Selenium Insertion into the M−C Bond (M = Ga, In): Syntheses and X-ray Crystal Structures of $[Np_2In(\mu\text{-}SeNp)]_2$, $[(Me_3SiCH_2)_2Ga(\mu\text{-}SeCH_2SiMe_3)]_2$, $[(Mes)C_6H_7N\cdot Ga\text{-}\mu\text{-}Se]_2$, and $(Mes)_2C_6H_7N\cdot GaSeMes$ (Np = $CH_2C(CH_3)_3$, Mes = 2,4,6-$Me_3C_6H_2$, C_6H_7N = 4-Picoline)

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The independent 1:1 reactions of $InNp_3$ (Np = CH_2CMe_3) and $Ga(CH_2SiMe_3)_3$ with elemental selenium resulted in the formation of novel dimeric compounds with the general formula $[R_2M(\mu\text{-}SeR)]_2$ (M = In, R = Np (**1**); M = Ga, R = CH_2SiMe_3 (**2**)) in a nearly quantitative yield. Reaction of $GaMes_3$ (Mes = 2,4,6-$Me_3C_6H_2$) with 2 mol of elemental Se, and subsequent addition of 4-picoline (C_6H_7N), resulted in the isolation of three compounds, $[(Mes)C_6H_7N\cdot Ga\text{-}\mu\text{-}Se]_2$ (**3**), $(Mes)_2C_6H_7N\cdot GaSeMes$ (**4**), and Se_2Mes_2. Compound **3** is a selenium-bridged dimer with two two-coordinate Se atoms and two 4-picoline (C_6H_7N) molecules in the dimeric unit. In related work, reaction of $InNp_3$ with S_2Ph_2 afforded the dimeric compound $[Np_2In(\mu\text{-}SPh)]_2$ (**5**) with elimination of NpSPh. The synthesis and characterization of **1**−**5**, including their solid-state structures, are presented.

Introduction

Unlike the chemistry of II−VI (12−16) compounds and the structural diversity that exists in such systems,[1−7] the chemistry of III−VI (13−16) compounds and materials is in its infancy. Semiconducting materials such as GaS have been made by metal−organic chemical vapor deposition (MOCVD) using the single-source precursor $[(^tBu)GaS]_4$,[8,9] and the cubic phase of GaS has been found to enhance the photoluminescence intensity of GaAs.[10] Syntheses of mixed-metal chalcogenides such as $CuInE_2$ (E = S, Se) from a single-source precursor[11,12] have been successful and their efficiency as photovoltaic cells are documented.[13,14]

There are several methods of synthesizing organometallic 13−16 compounds that have been previously reported in the literature.[15−18] However, there are only a handful of fully characterized compounds for the Ga−Se systems,[19−22] whereas more examples could be found for the Al−S and Ga−S systems.[23] Herein, we report the synthesis and characterization of five novel compounds, $[Np_2In(\mu\text{-}SeNp)]_2$ (Np = CH_2CMe_3) (**1**), $[(Me_3SiCH_2)_2Ga(\mu\text{-}SeCH_2SiMe_3)]_2$ (Mes = 2,4,6-$Me_3C_6H_2$) (**2**), $[(Mes)C_6H_7N\cdot Ga\text{-}\mu\text{-}Se]_2$ (**3**), $(Mes)_2C_6H_7N\cdot GaSeMes$ (**4**), and $[Np_2In(\mu\text{-}SPh)]_2$ (**5**).

Experimental Section

General Considerations. All manipulations of air- and moisture-sensitive materials were performed in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere and by general Schlenk techniques. Toluene and pentane were distilled over Na/K alloy.

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Elemental Se, S_2Ph_2, and 4-picoline (NC_6H_7) were purchased from Aldrich and were used as received. $InNp_3$,[24] $Ga(CH_2SiMe_3)_3$,[25] and $GaMes_3$[26] were prepared according to the literature methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a QE-300 spectrometer operating at 300 and 75.4 MHz, respectively. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to TMS by using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm, respectively, and the upfield pentet of C_7D_8 at δ 2.09 ppm for the ^1H NMR spectra and δ 20.4 ppm for $^{13}C\{^1H\}$ NMR spectra. All NMR samples were prepared in 5-mm tubes, which were septum-sealed under argon. Melting points (uncorrected) were obtained with a Thomas-Hoover Uni-melt apparatus, and capillaries were flame-sealed under argon. Elemental Analyses were performed by E + R Microanalytical Laboratory, Inc., Corona, NY. Mass spectral data were collected on a JEOL JMS-SX 102A spectrometer operating in the electron ionization mode at 20 eV. X-ray crystallographic data were obtained at 25 °C on a Siemens P4 diffractometer utilizing graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$ Å) radiation.

