SYNTHESIS OF INDIUM(III) SUPERMESITYL DERIVATIVES
(SUPERMESITYL = Mes* = 2,4,6-i-Bu₃(C₆H₃)). X-RAY CRYSTAL
STRUCTURES OF Mes*(Br)In[CH₃(CH₂)₂C₆H₃(Bu)₃] and Mes*In(SePh)₂

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ABSTRACT (Maximum 200 words)

Heating Mes*₂InBr (Mes* = 2,4,6-i-Bu₃(C₆H₃)) at 130-150 °C under reduced pressure afforded the new isomer Mes*(Br)In[CH₃(CH₂)₂C₆H₃(Bu)₃]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-Bu hydrogens on the Mes* groups. Reaction of In(SePh)₂I 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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X-RAY CRYSTAL STRUCTURES OF
Mes*(Br)In[CH\textsubscript{2}C(Me)\textsubscript{2}C\textsubscript{6}H\textsubscript{3}\textit{t}-Bu\textsubscript{2}] and Mes*In(SePh)\textsubscript{2}

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Synthesis of Indium(III) Supermesityl Derivatives
(Supermesityl = Mes* = 2,4,6-iBu3(C6H3)). X-ray Crystal Structures of Mes*(Br)In[CH2C(Me)2C6H3(iBu)2] and Mes*In(SePh)2

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Summary: Heating Mes*InBr (Mes* = 2,4,6-iBu3(C6H3)) at 130-150 °C under reduced pressure afforded the new isomer Mes*(Br)In[CH2C(Me)2C6H3(iBu)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-iBu hydrogen on the Mes* groups. Reaction of In(SePh)3 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 numbers1-3 or lower oxidation states of the metal center.4-12 The supermesityl ligand, 2,4,6-iBu3(C6H3), has been used successfully for the synthesis of various compounds which otherwise can be difficult to prepare. Several monomeric compounds of group 13-15 and group

13 are stabilized by the supermesityl ligand because the o-iBu groups of Mes* offer protection to the metal center. Supermesityl derivatives of monomeric monohalides16-18 and dihalides19-20 of Al, Ga, and In have been synthesized, and the stable hydrides of Al and Ga have also been isolated.19,21-22 In a recent work by Power and co-workers, the synthesis and characterization of MMes*2 (M = Mg, Mn, Fe) was reported16 and, in another paper,24 the formation of several monomeric group 13 compounds (e.g., Mes*GaMe and Mes*GaPh) was discussed. Meller et al. reported the formation of Mes*2GaCl and its transformation to Mes*(Cl)GaCl(CMes)-C6H3(iBu)220 and the cyclometalated product 5,7-di-tert-butyl-3,3-dimethyl-1-(2,4,6-tri-tert-butylphenyl)benzo[5]gallolane,27 where the activation of the C-H bond is achieved by the Ga center. Similarly, the reaction of Mes*2GaCl with LiGaH2 resulted in the formation of Mes*[GaCl2(CMes)-C6H3(iBu)2]25 and 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.22-27 In this note, we report our findings in utilizing the supermesityl group and present the synthesis and characterization of Mes*(Br)In[CH2C(Me)2C6H3(iBu)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*BrIn, 16 Mes*MgBr, 16 Mes*InBr, 16 and IntSePh 26 were made according to the literature. 1H and 13C{H} NMR spectra were recorded on a GE-300 spectrometer operating at 300 and 75.4 MHz, respectively. 1H and 13C{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 Ka (λ = 0.7107 Å) radiation.

Preparation of Mes*{Br}In(CH2=C(CH3)2)2C6H5(Bu) (1). Mes*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 I after several days: yield 55%; mp 141 °C. Anal. Calcd (found) for C30H31BrIn: C, 63.07 (63.21); H, 8.53 (8.66). 1H NMR (CD3)2SO: 1.29 (9H, s, p-C6H5), 1.26 (18H, s, o-C6H5), 3.5–3.6 Bu3C=CH2, 7.39 (2H, d, J = 18 Hz, 2.6–H), 7.33 (1H, t, J = 18 Hz, 4.7–H), 1.23 (8H, s, 2.6–Bu), 2.03 (2H, s, 3.5–Bu), 1.53 (6H, s, 2CH3).

13C{H} NMR (CD3)2SO: 31.6 (p-C6H5), 32.8 (o-C6H5), 34.0 (p-C6H5), 37.4 (o-C6H5), 122.1 (C-3,5), 128.2 (C-2,6), 156.2 (C-3,4), 31.4 (C=CH2), 34.8 (C=CH2), 39.3 (CH3), 3.5–3.6 Bu3C=CH2, 31.4 (C=CH2), 39.6 (C=CH2), 119.5 (C-4), 120.5 (C-2,6), 150.4 (C-3,5), 150.9 (C-1).

Final X-ray data: masses at m/e 665, 605, 493, 246, 231 corresponding to fragments of C30H31BrIn (M+), [M – Br]+, [M – Mes*]+, [Mes*In]+, [Mes*]+, respectively. IR (cm–1, KBr pellet): 2957, 2862, 1582, 1360, 1106, 1021, 874, 804, 704, 565, 495.

