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SYNTHESIS OF INDIUM(III) SUPERMESITYL DERIVATIVES (SUPERMESITYL = Mes* = 2,4,6-^{t}Bu$_3$(C_6H_2)). X-RAY CRYSTAL STRUCTURES OF Mes*(Br)In[$CH_2C(Me)_2C_6H_3{}^{t}Bu_2$] and Mes*In(SePh)$_2$

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Heating Mes*$_2$InBr (Mes* = 2,4,6-^{t}Bu$_3$(C_6H_2)) at 130-150 °C under reduced pressure afforded the new isomer Mes*(Br)In[$Ch_2C(CH_3)_2C_6H_3(^{t}Bu)_2$ (**1**) in 55% yield. The solid-state structure of **1** was determined by single-crystal X-ray crystallography. The resultant geomery around the indium center can be viewed as pseudo trogonal bupyramidal due to two close contacts of *o*-$_{t}$Bu hydrogens on the Mes* groups. Reaction of In(SePh)$_2$I with Mes*MgBr resulted in the quantitative formation of Mes*In(SePh)$_2$ (**2**). An X-ray structural analysis of 2 revealed a monomeric molecule.

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Notes

Synthesis of Indium(III) Supermesityl Derivatives (Supermesityl = Mes* = 2,4,6-^{t}Bu$_3$(C$_6$H$_2$)). X-ray Crystal Structures of Mes*(Br)In[CH$_2$C(Me)$_2$C$_6$H$_3$(^{t}Bu)$_2$] and Mes*In(SePh)$_2$

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Summary: Heating Mes$_2$InBr (Mes* = 2,4,6-^{t}Bu$_3$(C$_6$H$_2$)) at 130−150 °C under reduced pressure afforded the new isomer Mes*(Br)In[CH$_2$C(CH$_3$)$_2$C$_6$H$_3$(^{t}Bu)$_2$] (**1**) in 55% yield. The solid-state structure of **1** was determined by single-crystal X-ray crystallography. The resultant geometry around the indium center can be viewed as pseudo trigonal bipyramidal due to two close contacts of o-^{t}Bu hydrogens on the Mes* groups. Reaction of In(SePh)$_2$I with Mes*MgBr resulted in the quantitative formation of Mes*In(SePh)$_2$ (**2**). An X-ray structural analysis of **2** revealed a monomeric molecule.*

Introduction

Group 13 compounds possessing bulky alkyl or aryl groups have been studied by several research groups, and sterically demanding ligands have enabled the isolation of several group 13 species with low coordination numbers[1−3] or lower oxidation states of the metal center.[4−12] The supermesityl ligand, 2,4,6-^{t}Bu$_3$(C$_6$H$_2$), has been used successfully for the synthesis of various compounds which otherwise can be difficult to prepare. Several monomeric compounds of group 2[13−15] and group 13 are stabilized by the supermesityl ligand because the o-^{t}Bu groups of Mes* offer protection to the metal center. Supermesityl derivatives of monomeric monohalides[16−18] and dihalides[19,20] of Al, Ga, and In have been synthesized, and the stable hydrides of Al and Ga have also been isolated.[18,21−23] In a recent work by Power and coworkers, the synthesis and characterization of MMes*$_2$ (M = Mg, Mn, Fe) was reported[15] and, in another paper,[24] the formation of several monomeric group 13 compounds (e.g.- Mes*$_2$GaSMe and Mes*$_2$GaSPh) was discussed. Meller *et al.* reported the formation of Mes*$_2$GaCl and its transformation to Mes*(Cl)Ga[CH$_2$C(Me)$_2$C$_6$H$_3$(^{t}Bu)$_2$][17] and the cyclometalated product 5,7-di-*tert*-butyl-3,3-dimethyl-1-(2,4,6-tri-*tert*-butylphenyl)benzo[*b*]-gallolane,[17] where the activation of the C−H bond is achieved by the Ga center. Similarly, the reaction of Mes*$_2$GaCl with LiGaH$_4$ resulted in the formation of Mes*(H)Ga[CH$_2$C(Me)$_2$C$_6$H$_3$(^{t}Bu)$_2$].[23] The unusual ability of the gallium metal to activate the C−H bond has motivated us to examine whether the indium metal behaves in a similar fashion. To our knowledge, the activation of the C−H bond by the indium center is unprecedented but documented for gallium.[17,23,25] In this note, we report our findings in utilizing the supermesityl group and present the synthesis and characterization of Mes*(Br)In[CH$_2$C(Me)$_2$C$_6$H$_3$(^{t}Bu)$_2$] (**1**) and Mes*In(SePh)$_2$ (**2**).

