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Organobismuth Compounds. VI.[1] Preparation and Characterization of Cationic Complexes of Triphenylbismuth(V) Derivatives

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Pentacoordinate cationic complexes of the types $(Ph_3BiL_2)X_2$ and $[(Ph_3BiL)_2O]X_2$, where L = DMSO, pyO, Ph_3PO, or Ph_3AsO and X = ClO_4, BF_4, or PF_6, have been isolated and characterized by elemental analyses, infrared spectral, and conductance measurements. An unstable complex $[Ph_3Bi(Ph_3AsO)_2](NO_3)_2$ has also been prepared and characterized by infrared spectroscopy. The Bi–O stretching frequencies for these complexes have been assigned, except for complexes containing Ph_3PO. In dichloromethane, the complex $[Ph_3Bi(Ph_3AsO)_2]BF_4$ decomposes into Ph_3BiF_2 and Ph_3AsOBF_3 and the complexes $[(Ph_3BiL)_2O](ClO_4)_2$, where L = DMSO or pyO, appear to dissociate according to the equation $[(Ph_3BiL)_2O](ClO_4)_2 \rightleftharpoons [Ph_3Bi(OClO_3)]_2O + 2L$. No dissociation is indicated for other complexes. The complexes $Ph_3BiPh_3Bi(Ph_3AsO)_2X_2$, where X = BF_4 or PF_6, form solvates with ketones such as acetone, diethyl ketone, and acetylacetone. Infrared and nmr data for these solvates indicate that the ketone is not coordinated to bismuth.

Introduction

A number of pentacoordinate triphenylbismuth derivatives of the type Ph_3BiX_2[2] such as dihalides, dipseudohalides, dinitrate, and the dicarboxylates have been studied recently. For triphenylbismuth dichloride[3] a trigonal-bipyramidal structure has been established by a X-ray diffraction study. Very recently, triphenylbismuth derivatives of the type $(Ph_3BiX)_2O$[4] have also been prepared. These compounds also contain pentacoordinate bismuth as shown by infrared spectral and conductance studies,[4] as well as by a crystal structure determination[5] of oxybis(triphenylbismuth) diperchlorate, $[Ph_3Bi(OClO_3)]_2O$. The latter compound also forms a dihydrate[4] which appears to contain the pentacoordinate cation $[Ph_3Bi(H_2O)]_2O^{2+}$. Since complex organobismuth cations have hitherto been uncharacterized, the present study was undertaken to isolate and characterize compounds containing complex triphenylbismuth(V) cations.

Experimental Section

General Data. Triphenylbismuth dichloride[2] and oxybis(triphenylbismuth) diperchlorate[4] were prepared as described previously. All other chemicals were reagent grade and were used without further purification. Ethanol and methanol were dried by refluxing over magnesium and subsequent distillation. Nitromethane was refluxed over calcium hydride and distilled under reduced pressure. Dichloromethane was also distilled over calcium hydride. Carbon and hydrogen analyses were performed in this department and bismuth analyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Physical Measurements. Infrared spectra were recorded on a Beckman IR-12 double-beam spectrophotometer. Spectra in the solid state were measured on mulls in Nujol or Halocarbon oil, using KRS-5 and polyethylene windows. Sealed NaCl cells of 0.1-mm path length were used to obtain spectra in solution. Nmr spectra were recorded at ambient temperatures on a Varian A-60 spectrometer. Conductance measurements were made at 25° using a Beckman RC-18 conductivity bridge. Melting points were determined with a Gallenkamp apparatus and are uncorrected.

Preparation of Complexes. (a) $[(C_6H_5)_3BiL]_2O(ClO_4)_2$. Anhydrous oxybis(triphenylbismuth) diperchlorate and the ligand (DMSO, DMSO-d_6, pyO, Ph_3PO, or Ph_3AsO) in 1:2 mole ratio were mixed in absolute alcohol. The solution was allowed to stand overnight. The complexes of DMSO and DMSO-d_6 were prepared in a nitrogen-filled drybox and were isolated by removing the solvent *in vacuo* until the crystals of the complex appeared. The complexes of pyO, Ph_3PO, and Ph_3AsO were isolated by dropwise addition of petroleum ether (bp 35–60°) or diethyl ether to the solution until it became turbid. Upon refrigerating the turbid solution, crystals of the complexes were obtained. The complexes were recrystallized from absolute alcohol containing free ligand. The product was washed successively with benzene and petroleum ether and then dried *in vacuo.*