Preparation of Mes*In(SePh2) (2). A 250 mL Schlenk flask equipped with a magnetic stirbar was charged with IntSePh2 (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 syringes 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 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 C20H38Se2In: C, 53.59 (53.70); H, 5.65 (6.00). 1H NMR (CD2Cl2): δ 7.59 (4H, m, ortho CeH5), 7.43 (2H, s, meta CeH5), 6.81 (1H, m, and para CeH5), 1.37 (18H, s, p-C6H5), 1.22 (9H, s, p-C6H5), 3.5–3.6 Bu3C=CH2, 31.9 (p-C6H5), 33.0 (p-C6H5), 35.2 (p-C6H5), 122.6 (meta Mes* ring), 136.4 (para Mes* ring), 150.9 (para Mes* ring), 156.3 (ortho Mes* ring), 119.5, 118.6, 128.6, 128.2 (Ph ring). Mass spectral data (EI mode): peaks at m/e 1189, 789, 674, 444, 517, 487, 246, 231 corresponding to fragments of [2M – SePh]+, [M + In]+, C20H38Se2In (M*), [M – 2Me]+, [M – SePh]+, [M – (SePh + 2Me)]+, [Mes*H]+, [Mes* – }
of Mes*H was deposited on the outlet valve of the Schlenk flask and was identified by 1H NMR. No traces of the iodine analog of 5,7-di-tert-butyl-3,3-dimethyl-1-(2,4,6-tri-tert-butylphenyl)benzo[b]gallolane (vide supra) was detected. Similar to the mechanism proposed by Cowley et al. for the formation of Mes*(H)Ga-[CH2C(Me)2]C6H5(Bu)2,15 the transformation of Mes*2- InBr16 to 1 could occur through the activation of a C−H bond of one of the o-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-Bu groups of one of the Mes* ligands in Mes*2-InBr16 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*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*2InBr.

The reaction of In(SePh)2I and Mes*MgBr afforded 2 in high yield (eq 2). Compounds 1 and 2 are soluble in aromatic solvents and saturated hydrocarbons and decompose slowly when exposed to air. The 1H NMR spectrum of 1 clearly shows a complex pattern which matches that of Mes*(Cl)Ga(CH2C(Me)2)C6H5(Bu)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 isosstructural with the Ga analog Mes*(Cl)Ga(CH2C(Me)2)C6H5(Bu)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 very close to the center and 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

![Figure 1. Molecular structure of Mes*(Br)In(CH2C(CH3)2C6H5(Bu)2] (1) with atoms shown as 30% probability ellipsoids. Hydrogen atoms were omitted for clarity.](image1)

![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.](image2)

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>C−C(6)</th>
<th>C−C(26)</th>
<th>In−C(9)</th>
<th>In−C(18)</th>
<th>Br−Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>In−C(6)</td>
<td>2.152(9)</td>
<td>2.156(10)</td>
<td>2.98</td>
<td>2.84</td>
<td>2.550(3)</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Bond Angles</th>
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<tbody>
<tr>
<td>C(6)−In−C(26)</td>
</tr>
<tr>
<td>C(26)−In−Br</td>
</tr>
<tr>
<td>C(2)−C(1)−C(7)</td>
</tr>
<tr>
<td>C(5)−C(4)−C(3)</td>
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<tr>
<td>C(4)−C(5)−C(15)</td>
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<tr>
<td>C(1)−C(6)−In</td>
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<tr>
<td>C(1)−C(6)−In</td>
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molecule, Mes*InBr, also shows short In−C contact distances. These short In−C contacts support the existence of an agostic or steric interaction between the In and the o-Bu groups, and the resultant geometry around the indium center can be viewed as pseudo trigonal bipyramidal.

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

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

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Bond Angles</th>
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<tbody>
<tr>
<td>In–C(1)</td>
<td>2.160(7)</td>
</tr>
<tr>
<td>In–Se(1)</td>
<td>2.526(12)</td>
</tr>
<tr>
<td>In–Se(2)</td>
<td>2.550(7)</td>
</tr>
</tbody>
</table>

(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_3)InSe (Tp = tris(pyrazolyl)hydroborate; In–Se = 2.376(1) Å)31 but are comparable with those seen in In[SeC(SiMe_3)_3]_2 (average 2.527 Å)32 and In[SeMes^*]_3 (average 2.505 Å)33 and are significantly shorter than the In-Se bond lengths in [Mes^2In(µ-SePh)]_2 (average 2.732 Å),33 [Mes^2In(µ-SeMes)]_2 (average 2.715 Å),33 [(neo-Ph)_2In(µ-SePh)]_2 (average 2.743 Å),34 and polymeric [In(SePh)_3]_n (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^*^2InBr 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)_3I can provide a synthetic route to other heteroleptic compounds.

Acknowledgment. This work was funded by the Office of Naval Research

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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