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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. All solvents were distilled over Na/K alloy. Mes*MgBr,[16] Mes*$_2$InBr,[16] and In(SePh)$_2$I[26] were made according to the literature. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a GE-300 spectrometer operating at 300 and 75.4 MHz, respectively. ^{1}H and ^{13}C{^{1}H} spectra were referenced to TMS by using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm, respectively. 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. IR spectra were acquired for KBr pellets on a BOMEM Michelson MB-100 FT-IR spectrometer. X-ray crystallographic data were obtained at 25 °C on a Siemens P4 diffractometer utilizing graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation.

Preparation of Mes*(Br)In[CH$_2$C(CH$_3$)$_2$C$_6$H$_3$(^{t}Bu)$_2$] (1). Mes*$_2$InBr (3.00 g, 4.38 mmol) was placed in a 250 mL Schlenk flask. The flask was then submerged completely in a silicone oil bath and heated under reduced pressure at 130−150 °C for 12 h. After the mixture was cooled to room temperature, a white crystalline solid was obtained and recrystallized from hexane at room temperature to give X-ray-quality colorless crystals of **1** after several days: yield 55%; mp 141 °C. Anal. Calcd (found) for $C_{36}H_{58}InBr$: C, 63.07 (63.21); H, 8.53 (8.66). ^{1}H NMR (C_6D_6): ^{t}Bu$_3$C$_6$H$_2$, δ 7.44 (2H, s, 3,5-H); 1.29 (9H, s, *p*-^{t}Bu), 1.26 (18H, s, *o*-^{t}Bu); 3,5-^{t}Bu$_2$C$_6$H$_3$C(CH$_3$)$_2$CH$_2$, δ 7.39 [2H, d, (^4J = 1.8 Hz), 2,6-H], 7.33 [1H, t, (^4J = 1.8 Hz), 4-H], 1.23 (18H, s, 3,5-^{t}Bu), 2.03 (2H, s, CH$_2$), 1.53 (6H, s, 2CH$_3$). ^{13}C{^{1}H} NMR (C_6D_6): ^{t}Bu$_3$C$_6$H$_2$, δ 31.6 [*p*-C(*C*H$_3$)$_3$], 32.8 [*o*-C(*C*H$_3$)$_3$], 34.0 [*p*-*C*(CH$_3$)$_3$], 37.4 [*o*-*C*(CH$_3$)$_3$], 122.1 (C-3,5), 138.2 (In−C), 156.1 (C-2,6), 150.3 (C-4), 31.4 [C(*C*H$_3$)$_2$], 34.8 [*C*(CH$_3$)$_2$], 39.3 (CH$_2$); 3,5-^{t}Bu$_2$C$_6$H$_3$, δ 31.4 [C(*C*H$_3$)$_3$], 39.6 [*C*(CH$_3$)$_3$], 119.5 (C-4), 120.5 (C-2,6), 150.4 (C-3,5), 150.9 (C-1). Mass spectral data (EI mode): peaks at *m*/*e* 685, 605, 439, 246, 231 corresponding to fragments of $C_{36}H_{58}InBr$ (M^+), [M − Br]$^{\bullet+}$, [M − Mes*]$^{\bullet+}$, [Mes*H]$^{\bullet+}$, [Mes* − Me]$^{\bullet+}$, respectively. IR (cm^{-1}, KBr pellet): 2957 (s), 2862 (w), 1582 (w), 1360 (w), 1106 (w), 1021 (w), 874 (w), 804 (w), 704 (w), 565 (w), 495 (w).