Preparation of $[Np_2In(\mu\text{-}SeNp)]_2$ (1). Inside the Dri-Lab a 250 mL Schlenk flask equipped with a magnetic stirbar was charged with $InNp_3$ (1.00 g, 3.05 mmol) and ca. 25 mL of toluene. A 0.24 g (3.05 mmol) amount of Se was added to the solution, and the resulting mixture was refluxed. After 30 min, all the Se was consumed and a colorless solution was formed. The solution was allowed to reflux for 6 h to ensure complete reaction, after which all of the volatile materials were removed under *vacuo* and the resultant white residue was dissolved in 5 mL of pentane. The X-ray quality colorless crystals of **1** were deposited at the bottom of the flask at −30 °C. Yield: 90% based on Se. Mp: 156 °C. Anal. Calcd (found) for $C_{30}H_{66}In_2Se_2$: C, 44.24 (44.47); H, 8.17 (8.31). ^1H NMR (C_6D_6): δ 1.35 (18H, s, $Se{-}CH_2C\mathit{Me}_3$), 1.61 (36H, s, $In{-}CH_2C\mathit{Me}_3$), 1.85 (8H, s, $In{-}\mathit{CH}_2CMe_3$), 3.36 (4H, s, $Se{-}\mathit{CH}_2CMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 28.12 ($Se{-}CH_2C\mathit{Me}_3$), 31.09 ($Se{-}CH_2\mathit{C}Me_3$), 31.93 ($In{-}\mathit{CH}_2CMe_3$), 33.93 ($In{-}CH_2C\mathit{Me}_3$), 34.65 ($Se{-}\mathit{CH}_2CMe_3$), 36.62 ($In{-}CH_2\mathit{C}Me_3$). MS (EI mode): *m/e*, 1064 ($[(M + {}^{M}/_{2}) - (2Np + Me)]^{\bullet+}$), 986 ($[(M + {}^{M}/_{2}) - (2Np + Se + Me)]^{\bullet+}$), 743 ($[M - Np]^{\bullet+}$), 408 ($[{}^{M}/_{2}]^{\bullet+}$), 337 ($[{}^{M}/_{2} - Np]^{\bullet+}$), 257 ($[InNp_2]^{\bullet+}$), 114.9 ($[In]^{\bullet+}$).

Preparation of $[(Me_3SiCH_2)_2Ga(\mu\text{-}SeCH_2SiMe_3)]_2$ (2). Compound **2** was synthesized using a procedure similar to that used for **1**. Note: Reaction time was 24 h. Reactants: $Ga(CH_2SiMe_3)_3$ (0.50 g, 1.51 mmol), Se (0.12 g, 1.51 mmol). Yield: 0.67 g, 94% based on Se. Mp: 106 °C. Anal. Calcd (found) for $C_{24}H_{66}Ga_2Se_2Si_6$: C, 35.13 (35.19); H, 8.11 (8.07). ^1H NMR: δ 0.10 (18H, s, $Se{-}CH_2Si\mathit{Me}_3$), 0.27 (36H, s, $Ga{-}CH_2Si\mathit{Me}_3$), 0.15 (8H, s, $Ga{-}\mathit{CH}_2SiMe_3$), 1.91 (4H, s, $Se{-}\mathit{CH}_2SiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −1.29 ($Se{-}CH_2Si\mathit{Me}_3$), 2.19 ($Ga{-}\mathit{CH}_2SiMe_3$), 2.54 ($Ga{-}CH_2Si\mathit{Me}_3$), 5.38 ($Se{-}\mathit{CH}_2CSiMe_3$). MS (EI mode): *m/e* 735 ($[M - CH_2SiMe_3]^{\bullet+}$), 441 ($[{}^{M}/_{2}]^{\bullet+}$), 395 ($[{}^{M}/_{2} - Me]^{\bullet+}$), 323 ($[SeGa(CH_2SiMe_3)_2]^{\bullet+}$), 244 ($[Ga(CH_2SiMe_3)_2]^{\bullet+}$).

Preparation of $[(Mes)C_6H_7N{\cdot}Ga\text{-}\mu\text{-}Se]_2$ (3) and $(Mes)_2C_6H_7N{\cdot}GaSeMes$ (4). Inside the Dri-Lab 3.15 g (7.37 mmol) of $GaMes_3$ and 0.52 g (7.37 mmol) of Se were combined in a 250 mL Schlenk flask, and ca. 100 mL of toluene was added to the mixture. The flask was removed from the Dri-Lab, and the resultant mixture was refluxed for 24 h. After 20 min of refluxing, the color of the solution had changed to yellow and after 2 h all of the selenium was consumed. A second mole of selenium (0.52 g) was added to the homogeneous light orange solution, and the mixture was refluxed for another 24 h. At the end of this period, a white solid had precipitated out of the solution with the consumption of all the selenium. To this solution was added 1.44 mL (14.74 mmol) of 4-picoline *via* syringe in ca. 10 min while stirring the solution. The solution was then heated with a heat gun to dissolve all of the precipitate. The flask was left undisturbed overnight at room temperature, and the X-ray quality crystals of **3** were deposited at the bottom of the flask. The solution was separated from the crystals of **3**, and the solution was cooled to −20 °C to afford a powder which was identified as **4**. Recrystallization of the powder from toluene afforded the X-ray quality crystals of **4**.

Data for 3: Yield 0.96 g, 81% based on Se. Mp: >300 °C (dec). Anal. Calcd (found) for $C_{30}H_{36}Ga_2N_2Se_2$: C, 49.91 (49.88); H, 5.03 (5.15); N, 3.88 (3.92). ^1H NMR (C_6D_6): δ 1.47 (6H, s, 4-CH_3-pyridine), 2.22 (6H, s, *p*-Me of Mes), 3.02 (12H, s, *o*-Me of Mes), 6.17 (4H, d, $J_{H-H} = 4.2$ Hz, *m*-H of 4-picoline), 6.92 (4H, s, *m*-H of Mes), 8.88 (4H, d, $J_{H-H} = 4.5$ Hz, *o*-H of 4-picoline). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 20.56 (Me-pyridine), 21.27 (*p*-Me of Mes), 25.84 (*o*-Me of Mes), 125.52, 127.31, 128.56, 137.73, 146.23, 147.50 (aryl). MS (EI mode): *m/e* 307 ($[GaMes_2]^{\bullet+}$).