(b) $[Ph_3BiL_2](ClO_4)_2$. Triphenylbismuth dichloride (1 equiv) and 2 equiv of the ligand L were dissolved in acetone or methanol. Two equivalents of silver perchlorate was added to this solution with constant stirring. After 15 min the precipitated silver chloride was filtered off and the filtrate was concentrated on a rotary evaporator. Diethyl ether or petroleum ether was then added to the concentrated solution and the mixture was refrigerated to yield a white crystalline product, which was recrystallized from a mixture of acetone and diethyl ether. The product was finally dried *in vacuo.*

(c) $[Ph_3BiL_2](BF_4)_2$ and $[Ph_3BiL_2](PF_6)_2$. These complexes were prepared by a similar procedure, except that instead of acetone, anhydrous methanol was used as solvent. Also, the reactions were performed in a nitrogen-filled drybox. Upon using acetone as solvent the product was found to be $Ph_3BiL_2X_2(CH_3COCH_3)$. Solvated complexes were also isolated by using diethyl ketone or acetylacetone in place of acetone. Recrystallization of $[Ph_3Bi(Ph_3AsO)]X_2$, where X = BF_4 or PF_6, from these ketones also afforded the solvated complexes. Infrared and nmr spectra of the solvated complexes showed that the ketone was not coordinated.

(d) $[Ph_3Bi(Ph_3AsO)_2](NO_3)_2$. Triphenylbismuth dichloride and triphenylarsine oxide in a 1:2 mole ratio were dissolved in anhydrous methanol and 2 equiv of silver nitrate was added with stirring. The precipitated silver chloride was filtered off quickly. Petroleum ether was then added to the filtrate to precipitate $Ph_3Bi(Ph_3AsO)_2(NO_3)_2$ which was filtered off immediately and dried *in vacuo.*

All the compounds prepared in the present work are white crystalline solids, soluble in polar organic solvents. They are stable at room temperature for at least several months, with the exception of $[Ph_3Bi(Ph_3AsO)_2](NO_3)_2$, which decomposes at room temperature. The complex $[Ph_3Bi(DMSO)]_2O(ClO_4)_2$ is sensitive to moisture and the complex $[Ph_3Bi(Ph_3AsO)_2](BF_4)_2$ is slowly decomposed in solution according to

$$[Ph_3Bi(Ph_3AsO)_2](BF_4)_2 \rightarrow Ph_3BiF_2 + 2Ph_3AsOBF_3 \tag{1}$$

Ph_3AsOBF_3[6] was isolated from a dichloromethane solution of the complex and was characterized by its infrared spectrum and melting point. Analytical data for all the compounds, except $[Ph_3Bi(Ph_3AsO)_2](NO_3)_2$, are recorded in Table I. For $[Ph_3Bi(Ph_3AsO)_2](NO_3)_2$ satisfactory analysis could not be obtained due to its decomposition at room temperature.

Results and Discussion

Anhydrous $[Ph_3Bi(OClO_3)]_2O$ reacts with oxygen-donor neutral ligands such as dimethyl sulfoxide (DMSO), pyridine *N*-oxide (pyO), triphenylphosphine oxide (Ph_3PO), and triphenylarsine oxide (Ph_3AsO) to form complexes of the type