Preparation of Mes*In(SePh)$_2$ (2). A 250 mL Schlenk flask equipped with a magnetic stirbar was charged with In(SePh)$_2$I (2.00 g, 3.61 mmol) and ca. 40 mL of THF. To this was added 12.2 mL of Mes*MgBr (0.30 M solution in THF) by syringe over about 15 min at room temperature. The formation of salt was apparent after addition of half of the Mes*MgBr. After the complete addition, the solution was stirred overnight at room temperature. The THF was removed *in vacuo*, and the resultant yellowish solid was extracted with two 25 mL portions of hexane. X-ray quality crystals of **2** formed overnight at −20 °C. The crystals were isolated and washed with 20 mL of cold (−75 °C) pentane. Yield 90%; mp 115 °C. Anal. Calcd (found) for $C_{30}H_{39}InSe_2$: C, 53.59 (53.79); H, 5.85 (6.00). ^{1}H NMR (C_6D_6): δ 7.59 (4H, m, *ortho* C_6H_5), 7.43 (2H, s, *meta* C_6H_2), 6.81 (6H, m, *meta* and *para* C_6H_5), 1.37 (18H, s, *o*-^{t}Bu) 1.22 (9H, s, *p*-^{t}Bu). ^{13}C{^{1}H} NMR (C_6D_6): ^{t}Bu$_3$C$_6$H$_2$, δ 31.9 [*p*-C(*C*H$_3$)$_3$], 33.0 [*o*-C(*C*H$_3$)$_3$], 35.2 [*p*-*C*(CH$_3$)$_3$], 37.5 [*o*-*C*(CH$_3$)$_3$], 122.6 (*meta* Mes* ring), 136.4 (*ipso* Mes* ring), 150.9 (*para* Mes* ring), 156.3 (*ortho* Mes* ring), 119.5, 126.6, 129.2 (Ph ring). Mass spectral data (EI mode): peaks at *m*/*e* 1191, 789, 674, 644, 517, 487, 246, 231 corresponding to fragments of [2M − SePh]$^{\bullet+}$, [M + In]$^{\bullet+}$, $C_{30}H_{39}InSe_2$ (M^+), [M − 2Me]$^{\bullet+}$, [M − SePh]$^{\bullet+}$, [M − (SePh + 2Me)]$^{\bullet+}$, [Mes*H]$^{\bullet+}$, [Mes* − Me]$^{\bullet+}$. IR (cm^{-1}; KBr pellet): 3140 (w), 3063 (w), 2953 (s), 2866 (w), 1580 (w), 1242 (w), 1066 (w), 1018 (w), 808 (w), 691 (w), 570 (w).

Table 1. Crystal Data and Structure Refinement for Mes*(Br)In[CH$_2$C(CH$_3$)$_2$C$_6$H$_3$(^{t}Bu)$_2$] (1) and Mes*In(SePh)$_2$ (2)

	1	2
empirical formula	$C_{36}H_{58}InBr$	$C_{30}H_{39}InSe_2$
fw	685.55	672.35
temp, K	298(2)	298(2)
radiation (wavelength, Å)	Mo Kα (λ = 0.710 73)	Mo Kα (λ = 0.710 73)
cryst syst	orthorhombic	monoclinic
space group	*Fdd*2	$P2_1/n$
a, Å	14.968(1)	11.103(2)
b, Å	82.54(2)	18.375(1)
c, Å	11.596(2)	14.951(2)
β, deg	90.0(−)	102.99(1)
V, Å^3	14326(5)	2972.2(7)
D_{calcd}, g cm^{-3}	1.271	1.503
Z	16	4
abs coeff	1.796 mm^{-1}	3.259 mm^{-1}
F(000)	5728	1344
cryst dimens, mm	0.40 × 0.40 × 0.15	0.30 × 0.20 × 0.20
cryst habit	colorless plate	colorless block
θ range for data collecn, deg	2.24−23.49°	2.18−22.50°
no. of rflns collected	3273	4671
no. of independent rflns	2990 (R_{int} = 0.0361)	3838 (R_{int} = 0.0525)
no. of data/restraints/params	2990/1/343	3831/0/296
goodness of fit on F^2	1.285	1.132
final *R* indices ($I > 2\sigma(I)$)[a]	R1 = 0.0412	R1 = 0.0468
	wR2 = 0.0941	wR1 = 0.0966
R indices (all data)	R1 = 0.0503	R1 = 0.0859
	wR2 = 0.0963	wR2 = 0.1098
D(*r*) and hole, e Å^{-3}	0.510 and −0.624	0.700 and −0.511