Data for 4: Yield 1.52 g, 77% based on Se. Mp: 179 °C. Anal. Calcd (found) for $C_{33}H_{40}GaNSe$: C, 66.13 (66.02); H, 6.73 (6.82); N, 2.34 (2.25). ^1H NMR (C_6D_6): δ 1.47 (3H, s, 4-CH_3-pyridine), 2.10 (3H, s, *p*-Me of Mes−Se), 2.16 (6H, s, *p*-Me of Mes−Ga), 2.39 (12H, s, *o*-Me of Mes−Ga), 2.53 (6H, s, *o*-Me of Mes−Se), 6.16 (2H, d, $J_{H-H} = 3.6$ Hz, *m*-H of 4-picoline), 6.72 (2H, s, *m*-H of Mes−Se), 6.77 (4H, s, *m*-H of Mes−Ga), 8.70 (4H, b, *o*-H of 4-picoline). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 20.59 (Me-pyridine), 20.93 (*p*-Me of Mes−Se), 21.14 (*p*-Me of Mes−Ga), 25.76 (*o*-Me of Mes−Ga), 26.41 (*o*-Me of Mes−Se), 125.48, 130.96, 134.65, 136.95, 143.70, 143.32, 144.39, 144.89, 145.64, 148.55, 151.63 (aryl). MS (EI mode): *m/e* 666 ($[M + Se]^{\bullet+}$), 586 ($[M = C_{33}H_{40}GaNSe]^{\bullet+}$), 467 ($[M - Mes]^{\bullet+}$), 398 ($[Se_2Mes_2]^{\bullet+}$), 318 ($[MesSeMes]^{\bullet+}$), 200 ($[HSeMes]^{\bullet+}$), 120 ($[MesH]^{\bullet+}$).

Preparation of $[Np_2In(\mu\text{-}SPh)]_2$ (5). A 0.33 g (1.01 mmol) amount of $InNp_3$ and 0.22 g (1.01 mmol) of S_2Ph_2 were combined in a Schlenk flask equipped with a magnetic stirbar. Pentane (20 mL) was added to the mixture, and the resultant clear solution was stirred for 12 h. The volume of pentane was reduced to 5 mL *in vacuo*, and the X-ray quality colorless crystals of **5** were deposited at the bottom of the flask at −30 °C. Yield: 89% based on $InNp_3$. Mp: 83 °C. Anal. Calcd (found) for $C_{32}H_{54}In_2S_2$: C, 52.47 (52.54); H, 7.43 (7.60). ^1H NMR (C_6D_6): δ 1.61 (36H, s, $In{-}CH_2C\mathit{Me}_3$), 1.85 (8H, s, $In{-}\mathit{CH}_2CMe_3$), 7.01 (6H, m, *m*, *p*-H of Ph), 7.59 (4H, d, *o*-H of Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 32.71 ($In{-}\mathit{CH}_2CMe_3$), 34.90 ($In{-}CH_2C\mathit{Me}_3$), 40.66 ($In{-}CH_2\mathit{C}Me_3$), 126.20, 128.98, 133.69, 134.14 (aryl). MS (EI mode): *m/e* 699 ($[M - S]^{\bullet+}$), 661 ($[M - Np]^{\bullet+}$), 366 ($[{}^{M}/_{2}]^{\bullet+}$), 295 ($[{}^{M}/_{2} - Np]^{\bullet+}$), 258 ($[InNp_2]^{\bullet+}$), 324.

X-ray Structural Solution and Refinement. Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals of **1**−**5** were mounted in thin-walled capillaries and temporarily sealed with silicone grease under an argon atmosphere and then flame-sealed.

Preliminary photographic data indicated a primitive monoclinic crystal system for **1**, **4**, and **5**, an *I*-centered monoclinic system for **3**, and no symmetry higher than triclinic for **2**. The systematic absences in the diffraction data for **1**, **4**, and **5** are uniquely consistent with the reported space groups for **1**, **4**, and **5**. The centrosymmetric options were chosen for **2** and **3** which yielded chemically reasonable and computationally stable results of refinement.

The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semi-empirical ellipsoid absorption corrections were applied to **2** and **5** but not for **1**, **3**, and **4** because there was less than 10% variation observed in the ψ-scan data. The molecules of **1** and **3** are located on an inversion center, and **2** contains two independent but chemically equivalent molecules, each lying on an inversion center. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated

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Table 1. Crystal Data and Structure Refinement for $[Np_2In(\mu\text{-}SeNp)]_2$ (1), $[(Me_3SiCH_2)_2Ga(\mu\text{-}Se(CH_2SiMe_3)]_2$ (2), $[(Mes)C_6H_7N\cdot Ga\text{-}\mu\text{-}Se]_2$ (3), $(Mes)_2C_6H_7N\cdot GaSeMes$ (4), $[Np_2In(\mu\text{-}SPh])_2$ (5) ($Np = CH_2C(CH_3)_3$, Mes = 2,4,6-$(CH_3)_3C_6H_2$)