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Table I. Analytical Data

Compd	% C		% H		Mp, °C
	Calcd	Found	Calcd	Found	
$[Ph_3Bi(DMSO)_2](ClO_4)_2$	33.23	33.20	3.40	3.54	116[f]
$[Ph_3Bi(DMSO\text{-}d_6)_2](ClO_4)_2$	33.70	33.23	3.40	3.46	120[f]
$[Ph_3Bi(pyO)_2](ClO_4)_2$[a,b]	40.60	40.27	3.02	2.98	[h]
$[Ph_3Bi(Ph_3PO)_2](ClO_4)_2$[c]	54.60	54.49	3.80	3.91	169[f]
$[Ph_3Bi(Ph_3PO)_2](PF_6)_2$	50.30	50.20	3.50	3.78	167[f]
$[Ph_3Bi(Ph_3AsO)_2](ClO_4)_2$[d]	50.40	49.96	3.50	3.56	[h]
$[Ph_3Bi(Ph_3AsO)_2](BF_4)_2$	51.51	51.93	3.58	3.72	166[f]
$[Ph_3Bi(Ph_3AsO)_2](BF_4)_2(C_3H_6O)$	51.98	51.79	3.88	3.70	154
$[Ph_3Bi(Ph_3AsO)_2](PF_6)_2$	47.17	46.65	3.27	3.38	161-162[f]
$[Ph_3Bi(Ph_3AsO)_2](PF_6)_2(C_3H_6O)$	47.78	47.93	3.56	3.48	163-164[f]
$[Ph_3Bi(Ph_3AsO)_2](PF_6)_2(C_5H_{10}O)$	48.49	47.95	3.76	3.27	150[f]
$[Ph_3Bi(Ph_3AsO)_2](PF_6)_2(C_7H_8O_2)_{1/2}$	48.06	47.95	3.59	3.43	135[f]
$[Ph_3Bi(DMSO)]_2O(ClO_4)_2$[i]	38.52	37.92	3.34	3.52	[g]
$[Ph_3Bi(DMSO\text{-}d_6)]_2O(ClO_4)_2$[i]	38.01	38.21	3.34	3.53	[g]
$[Ph_3Bi(pyO)]_2O(ClO_4)_2$	42.97	42.83	3.13	3.04	135[f]
$[Ph_3Bi(Ph_3PO)]_2O(ClO_4)_2$[e]	52.34	52.21	3.66	4.18	[g]
$[Ph_3Bi(Ph_3AsO)]_2O(ClO_4)_2$	49.70	49.79	3.47	3.74	117[f]

[a] % Bi: calcd, 25.20; found, 25.39. [b] % N: calcd, 3.38; found, 3.09. [c] % Bi: calcd, 17.61; found, 17.20. [d] % Bi: calcd, 16.28; found, 16.26. [e] % N: calcd, 2.18; found, 2.06. [f] Decomposed. [g] Decomposed without melting. [h] Exploded on heating. [i] Hygroscopic.

$[(Ph_3BiL)_2O](ClO_4)_2$. However, other $(Ph_3BiX)_2O$ derivatives such as halides, pseudohalides, carboxylates, or the nitrate did not form any complexes. Similarly no complexes of the known Ph_3BiX_2 derivatives could be isolated but stable complexes of the type $(Ph_3BiL_2)X_2$, where X = ClO_4, BF_4, or PF_6, were obtained from

$$Ph_3BiCl_2 + 2L + 2AgX \rightarrow (Ph_3BiL_2)X_2 + 2AgCl \qquad (2)$$

An unstable complex $[Ph_3Bi(Ph_3AsO)_2](NO_3)_2$ was also formed in a similar manner.

Infrared spectra of all the compounds prepared in this study were examined in the solid state in the 4000-200-cm^{-1} region and the important infrared frequencies are recorded in Table II. As shown in Table II, the spectrum of each compound showed characteristic infrared bands due to the free anion.[7,8] Assignments for the infrared spectra of DMSO and DMSO-d_6,[9-14] pyO,[15-18] Ph_3PO,[19,20] Ph_3AsO,[20-22] and their complexes with metal ions have been well established. The ν(XO) frequency (X = S, N, P, or As) for each complex studied in the present work can, therefore, be assigned unambiguously by comparing the spectrum of the complex with that of the free ligand. As can be seen from the data presented in Table II, the ν(XO) frequency for each complex is significantly reduced from the free-ligand value. Thus the infrared data clearly show that all the compounds listed in Table II contain the pentacoordinate cation $Ph_3BiL_2^{2+}$ or $(Ph_3BiL)_2O^{2+}$ in which the ligands L are bonded to bismuth through their oxygen atoms. As expected, the ν(XO) frequency for the cation is unaffected by the nature of the counteranion.

