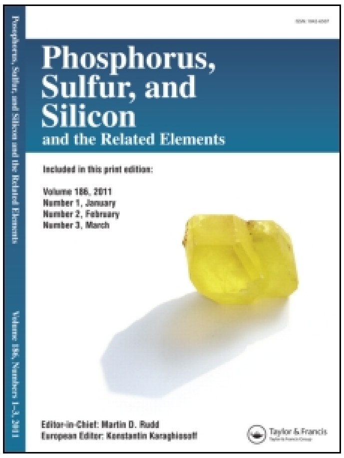

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An Improved Synthesis and Isolation of Tribenzylbismuth

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A much improved synthesis and isolation of tribenzylbismuth (Bn_3Bi where $Bn = CH_2C_6H_5$) compared to the previous literature preparation is presented. Using the described method, a $\geq$ 3-fold increase in yield of analytically pure compound is obtained, providing Bn_3Bi in synthetically useful quantities. Additionally, full spectral characterization has been achieved (^1H and ^{13}C NMR, IR) for the first time. Thermal analysis was performed via condensed phase pyrolysis and differential scanning calorimetry (DSC). The DSC data was used to estimate $\Delta H_f\,(Bn_3Bi)_{liquid}$.

Keywords Bismuth (Bi); benzyl; enthalpy of formation; organometallic

INTRODUCTION

Since the birth of organometallic chemistry with the synthesis of Cadet's organoarsenic compounds in 1760,[1] the organic chemistry of the group 15 elements has certainly flourished. Mainly, investigators have focused on the lighter congeners N, P and As with the chemistry of Sb and Bi lagging behind. Recently, interest in the structure and bonding of organostibines[2] and bismuthines,[3] coupled with their utility as precursors in the synthesis and chemical vapor deposition (CVD) of antimony and bismuth containing solid state materials has led to a resurgence of research in this area.

Bismuth alloys such as Bi_2Te_3 and Bi_xSb_{1-x} are thermoelectric cooling devices and are of interest in rewritable optical storage technologies.[4] 13/15 alloys containing Bi are important in many photonic and electronic devices such as infrared detectors in the 8–12 μm range and 2–5 μm lasers.[5,6] Moreover, bismuth-based superconductors of the type Bi-Sr-Ca-Cu-O (BSCCO) have a critical temperature (T_c)

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as high as 110 K.[7,8] Bismuth containing ferroelectric materials are another technologically important class of compounds.[9]

Organometallic chemical vapor deposition (OMCVD) is the method of choice for preparing these materials. As a result, much research has been focused on determining suitable precursor molecules that deliver bismuth efficiently and in high purity. The ideal OMCVD precursor to bismuth would be safer, easier to handle, and pyrolyze more efficiently at lower temperatures than standard precursors such as Me_3Bi ($Me = CH_3$). The thermal behavior of Me_3Bi,[10] and its use in the growth of $InSb_{1-x}Bi_x$ semiconducting materials[6] have been reported. It is the only trialkyl bismuthine that can be distilled at atmospheric pressure. Other OMCVD bismuthine precursors have included Ph_3Bi,[8,9a,b,d,e,g,11,12] which is volatile but has a relatively high thermal stability, $(alkoxide)_3Bi$,[13] and β-diketonate complexes.[9c,14] In general, these precursors produce films with high concentrations of carbon and oxygen contaminants. Recent studies have used triallyl bismuth, $(allyl)_3Bi$,[15] and salicylate complexes of Bi[9f,16] as precursors to Bi containing solid state materials.

Our group has been using benzylated main group compounds in the low temperature synthesis and CVD of solid state compound semiconductors[17] and metals.[17g,18] The benzyl ligand has been under utilized in materials chemistry despite having several distinct advantages over other organic ligands. Among these are low bond dissociation energies to heavy atoms,[19] and the ability to stabilize any development of charge (radical, cation, or anion) through resonance.[20] Indeed, we have shown that benzylated organometallics decompose under mild conditions giving rise to the innocuous, volatile organic byproduct, 1,2-diphenylethane, and the desired solid state product in high yield and purity.[17a,d,f,g,18]

With the need for suitable OMCVD precursors to Bi, we have investigated tribenzylbismuth, Bn_3Bi, where $Bn = CH_2C_6H_5$, as a safe, efficient CVD source of Bi.[18] Our results have shown that Bn_3Bi is an excellent OMCVD precursor to Bi providing elemental films of high crystallinity and purity. Additionally, Bn_3Bi has proved to be an excellent source of Bi in the bulk synthesis of Bi_2S_3 and $(Bi_xSb_{1-x})_2S_3$ materials at low temperatures.[18b]

Some factors to consider when searching for suitable CVD precursors are availability, volatility, ease of purification, reactivity, and decomposition temperature. Relatively, Bn_3Bi excels in all but one of the above categories, availability. Unlike the typical CVD sources of bismuth described above, Bn_3Bi is not commercially available. Unfortunately, the literature preparation of Bn_3Bi is very time intensive, requiring multi-steps, and providing the target compound in very low yields (ca.