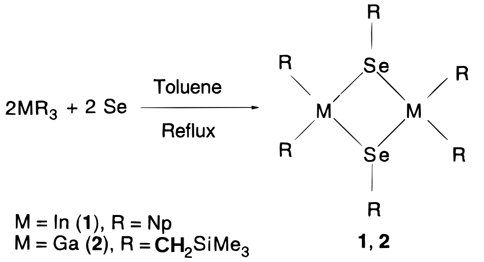
	1	2	3	4	5
empirical formula	$C_{30}H_{66}In_2Se_2$	$C_{24}H_{66}Ga_2Se_2Si_6$	$C_{30}H_{36}Ga_2N_2Se_2$	$C_{33}H_{40}GaNSe$	$C_{32}H_{54}In_2S_2$
fw	814.39	820.67	721.97	599.34	732.51
temp, K	233(2)	233(2)	298(2)	298(2)	237(2)
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
space group	$P2_1/c$	$P\bar{1}$	$I2/a$	$I2_1/n$	$P2_1/c$
a, Å	10.241(2)	10.058(2)	14.771(2)	14.080(2)	18.778(3)
b, Å	10.393(3)	11.506(2)	13.336(1)	15.413(1)	10.050(1)
c, Å	18.501(4)	19.826(4)	15.924(2)	14.577(1)	19.880(2)
α, deg		82.44(1)			
β, deg	102.25(2)	89.80(2)	99.187(8)	108.186(8)	104.31(1)
γ, deg		73.49(1)			
V, Å^3	1924.3(3)	2179.4(7)	3096.8(6)	3005.4(5)	3635.4(6)
D_{calcd}, g cm^{-3}	1.406	1.251	1.549	1.325	1.338
Z	2	2	4	4	4
abs coeff cm^{-1}	31.04	30.83	41.11	21.47	14.00
cryst dimens mm	0.30 × 0.20 × 0.20	0.40 × 0.25 × 0.15	0.40 × 0.10 × 0.10	0.40 × 0.30 × 0.30	0.40 × 0.40 × 0.25
cryst habit	colorless block	colorless block	colorless rod	colorless block	colorless block
q range for data collection, deg	2.11−21.49	2.01−22.50	2.00−22.49	2.02−22.49	2.11−33.50
no. of rflns collected	3014	6845	2447	4819	5985
no. of independent rflns	2196 (R_{int} = 0.0254)	5677 (R_{int} = 0.0469)	2009 (R_{int} = 0.0617)	3876 (R_{int} = 0.0677)	4750 (R_{int} = 0.0393)
goodness-of-fit on F^2	1.173	1.498	1.237	1.008	1.313
final R indices[a] $[I > 2\alpha(I)]$	R1 = 0.0491 wR2 = 0.1039	R1 = 0.0627 wR2 = 0.1441	R1 = 0.0457 wR2 = 0.1035	R1 = 0.0460 wR2 = 0.0914	R1 = 0.0397 wR2 = 0.0939

[a] Quantity minimized = $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = -|F_o - F_c)|$; $R(wF^2) = \Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[(wF_o{}^2)^2]^{1/2}$.

as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL(5.3) program libraries.[27]

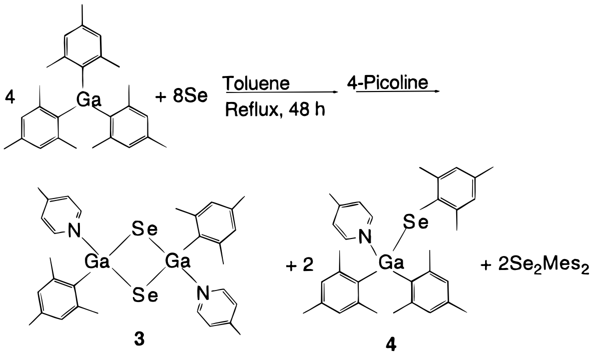
Results and Discussion

Syntheses. Independent reactions of $InNp_3$ ($Np = CH_2C(CH_3)_3$) and $Ga(CH_2SiMe_3)_3$ with elemental selenium in a 1:1 ratio in refluxing toluene resulted in the formation of $[Np_2In(\mu\text{-}SeNp)]_2$ (**1**) and $[(Me_3SiCH_2)_2Ga(\mu\text{-}Se(CH_2SiMe_3)]_2$ (**2**) in nearly quantitative yields (eq 1). In the formation of **1**, all of the selenium is consumed within $^1/_2$ h, whereas for compound **2** the elemental selenium was consumed over the course of several hours under similar conditions.



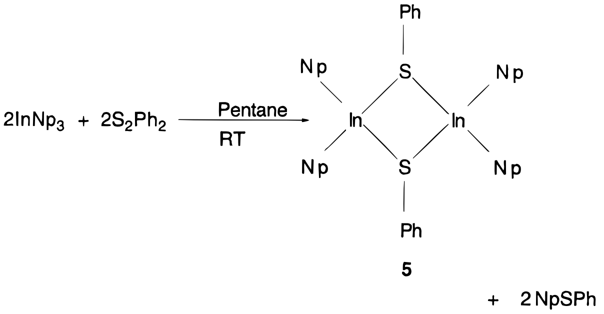
(1)

The reaction of $GaMes_3$ with 2 mol of elemental Se resulted in the formation of a precipitate which was insoluble in toluene. We did not attempt to isolate and characterize the white precipitate, however, upon molar addition of the base, 4-picoline (C_6H_7N), to the original reaction flask and heating the reaction mixture, all of the precipitate was dissolved to form a homogeneous orange solution. Leaving the flask undisturbed at room temperature for several hours resulted in the formation of X-ray quality crystals (colorless rods) of **3**. X-ray quality crystals (colorless blocks) of **4** were isolated from recrystallization of a white powder obtained from the original orange solution at −20 °C. Inside the Dri-Lab the orange solution was evaporated to leave an orange residue, which was completely dissolved in pentane. The pentane solution yielded crystals (golden blocks) which were identified by ^1H NMR and MS data to be Se_2Mes_2 (eq 2). The white insoluble precipitate, from which compounds **3** and **4** were isolated, could have consisted of the large aggregate $(MesGaSe)_n$ as well as $(Mes_2GaSeMes)_n$, which upon addition of the base (C_6H_7N) yielded the more soluble adducts (eq 2).