The shifts in the ν(XO) frequencies, $\Delta\nu$(XO) [$\nu(XO) = \nu(XO)_{ligand} - \nu(XO)_{complex}$], for the $(Ph_3BiL)_2O^{2+}$ cations are comparable to those reported for the cationic complexes[11,12,14-16,18-22] of divalent transition metals. They are also very similar to those for the analogous organoantimony(V) cations,[23] $(Ph_3SbL)_2O^{2+}$, which have been studied very recently. The $\Delta\nu$(XO) values for the $Ph_3BiL_2^{2+}$ cations are, however, about 50% larger than those for the $(Ph_3BiL)_2O^{2+}$ cations. They are even slightly higher than those reported for complexes[11,12,16,21,24,25] of trivalent transition metals. Accordingly, the cation Ph_3Bi^{2+} is indicated to be a stronger electron pair acceptor than the cation $(Ph_3Bi)_2O^{2+}$.

The spectra of the DMSO, pyO, and Ph_3AsO complexes show an additional band in the low-frequency region which can be assigned to the Bi-O(ligand) stretching frequency. In the spectrum of the complex $[Ph_3Bi(DMSO)_2](ClO_4)_2$ a strong band is observed in the 450-400-cm^{-1} region which shows maxima at 450 and 430 cm^{-1}. The 450-cm^{-1} band is due to the y vibration of the phenyl groups and the 430-cm^{-1} band can be assigned to the Bi-O stretching frequency. For $Ph_3Bi(DMSO\text{-}d_6)_2(ClO_4)_2$, the absorption due to the y mode remains unchanged at 450 cm^{-1} and the ν(Bi-O) frequency is observed as a medium band at 415 cm^{-1}. The ratio of the ν(Bi-O) frequencies for the DMSO and DMSO-d_6 complexes, 430/415 = 1.036, is in very good agreement with the expected value of 1.035. The ν(Bi-O) frequency for the $[Ph_3Bi(DMSO)]_2O^{2+}$ cation is observed as a medium intensity band at 405 cm^{-1} and this frequency is shifted to 370 cm^{-1} in the cation $[Ph_3Bi(DMSO\text{-}d_6)]_2O^{2+}$. For the cations $Ph_3Bi(pyO)_2^{2+}$ and $[Ph_3Bi(pyO)]_2O^{2+}$, a medium band is observed at 350 and 300 cm^{-1}, respectively, which can be assigned to the ν(Bi-O) frequency. The ν(Bi-O) frequency for the cations $Ph_3Bi(Ph_3AsO)_2^{2+}$ and $[Ph_3Bi(Ph_3AsO)]_2O^{2+}$ is observed at 390 and 380 cm^{-1}, respectively. The proposed assign-

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Table II. Infrared Spectroscopic Data[a] (cm^{-1}) for $Ph_3BiL_2X_2$ and $(Ph_3BiL)_2OX_2$ Complexes

Compd	ν(XO)[d]	$\Delta\nu$(XO)[e]	ν(Bi-O)	Anion freq
$[Ph_3Bi(DMSO)_2](ClO_4)_2$	900 s	155	430 m	1090 vs, 625 m
$[Ph_3Bi(DMSO\text{-}d_6)_2](ClO_4)_2$	895 s	160	415 m	1090 vs, 625 m
$[Ph_3Bi(pyO)_2](ClO_4)_2$	1194 m	51	350 m	1090 vs, 625 m
$[Ph_3Bi(Ph_3PO)_2](ClO_4)_2$	1120 s 1125[b,c] s	70		1090 vs, 628 m
$[Ph_3Bi(Ph_3PO)_2](PF_6)_2$	1120 s 1125[b,c] s	70		840 vs, 560 m
$[Ph_3Bi(Ph_3AsO)_2](ClO_4)_2$	810 s 815[c] s	70	390 m	1090 vs, 625 m
$[Ph_3Bi(Ph_3AsO)_2](BF_4)_2$	810 s 815[c] s	70	390 m	1020 vs, b, 520 m
$[Ph_3Bi(Ph_3AsO)_2](PF_6)_2$	810 s	70	390 m	840 vs, 560 m
$[Ph_3Bi(Ph_3AsO)_2](NO_3)_2$	805 s	75	395 m	1350 vs
$[Ph_3Bi(DMSO)]_2O(ClO_4)_2$	940 s 950[c] m	115	405 m	1090 vs, 625 m
$[Ph_3Bi(DMSO\text{-}d_6)]_2O(ClO_4)_2$	960 s, b 970[c] m	95	370 m	1090 vs, 625 m
$[Ph_3Bi(pyO)]_2O(ClO_4)_2$	1212 m 1215[b] w, 1250[b] m	37	300 m	1090 vs, 625 m
$[Ph_3Bi(Ph_3PO)]_2O(ClO_4)_2$	1145 s 1145[c] m	45		1090 vs, 625 m
$[Ph_3Bi(Ph_3AsO)]_2O(ClO_4)_2$	840 s 860–850[c] s	40	380 m	1100 vs, 628 m