20%).[21] In light of the utility of Bn_3Bi in materials chemistry (*vide supra),* it has become necessary to obtain Bn_3Bi in synthetically useful quantities. Herein we report a much improved synthesis and isolation of the title compound. The synthesis provides Bn_3Bi in high yields ($\geq$ 60%) and in a minimum number of steps, allowing for complete spectral characterization for the first time.

RESULTS AND DISCUSSION

In 1957, Bähr and Zoche reported the synthesis of Bn_3Bi as shown in Eq. (1).[21]

$$\text{xs BnMgCl} + BiCl_3 \rightarrow Bn_3Bi \tag{1}$$

As a consequence of their use of excess Grignard reagent an aqueous quench step must be employed for the ultimate isolation of the organometallic. This procedure requires a steam distillation before the product is extracted. After the initial reaction, four additional steps are required before one acquires the desired product. The reported yield of their procedure is 21%, while in our laboratory we have observed isolated yields from as low as 14% to about 22%, usually significantly contaminated with 1,2-diphenyl ethane, bibenzyl. The procedure is very time intensive and the outcome results in a minimum amount of material.

With the importance of benzylated organometallics in our research program, it was necessary to minimize the effort and maximize the yield in the synthesis of Bn_3Bi. By simply following Eq. (2), followed by filtration and concentration, Bn_3Bi can be isolated in analytical yield, in $\geq$ 60%, a three-fold increase in yield.

$$3.0\ \text{BnMgCl} + BiCl_3 \rightarrow Bn_3Bi \tag{2}$$

The stoichiometry is ensured by accurately titrating the Grignard reagent. We have found the colorimetric reagent, Ph_2Te_2, to be useful for this purpose.[22] The reaction is carried out at room temperature in dry Et_2O in a fume hood using standard Schlenk techniques to ensure the exclusion of H_2O and O_2. The reaction is stirred for 8–12 h then filtered under an inert gas by using a glass frit. The yellow solution is concentrated to about 0.75 of the original volume and placed in a freezer (−20°C) overnight. Bright yellow crystalline material is isolated from the solution by decanting. The remaining solution can be further concentrated and placed in the freezer for additional crystallization. However, it should be noted that the product becomes increasingly contaminated with bibenzyl the more times the product is isolated and the solution is concentrated. No distillations or extractions are necessary.

Bn_3Bi was characterized in solution by using ^1H and ^{13}C spectrometries. An interesting feature of the benzylic methylene proton resonance is the presence of ^1H-^{209}Bi coupling with a measured ^2J of ca. 70 Hz. The benzylic methylene carbon resonance is broadened and decreased in intensity due to its connectivity to a highly quadrupolar nuclei (^{209}Bi, $I = 9/2$).[23] Inspection of the aromatic region shows only three distinct carbon signals. However, the lowest field signal of the C_6D_6 multiplet is substantially greater in intensity compared to the other two suggesting that the fourth signal of Bn_3Bi is coincidental with this resonance.

Although it has been difficult to obtain reliable thermogravimetric analysis (TGA) on Bn_3Bi due to its sensitivity to O_2, condensed phase pyrolysis (1.0 g) under N_2 shows an onset of decomposition at ca. 110°C demonstrated by a color change from yellow to black/green. No further weight loss occurs after 180°C. The resulting product is phase-pure polycrystalline bismuth (99% yield) with no traces of its oxides as determined from x-ray powder diffraction (XRPD). Contamination from carbon was ca. 0.7 wt. % and from hydrogen < 0.5 wt. %. Analysis of the organic residue recovered from the pyrolysis *via* ^1H NMR spectrometry and GC-MS showed bibenzyl as the only product. The combined yields (organic + inorganic) account for a total mass recovery of $\geq 90\%$.

