Films. Thin films of ZnS and ZnSe were deposited onto glass microscope slides. Samples of the precursors (30–40 mg) were placed at one end of a Schlenk tube (12 mm o.d.) which was inserted into a tube furnace. The sample tube was kept under a continuous vacuum (10^{-2} Torr) at 450 °C. The precursor-containing end of the tube was allowed to protrude slightly outside the furnace, keeping the precursor at somewhat lower temperature than the furnace. The glass slide was placed at the center (hottest part) of the furnace. Thin specular films were grown over about 30 min.

Results and Discussion

The compounds of stoichiometry $Me_3CCH_2ZnS_2CNEt_2$ (1), $Me_3CCH_2ZnSe_2CNEt_2$ (2), $Me_3CZnS_2CNEt_2$ (3), and $Me_3CZnSe_2CNEt_2$ (4) were prepared as described in the Experimental Section. All are air-sensitive white crystalline solids with well-defined melting points. They can be recrystallized from hot toluene or benzene. The thiocarbamato derivatives are more soluble in common organic solvents than those of the selenocarbamates.

Structure of $Me_3CCH_2ZnSe_2CNEt_2$. The structure of compound 2 was determined from a single crystal by X-ray methods and is shown in Figure 1. Selected bond lengths and angles are summarized in Table III. The structure consists of discrete centrosymmetric dimeric molecules, $[Me_3CCH_2ZnSe_2CNEt_2]_2$; each diselenocarbamate chelates one zinc atom and bridges to the next.

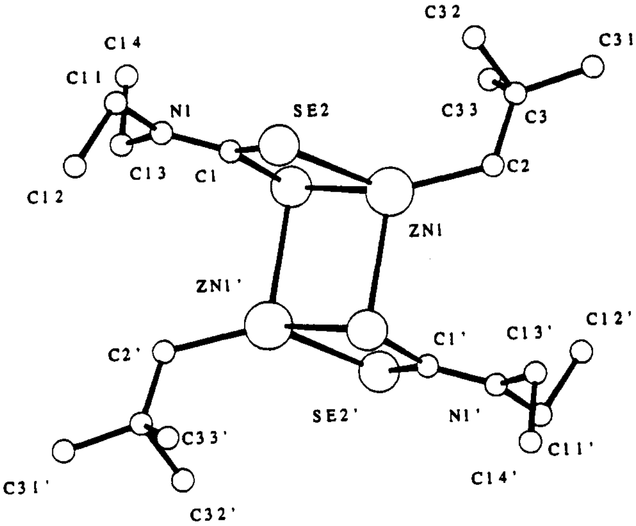

Figure 1. Molecular structure of $[Me_3CCH_2ZnSe_2CNEt_2]_2$ (2) with the atom-numbering scheme.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Me_3CCH_2ZnSe_2CNEt_2$ (2)

Se(1)–Zn(1)	2.578 (5)	Se(2)–Zn(1)	2.486 (5)
Se(3)–Zn(2)	2.588 (5)	Se(4)–Zn(2)	2.475 (4)
Se(1′)–Zn(1)	2.630 (5)	Se(1)–Zn(1′)	2.630 (5)
Se(3′)–Zn(2)	2.656 (5)	Se(3)–Zn(2′)	2.656 (5)
C(2)–Zn(1)	1.917 (16)	C(1)–Se(1)	1.915 (16)
C(1)–Se(2)	1.802 (15)	C(1)–N(1)	1.316 (16)
C(4)–Se(3)	1.864 (5)	C(4)–Se(4)	1.826 (2)
Se(2)–Zn(1)–Se(1)	77.7 (2)	C(2)–Zn(1)–Se(1)	129.5 (6)
Se(1)–Zn(1)–Se(1′)	95.2 (8)	Se(2)–Zn(1)–Se(1′)	94.8 (7)
Se(1′)–Zn(1)–C(2)	114.8 (5)	Se(2)–Zn(1)–C(2)	133.8 (5)
Se(3)–Zn(2)–Se(3′)	92.7 (11)	Se(3)–Zn(2)–Se(4)	77.5 (2)
Se(3′)–Zn(2)–Se(4)	96.4 (6)	Zn(1′)–Se(1)–Zn(1)	84.7 (2)
Zn(1)–Se(1)–C(1)	80.1 (5)	Zn(1′)–Se(1)–C(1)	92.6 (4)
Zn(1)–Se(2)–C(1)	84.9 (6)	Zn(2)–Se(3)–Zn(2′)	87.2 (9)
Zn(2)–Se(3)–C(4)	80.1 (5)	Zn(2′)–Se(3)–C(4)	96.2 (6)
Zn(2)–Se(4)–C(4)	83.9 (6)	Se(1)–C(1)–Se(2)	117.3 (4)
Se(1)–C(1)–N(1)	118.2 (1)	Se(2)–C(1)–N(1)	124.4 (12)
Zn(1)–C(2)–C(3)	124.9 (6)	Se(3)–C(4)–Se(4)	118.4 (8)
Se(3)–C(4)–N(2)	119.6 (1)	Se(4)–C(4)–N(2)	121.8 (11)
C(2)–Zn(1)–Se(2)	133.8 (5)	C(1)–Se(1)–Zn(1)	80.1 (5)
C(1)–Se(2)–Zn(1)	84.9 (6)	Se(2)–C(1)–Se(1)	117.3 (8)
N(1)–C(1)–Se(1)	118.2 (11)	N(1)–C(1)–Se(2)	124.4 (12)