(2)

Compound **5** was synthesized according to eq 3 (*vide infra*), with the byproduct NpSPh being identified by GC/MS. The formation of $[Np_2In(\mu\text{-}SPh)]_2$ and NpSPh



(3)

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(27) *SHELXTL PC*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

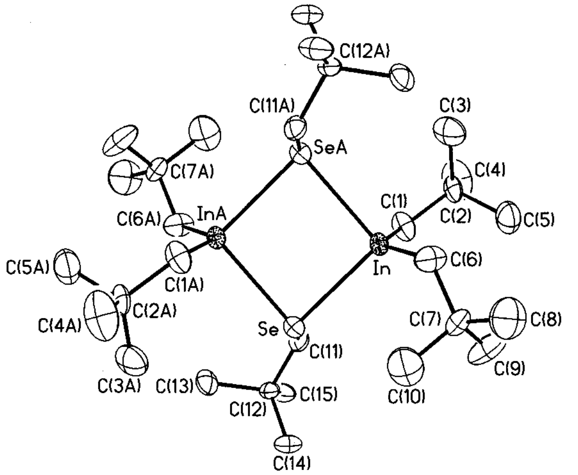

Figure 1. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of [Np$_2$In(μ-SeNp)]$_2$ (**1**).

suggest that the reaction mechanism is similar to the reactions of InMes$_3$ with diselenides and ditellurides reported earlier.[20,28,29]

Compounds **1**, **2**, and **5** are extremely soluble in pentane, whereas **3** is slightly soluble and **4** shows better solubility in toluene. Compounds **1**−**5** are air sensitive and decomposed slowly in the presence of air.

We have observed that the independent insertion reactions of GaR$_3$ and elemental Se are much slower when compared to similar reactions with InR$_3$ and elemental Se under similar forcing conditions, keeping in mind the similar bulk of the R groups. This behavior is also observed by Uhl and co-workers.[21] One explanation might be that when we compare InR$_3$ to GaR$_3$ (R is a bulky group such as mesityl or neopentyl), the bulky substituent can offer much more protection to the smaller Ga center making it a much more hindered molecule and, therefore, less reactive toward Se insertion.

Spectroscopic Studies. The mass spectrum of **1** shows larger fragments than the dimeric unit observed in the solid state, suggesting the existence of a larger aggregate in the vapor phase. Compounds **1**, **2**, and **4** are reasonably volatile and their mass spectra show isotope patterns that match with the calculated isotope patterns well.

The ^{1}H NMR spectrum of **4** shows two sharp doublets for the *ortho* and *meta* protons on the picoline group, whereas in compound **5** these signals are much broader, suggesting an exchange process in solution.[30] Variable-temperature NMR studies (−85 to 80 °C) were carried out for compounds **2**, **3**, and **5** but no significant changes were observed.

Structures of [Np$_2$In(μ-SeNp)]$_2$ (1) and [(Me$_3$SiCH$_2$)$_2$Ga(μ-SeCH$_2$SiMe$_3$)]$_2$ (2). Thermal ellipsoid diagrams of **1**−**5** are shown in Figures 1−6. Crystal data and structure refinement for **1**−**5** are given in Table 1. Selected interatomic bond distances and bond angles for **1**−**5** are presented in Tables 2−6. Compounds **1** and **2** have a central (MSe)$_2$ core with the substituent on the Se in the *anti* conformation, with this orientation of ligands presumably minimizing the steric interaction. Both compounds possess a planar four-membered ring and the metal centers have to quasi-tetrahedral geometry. A planar core is found in [Mes$_2$In(μ-Cl)]$_2$;[31] however, a folded conformation is reported

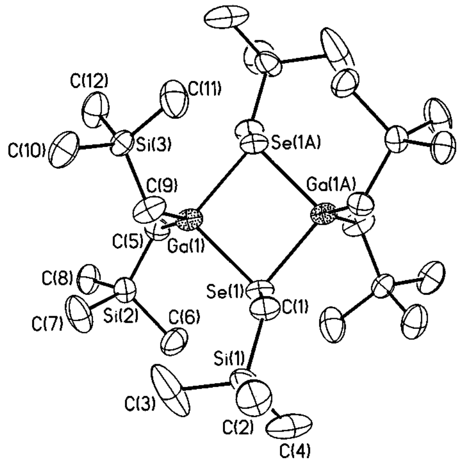

Figure 2. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of [(Me$_3$SiCH$_2$)$_2$Ga(μ-Se(CH$_2$SiMe$_3$)]$_2$ (molecule 1) (**2**). Hydrogen atoms are omitted for clarity.

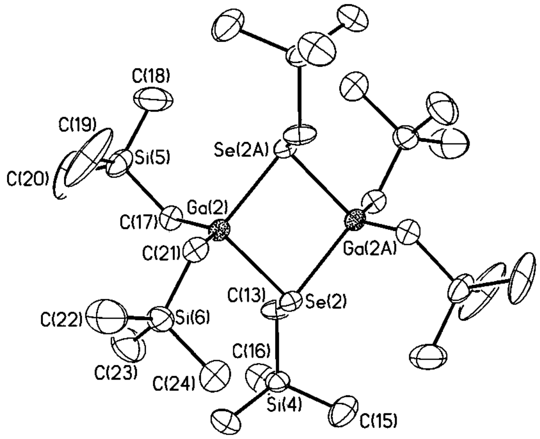

Figure 3. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of [(Me$_3$SiCH$_2$)$_2$Ga(μ-Se(CH$_2$SiMe$_3$)]$_2$ (molecule 2) (**2**). Hydrogen atoms are omitted for clarity.