Differential scanning calorimetry (DSC) provides some further insight into the thermal behavior of Bn_3Bi. Figure 1 shows a typical DSC trace of Bn_3Bi. An endothermic peak at 73°C corresponds to the melting point of Bn_3Bi (lit: 65°C).[21] A large exothermic peak beginning at 120°C

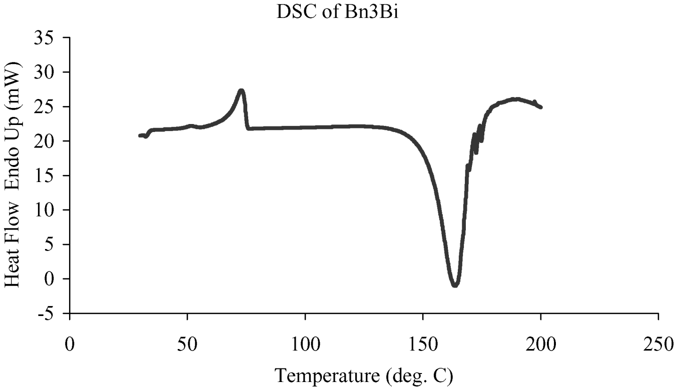

FIGURE 1 Typical DSC trace of Bn_3Bi. Conditions: Held at 30°C for 1.0 min.; Heat from 30°C to 200°C at 5.00°C min^{-1}; 16 mg

and ending ca. 185°C with its center at 163°C is also present. This peak corresponds to decomposition and ΔH_{rxn} for the decomposition reaction is given by Eq. (3). The temperature values measured in the DSC experiments correspond well with the observations and results from the condensed phase pyrolysis of Bn_3Bi as described above.

$$\Delta H_{\text{rxn}} = \Delta H_{\text{f}}(\text{Bi}) + 3\,/\,2\Delta H_{\text{f}}(\text{Bn}_2)_{\text{liquid}} - \Delta H_{\text{f}}(\text{Bn}_3\text{Bi})_{\text{liquid}} \tag{3}$$

The $\Delta H^{\circ}_{\text{rxn}}$was found to be, with three replicate trials, −297.1, −303.6, and −328.6 J/g giving a mean $\Delta H^{\circ}_{\text{rxn}}$of -309.8 J/g (-149.3 kJ/mol) with a standard deviation of 16.6 J/g (8.0 kJ/mol). By rearranging Eq. (3) one can solve for $\Delta H^{\circ}_{f}(\text{Bn}_3\text{Bi})_{\text{liquid}}$. $\Delta H_{f}(\text{Bn}_2)_{\text{solid}}$ is 51.5 kJ/mol while in the gaseous state it is 142.9 kJ/mol.[24] At the temperature of the experiment, bibenzyl should be in the liquid state (mp of bibenzyl: 52°C, bp of bibenzyl: 285°C). To estimate $\Delta H_{f}(\text{Bn}_2)_{\text{liquid}}$ one can utilize the known $\Delta H_{f}(\text{Bn}_2)$ values in concert with heat of fusion or heat of vaporization data according to Eq. (4).

$$\begin{aligned} \Delta H_{\text{fus}} &= \Delta H_{\text{f}}(\text{Bn}_2)_{\text{liquid}} - \Delta H_{\text{f}}(\text{Bn}_2)_{\text{solid}}\ \text{OR} \\ \Delta H_{\text{vap}} &= \Delta H_{\text{f}}(\text{Bn}_2)_{\text{gas}} - \Delta H_{\text{f}}(\text{Bn}_2)_{\text{liquid}} \end{aligned} \tag{4}$$

Utilizing a $\Delta H_{vap}(\text{Bn}_2)$ value of 67.5 kJ/mol[25] or a $\Delta H_{fus}(\text{Bn}_2)$ of 22.7 kJ/mol[26] one obtains values for $\Delta H_{f}(\text{Bn}_2)_{\text{liquid}}$ of 75.4 kJ/mol and 74.2 kJ/mol, respectively. An average of 74.8 kJ/mol is a good estimate for $\Delta H_{f}(\text{Bn}_2)_{\text{liquid}}$. Solving Eq. (3) for $\Delta H^{\circ}_{f}(\text{Bn}_3\text{Bi})_{\text{liquid}}$ provides a value of 261.5 kJ/mol with an estimated error of ± 35 kJ/mol.[27]

In summary, a much improved synthesis and isolation of Bn_3Bi has been achieved by accurately controlling the ratio, BnMgCl:$BiCl_3$, to 3.0:1. This results in a $\geq$ 3 times increase in yield in a "one-pot" synthesis. Characterization of Bn_3Bi has been achieved in solution for the first time *via* NMR spectrometry. The ^{1}H NMR spectrum displays ^{1}H-^{209}Bi coupling and the^{13}C NMR spectrum demonstrates the effect of a highly quadrupolar nuclei on the methylene carbon of the benzyl ligand. Thermal analysis reveals that Bn_3Bi exhibits both a low melting point and decomposition temperature, making it an ideal OMCVD source for low pressure, low temperature CVD applications. The DSC results suggest that an estimate for $\Delta H^{\circ}_{f}(\text{Bn}_3\text{Bi})_{\text{liquid}}$ is about 261.5 ± 35 kJ/mol.