[a] Quantity minimized: $\sum[w(|F_o^2 - F_c^2)^2]/\sum[(wF_o^2)_2]]^{1/2}$. $R = \sum\Delta/\sum(F_o)$. $R_w = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$. $\Delta = |(F_o - F_c)|$.

X-ray Structural Solution and Refinement. Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals were mounted in thin-walled capillaries and flame-sealed under argon.

The photographic data, unit cell parameters, and occurrences of equivalent reflections and systematic absences in the diffraction data are uniquely consistent with the space group *Fdd*2 for **1** and $P2_1/n$ for **2**.

The structures were solved using direct methods, completed by difference Fourier syntheses, and refined by full-matrix least-squares procedures. A semiempirical absorption correction was applied for **1**; all data with a glancing angle of ≤3° to the prominent face [001] were rejected, affecting 169 reflections. Semiempirical absorption corrections were applied for **2**. All non-hydrogen atoms were refined with anisotropic displacement coefficients, except for the *para* ^{t}Bu group on the Mes* moiety in **2**. Carbon atoms, C(16), C(17), and C(18) are disordered over two positions with an occupancy distribution of 60/40 and were refined isotropically. The hydrogen atoms on these carbons were ignored. All other hydrogen atoms were treated as idealized contributions.

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

Results and Discussion

Heating Mes*$_2$InBr at 130−150 °C under reduced pressure afforded **1** in 55% yield (eq 1). A small amount

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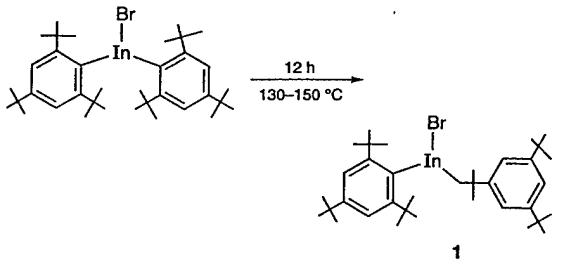
(27) SHELXTL PC; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1990.



(1)

1

of Mes*H was deposited on the outlet valve of the Schlenk flask and was identified by ^{1}H NMR. No traces of the indium analog of 5,7-di-*tert*-butyl-3,3-dimethyl-1-(2,4,6-tri-*tert*-butylphenyl)benzo[*b*]gallolane[17] (*vide supra*) was detected. Similar to the mechanism proposed by Cowley *et al.* for the formation of Mes*(H)Ga[$CH_2C(Me)_2C_6H_3(^tBu)_2$],[23] the transformation of Mes*$_2$InBr[16] to **1** could occur through the activation of a C–H bond of one of the *o*-^{t}Bu groups of Mes* with subsequent protonation of the *ipso* carbon. This is a good indication that an agostic interaction between the In center and the *o*-^{t}Bu groups of one of the Mes* ligands in Mes*$_2$InBr[16] does exist and this agostic interaction might be responsible for the formation of **1**. The deviation of one of the Mes* groups from planarity (15°) in Mes*$_2$InBr (Mes* group with close C–H···In contact) is not observed in the molecular structure of **1**. This is perhaps due to relief of steric hindrance in **1** compared to the parent isomer, Mes*$_2$InBr.