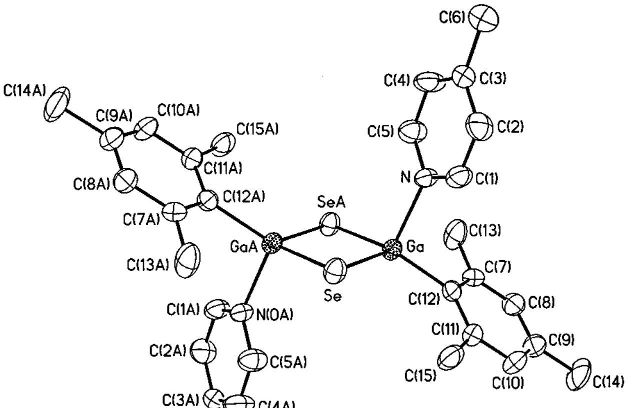

Figure 4. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of [(Mes)C$_6$H$_7$N·Ga-μ-Se]$_2$ (**3**). Hydrogen atoms are omitted for clarity.

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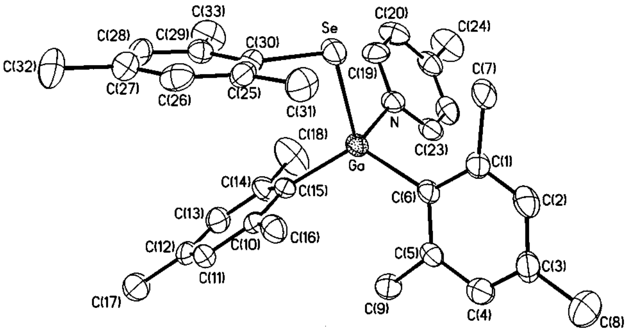

Figure 5. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of $(Mes)_2C_6H_7N\cdot GaSeMes$ (**4**). Hydrogen atoms are omitted for clarity.

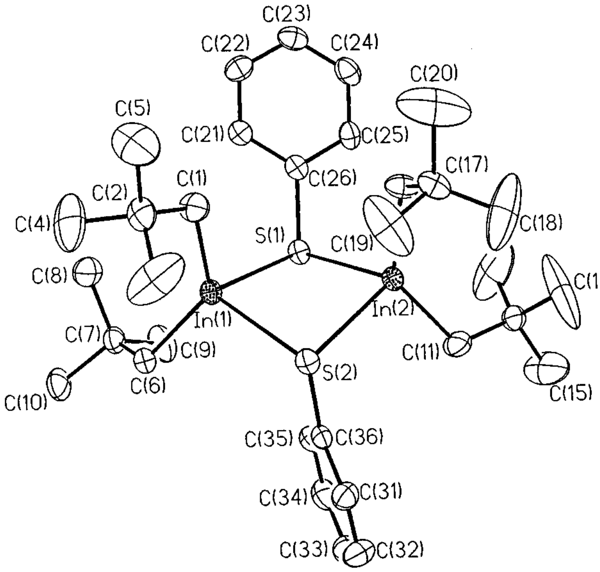

Figure 6. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of $[Np_2In(\mu\text{-}SPh)]_2$ (**5**). Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Np_2In(\mu\text{-}SeNp)]_2$ (1), with Estimated Standard Deviations in Parentheses[a]

Bond Lengths			
In−C(1)	2.197(11)	In−C(6)	2.198(9)
In−Se	2.7053(14)	In−SeA	2.719(2)
Se−C(11)	1.972(10)	Se−InA	2.719(2)
C(1)−C(2)	1.50(2)	C(2)−C(3)	1.51(2)
Bond Angles			
C(6)−In−C(1)	134.5(4)	C(6)−In−Se	109.1(3)
C(1)−In−Se	104.2(3)	C(6)−In−SeA	107.5(4)
C(1)−In−SeA	99.9(3)	Se−In−SeA	94.06(4)
C(11)−Se−In	103.1(3)	C(11)−Se−InA	108.1(3)
In−Se−InA	85.94(4)	C(2)−C(1)−In	118.4(7)

[a] Symmetry transformation used to generate equivalent atoms: −x, −y + 2, −z + 2.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[(Me_3SiCH_2)_2Ga(\mu\text{-}Se(CH_2SiMe_3)]_2$ (2) (Molecule 1 and 2), with Estimated Standard Deviations in Parentheses[a]

Bond Lengths			
Se(1)−C(1)	1.983(9)	Se(1)−Ga(1)	2.523(2)
Se(1)−Ga(1A)	2.539(2)	Se(2)−C(13)	1.978(9)
Se(2)−Ga(2A)	2.529(2)	Se(2)−Ga(2)	2.5329(14)
Ga(1)−C(5)	1.959(9)	Ga(1)−C(9)	1.975(9)
Ga(1)−Se(1A)	2.539(2)	Ga(2)−C(21)	1.954(9)
Ga(2)−C(17)	1.961(9)	Ga(2)−Se(2A)	2.529(2)
Si(1)−C(2)	1.856(12)	Si(1)−C(1)	1.865(10)
Si(1)−C(4)	1.880(13)	Si(1)−C(3)	1.884(14)
N(1)−C(9)	1.468(3)	C(15)−C(20)	1.388(4)
Bond Angles			
C(1)−Se(1)−Ga(1)	105.3(3)	C(1)−Se(1)−Ga(1A)	102.4(3)
Ga(1)−Se(1)−Ga(1A)	85.35(5)	C(13)−Se(2)−Ga(2A)	102.9(3)
C(13)−Se(2)−Ga(2)	103.5(3)	Ga(2A)−Se(2)−Ga(2)	84.14(5)
C(5)−Ga(1)−C(9)	125.1(5)	C(5)−Ga(1)−Se(1)	107.5(3)
C(9)−Ga(1)−Se(1)	110.8(3)	C(5)−Ga(1)−Se(1A)	106.4(3)
C(9)−Ga(1)−Se(1A)	108.1(4)	Se(1)−Ga(1)−Se(1A)	94.65(5)
C(21)−Ga(2)−C(17)	125.6(4)	C(21)−Ga(2)−Se(2A)	109.7(3)
C(17)−Ga(2)−Se(2A)	106.7(3)	C(21)−Ga(2)−Se(2)	106.0(3)
C(17)−Ga(2)−Se(2)	108.9(2)	Se(2B)−Ga(2)−Se(2)	95.86(5)
C(2)−Si(1)−C(1)	107.8(6)	C(2)−Si(1)−C(4)	111.3(6)
C(1)−Si(1)−C(4)	108.0(6)	C(2)−Si(1)−C(3)	108.1(7)
Si(1)−C(1)−Se(1)	111.5(5)	Si(2)−C(5)−Ga(1)	121.0(5)
Si(3)−C(9)−Ga(1)	120.6(5)	Si(4)−C(13)−Se(2)	112.2(5)
Si(5)−C(17)−Ga(2)	118.8(4)	Si(6)−C(21)−Ga(2)	118.6(5)