The zinc atoms are four-coordinate, and the coordination can be described as distorted tetrahedral. The structure is similar to those recently reported for a methylzinc dithiocarbamate dimer[13] and methyl- and ethyl(diethylselenocarbamato)zinc(II).[15] The structure also resembles the dimeric units found in bis(thiocarbamates) and bis(selenocarbamates),[22-24] but with the alkyl group replacing the chelating-only carbamato group. The bond distances and angles are similar to those in other alkylzinc diethylselenocarbamates.[15] The Zn–Se bond lengths (2.58, 2.49, 2.63 Å) are almost same as those found in methyl- or ethylzinc diethyldiselenocarbamates. However, the Zn–C bond length (1.92 Å) is slightly shorter than those reported[15] (1.95 Å (methyl) and 1.97 Å (ethyl) for the above compounds. The Zn–Se bond lengths are slightly longer than those in bis(diethyldiselenocarbamato)zinc(II) (Zn–Se = 2.57, 2.45, 2.44, 2.40 Å). Neopentylzinc diethyldiselenocarbamate has longer E–Zn and E–C bond lengths than methylzinc diethyldithiocarbamate (S–Zn = 2.51, 2.37, 2.50 Å; S–C = 1.73 Å),[13] which is as expected on the basis of the accepted difference in radii between sulfur (r_{ion}

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= 1.70 Å and r_{cov} = 1.02 Å) and selenium (r_{ion} = 1.84 Å and r_{cov} = 1.17 Å). The zinc–carbon bond length (1.92 Å) is within the limits reported for other zinc alkyls.[12,25–28]

The packing involves two independent molecules with different orientations with respect to each other within the unit cell; there are no short or unusual contacts between the molecules. We had hoped that the use of the larger neopentyl alkyl group might lead to a structure different from that observed for the earlier compounds we have studied; unfortunately, this is not found to be the case.

Spectroscopic Studies. ^{1}H NMR spectra show a quartet and triplet for the *N*-ethyl groups (1–4), singlets for the methylene and methyl protons of neopentyl (1 and 2), and a singlet for the methyl protons of the *tert*-butyl group (3 and 4). These singlets can easily be assigned to the corresponding protons by the differences in their intensities. Only a small change in chemical shift is observed from thio- to selenocarbamates, but a significant shift to lower field is noted for the methyl protons as one goes from the neopentyl to the *tert*-butyl group. A slight change is noted in the chemical shift of *N*-ethyl protons as the alkyl substituent at the metal is varied.[13,15]

Proton-decoupled ^{13}C NMR spectroscopy reveals six- and five-line spectra for neopentyl and *tert*-butyl derivatives, respectively. A considerable difference in chemical shift is observed in the ^{13}C spectra between the thio- and selenocarbamates, especially for the $-CS_2-/-CSe_2-$ carbons. Similar differences in chemical shift have been noted for the methyl- and ethylzinc derivatives of thio- and selenocarbamates.[13,15] The quaternary carbons appear at lower field in the neopentyl derivatives than in the *tert*-butyl derivatives as the quaternary carbon in the *tert*-butyl group is more shielded.

The infrared spectra show the expected bands for Zn–S/Zn–Se, Zn–C, C–S/C–Se, and C–N stretching. A large decrease in stretching frequency is observed from Zn–S to Zn–Se, as expected, due to the larger mass of Se.

The similarity of the spectroscopic properties of all of the compounds strongly suggests that all the solids contain similar dimeric units.

Deposition of Thin Films. Using compounds 1–4, thin specular films of zinc chalcogens were deposited onto glass at 450 °C, under continuous vacuum, as described previously.[14] Electron microscopy showed these films to be polycrystalline with ca. 1-μm crystallites. The optical band gaps measured at room temperature were 2.70 eV for ZnSe films grown from either 1 or 3 (lit.[29] 2.70 eV; and 3.72 eV for ZnS film grown from 2 and 3.70 eV for the film grown from 4 (lit.[29] 3.68 eV). The elemental composition of the films was confirmed by elemental detection analytical X-ray methods (EDAX).

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Supplementary Material Available: Tables listing fractional atomic coordinates, anisotropic temperature factors, bond distances and angles, and selected inter- and intramolecular nonbonded distances (9 pages). Ordering information is given on any current masthead page.

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Base-Induced Migrations from Iron to the η^5-Indenyl Ligand in the Complexes $(\eta^5\text{-}C_9H_7)Fe(CO)_2R$ (R = Silyl, Oligosilyl)[1]

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Summary: The complexes $(\eta^5\text{-}C_9H_7)Fe(CO)_2R$ (R = $SiMe_3$, Si_2Me_5, Si_3Me_7, Si_4Me_9, c-Si_6Me_{11}) have been synthesized, and their reactivity toward *i*-Pr_2NLi (LDA) has been examined. Intermediate salts, $[(\eta^5\text{-R-}C_9H_6)Fe(CO)_2]^-Li^+$, were formed and quenched with MeI or Ph_3SnCl. The resulting complexes were shown by spectroscopy to involve migration of the R group to the 1-position of the indenyl ligand. In the case of the migrated product $(\eta^5\text{-1-}SiMe_3\text{-}C_9H_6)Fe(CO)_2SnPh_3$ a second treatment with LDA followed by addition of Ph_3SnCl or MeI produced $(\eta^5\text{-1-}SiMe_3\text{-3-}SnPh_3\text{-}C_9H_5)Fe(CO)_2R''$ (R'' = Ph_3Sn, Me). The complex with R'' = Ph_3Sn was characterized by single-crystal X-ray analysis to confirm the location of the migrated groups.

Migration of silyl, germyl, stannyl, and plumbyl groups from transition-metal centers to η^5-cyclopentadienyl ligands upon initial deprotonation of the cyclopentadienyl ligand has been studied extensively.[2] Related migrations of certain acyl and substituted alkyl groups have also been reported.[3] Given the relationship between the cyclopentadienyl and indenyl ligands, and the often greater reactivity of the indenyl system due to the η^5–η^3 ring-

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