The reaction of In(SePh)$_2$I and Mes*MgBr afforded **2** in high yield (eq 2). Compounds **1** and **2** are soluble in

$$\text{Mes*MgBr} + \text{In(SePh)}_2\text{I} \xrightarrow[25\ ^\circ\text{C}]{\text{THF}} \underset{\mathbf{2}}{\text{Mes*In(SePh)}_2} + \text{"MgBrI"} \quad (2)$$

aromatic solvents and saturated hydrocarbons and decompose slowly when exposed to air. The ^{1}H NMR spectrum of **1** clearly shows a complex pattern which matches that of Mes*(Cl)Ga[$CH_2C(Me)_2C_6H_3(^tBu)_2$].[17] The mass spectrum of **1** showed a fragment corresponding to the parent ion, while the mass spectrum of **2** showed fragments associated with a dimeric species of **2** as well as monomeric M^+ for **2**. Compounds **1** and **2** are volatile, and their mass spectra show isotope patterns that match well with calculated isotope patterns.

The structures of compounds **1** and **2** were determined by single-crystal X-ray diffraction methods, and their molecular drawings are shown in Figures 1 and 2, respectively. Selected bond distances and angles for **1** and **2** are listed in Tables 2 and 3, respectively. The structure of **1** shows it to be a monomer and to be isostructural with the Ga analog Mes*(Cl)Ga[$CH_2C(Me)_2C_6H_3(^tBu)_2$].[17] The bond distances and angles are comparable to many examples in the literature.[16,18–20] One interesting feature is the close proximity of the methyl groups on the Mes* moiety to the indium center. C(9) and C(18) are almost directly above and below the indium atom with In···C(9) = 2.98 Å and In···C(18) = 2.84 Å. Such close In···C contact distances have been documented for several species.[16,18,20,28–30] The parent molecule, Mes*$_2$InBr, also shows short In···C contact distances.[16] These short In···C contacts support the existence of an agostic or steric interaction between the In and the *o*-^{t}Bu groups, and the resultant geometry around the indium center can be viewed as pseudo trigonal bipyrimidal.

Similar to compound **1**, compound **2** is a monomeric base-free molecule with close In–C contact distances

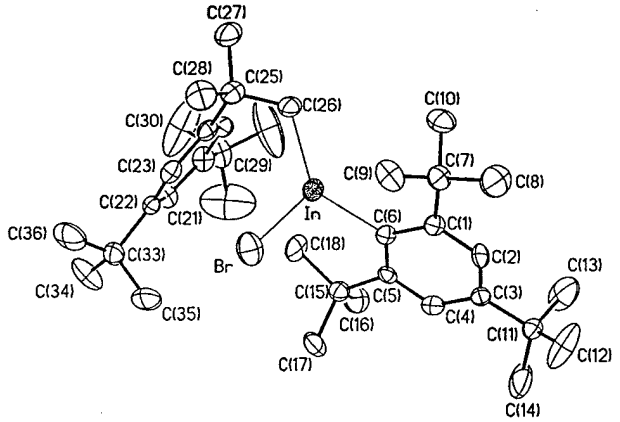


Figure 1. Molecular structure of Mes*(Br)In[$CH_2C(CH_3)_2C_6H_3(^tBu)_2$] (**1**) with atoms shown as 30% probability ellipsoids. Hydrogen atoms were omitted for clarity.

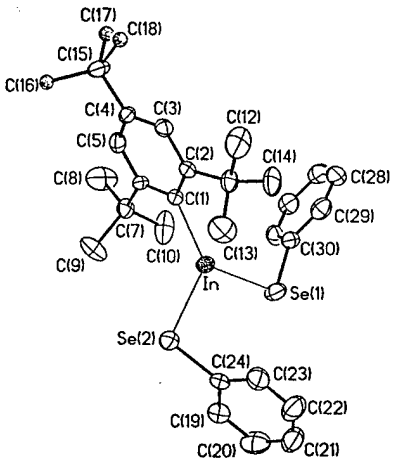


Figure 2. Molecular structure of Mes*In(SePh)$_2$ (**2**) with carbon atoms C(16), C(17), and C(18) disordered over two positions, with the major contribution shown isotropically. All other atoms are shown as 30% probability ellipsoids. Hydrogen atoms were omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Mes*(Br)In[$CH_2C(CH_3)_2C_6H_3(^tBu)_2$] (1), with Estimated Standard Deviations in Parentheses