[a] Symmetry transformation used to generate equivalent atoms: 1A −x + 2, −y, −z + 1; 2A −x − 1, −y + 3, −z.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $[(Mes)C_6H_7N\cdot Ga\text{-}\mu\text{-}Se]_2$ (3), with Estimated Standard Deviations in Parentheses[a]

Bond Lengths			
Se−Ga(1A)	2.3784(12)	Se−Ga	2.3872(13)
Ga−C(12)	1.988(7)	Ga−N	2.090(6)
Ga−Se(A)	2.3784(12)	N−C(1)	1.306(10)
N−C(5)	1.313(10)	C(1)−C(2)	1.382(11)
Bond Angles			
Ga(A)−Se−Ga	79.87(4)	C(12)−Ga−N	103.3(3)
C(12)−Ga−Se(A)	120.5(2)	N−Ga−Se(A)	104.7(2)
C(12)−Ga−Se	125.2(2)	N−Ga−Se	99.6(2)
Se(A)−Ga−Se	100.13(4)	C(1)−N−C(5)	116.8(7)
C(1)−N−Ga	118.6(6)	C(5)−N−Ga	123.9(6)
N−C(1)−C(2)	121.9(8)	C(3)−C(2)−C(1)	122.3(9)

[a] Symmetry transformation used to generate equivalent atoms: −x + 1, −y, −z + 1.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for $(Mes)_2C_6H_7N\cdot GaSeMes$ (4), with Estimated Standard Deviations in Parentheses[a]

Bond Lengths			
Se−C(30)	1.922(6)	Se−Ga	2.4383(9)
Ga−C(15)	2.004(5)	Ga−C(6)	2.004(6)
Ga−N	2.095(5)	C(1)−C(2)	1.384(8)
N−C(23)	1.347(7)	C(14)−C(18)	1.500(9)
Bond Angles			
C(30)−Se−Ga	106.7(2)	C(15)−Ga−C(6)	119.9(2)
C(15)−Ga−N	112.5(2)	C(6)−Ga−N	100.0(2)
C(15)−Ga−Se	111.3(2)	C(6)−Ga−Se	114.8(2)
N−Ga−Se	94.84(14)	C(1)−C(6)−Ga	122.5(5)
C(5)−C(6)−Ga	120.8(4)	C(10)−C(15)−Ga	117.3(4)
C(14)−C(15)−Ga	125.7(5)	C(23)−N−Ga	117.6(4)
C(29)−C(30)−Se	121.5(5)	C(25)−C(30)−Se	117.9(5)

for $[Np_2In(\mu\text{-}SePh)]_2$,[32] $[Mes_2In(\mu\text{-}I)]_2$,[33] and $Np_2In(\mu\text{-}SePh)(\mu\text{-}P^tBu_2)InNp_2$.[34] The In−Se bond lengths in **1** (average 2.71 Å) are comparable with those seen in $[Mes_2In(\mu\text{-}SePh)]_2$ (average 2.732 Å),[29] $[Mes_2In(\mu\text{-}SeMes)]_2$ (average 2.715 Å),[29] $[Np_2In(\mu\text{-}SePh)]_2$ (average 2.743 Å),[32] $[^tBu_2In(\mu\text{-}Se^tBu)]_2$ (2.70 Å),[35] and polymeric $[In(SePh)_3]_\infty$ (average 2.78 Å)[36] but longer than those observed in polymeric $[MeIn(SePh)(\mu\text{-}SePh)]_\infty$ (bridging

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Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for $[Np_2In(\mu\text{-}SPh)]_2$ (5), with Estimated Standard Deviations in Parentheses[a]

Bond Lengths			
In(1)−C(1)	2.162(6)	In(1)−C(6)	2.171(6)
In(1)−S(2)	2.618(2)	In(1)−S(1)	2.6318(14)
In(2)−C(16)	2.143(6)	In(2)−C(11)	2.155(6)
In(2)−S(2)	2.623(2)	In(1)−S(1)	2.651(2)
S(1)−C(26)	1.788(6)	S(2)−C(36)	1.783(6)
C(1)−C(2)	1.518(8)	C(2)−C(4)	1.521(12)