EXPERIMENTAL

General: 1.0 *M* BnMgCl and Ph_2Te_2 were purchased from Aldrich (Milwaukee, WI). The Grignard was titrated with Ph_2Te_2 to obtain a more accurate concentration.[22] Anhydrous bismuth trichloride (99+%) was purchased from Strem Chemicals, Inc. (Newburyport, MA) and used as received. The purity of the bismuth trichloride was monitored by measuring the melting point. Diethyl ether was distilled from sodium benzophenone ketyl under a dry nitrogen atmosphere immediately before use.

NMR spectra were obtained on a JEOL GSX270 or JEOL GSX400 spectrometer at the following frequencies: ^{1}H (270.17 or 399.78 MHz),^{13}C (67.94 or 100.53 MHz). Typical samples were prepared as 0.1–0.2 *M* solutions in $CDCl_3$. Chemical shifts are reported relative to Me_4Si and are in ppm. Infrared spectra were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}.

DSC measurements were obtained by using a Perkin-Elmer 7 Series/Unix Differential Scanning Calorimeter. X-ray diffraction experiments were carried out on a Philips X'Pert MPD Diffractometer using Cu K_α ($\lambda = 1.54059$ Å) x-rays, diffracted beam monochromator, variable divergence slit, and sealed proportional counter.

Condensed phase pyrolysis experiments were performed on 1 g samples of Bn_3Bi at atmospheric pressure under flowing N_2 as described elsewhere.[17a–c,e–h] These experiments were run until decomposition was assumed to be complete by visual inspection. The sample was then allowed to cool and was weighed. The experiment was repeated until a temperature was reached where no further loss in mass occurred. The inorganic residue was then analyzed by XRPD and trace carbon and hydrogen analysis.

C, H, N analysis was performed by using a Perkin Elmer Series II 2400 CHNS/O Analyzer. Trace carbon and hydrogen analyses on bismuth powders were performed by Galbraith Laboratories (Knoxville, TN, USA). In all cases, carbon was ≤ 0.7 wt. % with hydrogen ≤ 0.5 wt.%.

Synthesis of Bn_3Bi

BnMgCl is titrated with Ph_2Te_2 in ether with at least two different aliquots and the concentration is averaged. The BnMgCl (90 mmol, 1.0 *M* solution in ether) is added to a suspension of $BiCl_3$ (9.2 g, 29.2 mmol) in 150 mL of ether over a period of 1.25 h in the absence of light. The color of the suspension changes from white to bright yellow, to dark yellow, and finally to an orange during the addition. The reaction mixture is allowed to stir for 12 h at room temperature and then allowed to settle giving a bright yellow solution and a grey-white precipitate. The mixture is filtered through an air-free glass frit to provide a clear, bright yellow solution that is concentrated in vacuo to about 0.75 the original volume. Placing the solution in a freezer overnight (−20 °C) provides Bn_3Bi (8.0 g, 57%) as bright yellow crystals. The remaining solution from isolation of the crystals can be concentrated to about 0.75 of the volume and replaced in the freezer. Within 2 days another 1.6 g of pure Bn_3Bi can be isolated bringing the total yield to 69%. Repeating the procedure provides a third crop of Bn_3Bi. Analysis of this third crop by ^1H and ^{13}C NMR reveal the presence of 1,2- diphenylethane (^1H (C_6D_6): 2.73 ppm CH_2Ph; ^{13}C (C_6D_6): 37.96 ppm CH_2Ph) which was confirmed by the NMR of an authentic sample of 1,2-diphenylethane. ^1H NMR (C_6D_6, 399.78 MHz) δ 2.72 (s, $^2J_{H-Bi} = 69.7$ Hz, CH_2Ph, 6 H), 6.72 (d,$^3J_{H-H} = 7.0$ Hz, PhH, 6H), 6.83 (t, $^3J_{H-H} = 7.4$ Hz, PhH, 3H), 7.14 (t,$^3J_{H-H} = 7.4$ Hz, PhH, 6H);^{13}C NMR (C_6D_6, 100.53 MHz) δ 36.19 (CH_2Ph), 124.81, 128.03 (Ph coincidental with the lowest field signal of the "triplet" from C_6D_6), 128.28, 141.83 (Ph); IR (KBr, cm^{-1}) 3057 s, 3017 vs, 2967 s, 2926 s, 1944 m, 1865 m, 1805 m, 1742 m, 1593 vs, 1487 vs, 1449 vs, 1408 s, 1262 s, 1208 vs, 1179 s, 1038 vs, 754 vs, 712 vs, 538 m, 424 s; analysis for $C_{21}H_{21}Bi$, calcd. (found) C 52.29 (52.85), H 4.39 (4.44), N 0.00 (0.10).

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