Bond Lengths			
In–C(6)	2.152(9)	In···C(9)	2.98
In–C(26)	2.166(10)	In···C(18)	2.84
In–Br	2.5503(14)		
Bond Angles			
C(6)–In–C(26)	131.2(4)	C(6)–In–Br	111.0(2)
C(26)–In–Br	117.6(3)	C(2)–C(1)–C(6)	119.8(8)
C(2)–C(1)–C(7)	118.7(7)	C(6)–C(1)–C(7)	121.5(8)
C(5)–C(4)–C(3)	122.7(9)	C(4)–C(5)–C(6)	119.3(7)
C(4)–C(5)–C(15)	116.4(8)	C(6)–C(5)–C(15)	123.9(8)
C(1)–C(6)–C(5)	117.2(8)	C(1)–C(6)–In	120.7(6)
C(5)–C(6)–In	122.1(6)		

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Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Mes*In(SePh)$_2$ (2), with Estimated Standard Deviations in Parentheses

Bond Lengths			
In–C(1)	2.160(7)	Se(1)–C(30)	1.917(8)
In–Se(1)	2.5261(12)	Se(2)–C(24)	1.921(9)
In–Se(2)	2.5507(11)		

Bond Angles			
C(1)–In–Se(1)	134.9(2)	C(1)–In–Se(2)	121.8(2)
Se(1)–In–Se(2)	103.34(4)	C(30)–Se(1)–In	102.1(2)
C(24)–Se(2)–In	98.0(2)	C(2)–C(1)–In	120.1(5
C(6)–C(1)–In	119.2(5)	C(19)–C(24)–Se(2)	120.6(7)
C(23)–C(24)–Se(2)	120.5(7)	C(29)–C(30)–Se(1)	121.6(7)
C(25)–C(30)–Se(1)	121.5(7)		

(In···C(10) = 3.054 Å and In···C(13) = 3.230 Å). The In–Se bond lengths in **2** (2.526 and 2.551 Å) are longer than the In–Se bond length in the terminal selenido complex [Tp('Bu$_2$)]InSe (Tp = tris(pyrazolyl)hydroborate; In–Se = 2.376(1) Å)[31] but are comparable with those seen in In[SeC(SiMe$_3$)$_3$]$_3$ (average 2.527 Å)[30] and In(SeMes*)$_3$ (average 2.505 Å)[32] and are significantly shorter than the In-Se bond lengths in [Mes$_2$In(μ-SePh)]$_2$ (average 2.732 Å),[33] [Mes$_2$In(μ-SeMes)]$_2$ (average 2.715 Å),[33] [(neo-Pe)$_2$In(μ-SePh)]$_2$ (average 2.743 Å),[34] and polymeric [In(SePh)$_3$]$_\infty$ (average 2.78 Å).[35] The Se-In-Se angle in **2** is 103.35°, which deviates from trigonal geometry but is in good accordance with a similar angle in In[SeC(SiMe$_3$)$_3$]$_3$ (103.86°).[30] The geometry of the In center is trigonal planar, with the sum of the angles around In being 359.95°. The In–C bond distance of 2.160(7) Å in **2** is in the same range as for several reported compounds in the literature.[36]

Conclusion. Compounds **1** and **2** are monomeric compounds, and the resultant geometry around the indium centers can be viewed as pseudo trigonal bipyramidal. The transformation of Mes*$_2$InBr to **1** in moderate yield can present opportunities to study the reactivity of **1** toward various reagents. The formation of **2** by arylation of In(SePh)$_2$I can provide a synthetic route to other heteroleptic compounds.

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Supporting Information Available: For **1** and **2**, complete listings of crystal and X-ray data collection parameters, bond distances and angles, atomic coordinates and anisotropic thermal parameters for the non-hydrogen atoms, and atomic coordinates and isotropic thermal parameters for the hydrogen atoms (14 pages). Ordering information is given on any current masthead page.

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