Bond Angles			
C(1)−In(1)−C(6)	131.7(2)	C(1)−In(1)−S(2)	101.2(2)
C(6)−In(1)−S(2)	108.8(2)	C(1)−In(1)−S(1)	105.6(2)
C(6)−In(1)−S(1)	112.4(2)	S(2)−In(1)−S(1)	87.48(5)
C(16)−In(2)−C(11)	136.3(3)	C(16)−In(2)−S(2)	108.1(2)
C(11)−In(2)−S(2)	103.9(2)	C(16)−In(2)−S(1)	103.1(2)
C(11)−In(2)−S(1)	107.5(2)	S(2)−In(2)−S(1)	86.98(5)
C(26)−S(1)−In(1)	110.0(2)	C(26)−S(1)−In(2)	106.3(2)
In(1)−S(1)−In(2)	88.25(5)	C(36)−S(2)−In(1)	110.2(2)
C(36)−S(2)−In(2)	102.3(2)	In(1)−S(2)−In(2)	89.14(5)
C(2)−C(1)−In(1)	119.2(5)	C(3)−C(2)−C(4)	108.5(9)

SePh 2.682 Å and terminal SePh 2.541 Å),[29] $[In_2Se_{21}]^{4-}$ (average 2.67 Å),[37] $In[SeC(SiMe_3)_3]_3$ (average 2.527Å),[38] $In(SeMes^*)_3$ ($Mes^* = 2,4,6\text{-}{}^tBu_3\text{-}C_6H_2$; average 2.505 Å),[39] $Mes^*In(SePh)_2$ (2.526 and 2.551 Å),[40] and $[Tp^tBu_2]$-InSe (Tp = tris(pyrazolyl)hydroborate) (In−Se = 2.376(1) Å).[41]

Only a few examples of Ga−Se bond distances are found in the literature. For **2**, the average Ga−Se bond distance of 2.53 Å is comparable to that of $[Ph_2Ga(\mu\text{-}SeMe)]_2$ (2.51 Å)[20] but slightly longer than those found in cubane $[{}^tBuGaSe]_4$ (2.48 Å),[19] monomeric $Ga(SeMes^*)_3$ (average 2.324 Å),[42] $[(Mes)C_6H_7N{\cdot}Ga\text{-}\mu\text{-}Se]_2$ (**3**) (average 2.383 Å), and $(Mes)_2C_6H_7N{\cdot}GaSeMes$ (**4**) (2.428 Å). The average M−C bond distances and exocyclic C−M−C angles for **1** and **2** are in accordance with those of similar structures reported in the literature.[23] The bridging Se atoms in **1** and **2** are three-coordinate and have pyramidal geometry ($\sum Se = 297.14°$ for **1** and $\sum Se1 = 293.05°$ for **2**).

Structures of $[(Mes)C_6H_7N{\cdot}Ga\text{-}\mu\text{-}Se]_2$ (3) and $(Mes)_2C_6H_7N{\cdot}GaSeMes$ (4). Compound **3** is dimeric with the central core consisting of planar $(GaSe)_2$. The selenium atoms are in the bridging position and are two-coordinate. The gallium atoms have a distorted tetrahedral geometry. The Ga−Se bond distance of 2.38 Å is shorter than the Ga−Se bond distance for **2** but similar to Ga−Se bond length in monomeric $R_2Ga{-}Se{-}GaR_2$ ($R = CH(SiMe_3)_2$; 2.34 Å).[21] This is understandable since the coordination number for Se atom is two in **3** rather than three for **2**. The Ga−Se bond length of 2.38 Å in **3** is almost identical to the covalent radii reported for Ga−Se (2.37 Å).[43]

Compound **4** is a simple adduct with a distorted tetrahedral geometry around the Ga center. The Ga−Se bond length of 2.44 Å is longer than the bond length observed for **3** but comparable to the Ga−Se bond length reported for $[{}^tBuGaSe]_4$ (2.48 Å).[19] The Ga−N bond lengths of 2.090(6) Å for **3** and 2.095(5) Å for **4** are normal, when compared to the several Ga−N adduct bond lengths reported in the literature.[44]

Structure of $[Np_2In(\mu\text{-}SPh)]_2$ (5). Compound **5** also has an *anti* conformer with a puckered core consisting of $(InS)_2$. This molecule possess no crystallographic symmetry. Crystals of **5** are isomorphous with previously reported dimeric compounds $[Np_2In(\mu\text{-}SePh)]_2$[32] and $[Np_2Ga(\mu\text{-}TePh)]_2$.[45] The In−S bond distances in **5** range from 2.618(2) to 2.651(2) Å. These values are in close agreement with the bond lengths in $[Mes_2In(\mu\text{-}S^tBu)]_2$ (average 2.62 Å),[46] $[Me_2In(\mu\text{-}SSiPh_3)]_3$ (average 2.609Å),[46] and $[{}^tBu_2In(\mu\text{-}S^tBu)]_2$ (2.60 Å)[35] but slightly longer than the similar bond lengths reported for $[Ph_2In(\mu\text{-}SSn(C_6H_{11})_3]_2$ (average 2.551 Å),[47] $[Mes_2In(\mu\text{-}SSiPh_3)]_2$ (average 2.498 Å),[46] and $[Mes_2In(\mu\text{-}S^tamyl)]_2$ (average 2.592 Å).[46] The overall geometry around the S atoms in **5** are also pyramidal ($\sum S(1) = 304.6°$ and $\sum S(2) = 301.6°$).

Conclusion

From the previously reported data in the literature and the data gathered here, we can conclude that the insertion of elemental selenium into the Ga−C and In−C bonds can occur with relative ease to produce the seleno-derivatives of these metals in good yield, if the substituent on the metal is sufficiently bulky. However, the insertion of more than one Se atom needs further investigation.

Acknowledgment. We are grateful for the financial support of this work provided by the Office of Naval Research.

Supporting Information Available: Tables of crystal and X-ray data collection parameters, bond distances and angles, anisotropic thermal parameters for the non-hydrogen atoms, and atomic coordinates and isotropic thermal parameters for the hydrogen atoms (27 pages). Ordering information is given on any current masthead page.

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