[a] In the solid state unless stated otherwise. Key: b, broad; m, medium; s, strong; vs, very strong; w, weak. [b] In $CDCl_3$. [c] In CH_2Cl_2. [d] X = S, N, P, or As. [e] $\Delta\nu(XO) = \nu(XO)_{\text{free ligand}} - \nu(XO)_{\text{complex}}$.

ments for the ν(Bi–O) frequencies for the $(Ph_3BiL)_2O^{2+}$ cations can be compared with the ν(Sb–O) frequencies for analogous antimony complexes.[23] The assignments for the ν(Bi–O) frequencies for the $Ph_3BiL_2{}^{2+}$ cations are also consistent with the ν(Sb–O) frequencies for the analogous antimony complexes[26] which are currently under investigation in this laboratory. The infrared spectra of the cations $Ph_3Bi(Ph_3PO)_2{}^{2+}$ and $[Ph_3Bi(Ph_3PO)]_2O^{2+}$ also show an additional band at *ca.* 410 cm^{-1}. Since a similar band is also observed for analogous antimony compounds,[23,26] it is very unlikely that this band is due to the ν(Bi–O) frequency. Bands in the 400–420-cm^{-1} region are also observed for Ph_3PO complexes of several other metals,[20,25,27-30] including the complexes of $SbCl_3$[29] and $BiCl_3$.[29] Although some workers[25,27,29,30] have assigned these bands to the ν(M–O) frequency, we believe that definite assignments for the ν(M–O) frequency cannot be made for Ph_3PO complexes.

As expected from the relative shifts in the ν(XO) frequencies, the ν(Bi–O) frequencies for the $Ph_3BiL_2{}^{2+}$ cations are higher than those for the $(Ph_3BiL)_2O^{2+}$ cations. For both types of cations the ν(Bi–O) frequencies are in the order DMSO > Ph_3AsO > pyO. The $\Delta\nu$(XO) values for these complexes also follow the same order, *i.e.*, $\Delta\nu(SO) > \Delta\nu(AsO) \sim \Delta\nu(PO) > \Delta\nu(NO)$.

The idealized geometries for pentacoordinate structures include a trigonal bipyramid and a tetragonal pyramid and for species of the type Ph_3BiX_2 there are three possible isomers in each geometry. However, all the neutral Ph_3BiX_2 compounds, for which structural information is available,[31] are indicated to possess a trigonal-bipyramidal skeleton with the X groups in the axial positions. Bismuth atoms in $[Ph_3Bi(OClO_3)]_2O$ also adopt a slightly distorted trigonal-bipyramidal configuration in which the bridging oxygen and a perchlorate oxygen occupy the axial positions. The observation of only one ν(Bi–O) frequency in the infrared indicates that the ligands L in the $Ph_3BiL_2{}^{2+}$ cations are also in the trans positions. Also, the infrared bands associated with the Bi–C_6H_5 skeletal modes for the $Ph_3BiL_2{}^{2+}$ and $(Ph_3BiL)_2O^{2+}$ cations are very similar to those for the Ph_3BiX_2 and $(Ph_3BiX)_2O$ derivatives. In view of these results the $Ph_3BiL_2{}^{2+}$ and $(Ph_3BiL)_2O^{2+}$ cations appear to be structurally similar to the neutral Ph_3BiX_2 and $(Ph_3BiX)_2O$ derivatives.

To examine the behavior of these complexes in solution, the ν(XO) frequencies were also determined in deuterated chloroform or dichloromethane, and the data are included in Table II. The complexes $[Ph_3Bi(DMSO)_2](ClO_4)_2$ and $[Ph_3Bi(pyO)_2](ClO_4)_2$ are not sufficiently soluble in either solvent but the infrared data for the complexes $[Ph_3Bi(Ph_3PO)_2](ClO_4)_2$ and $[Ph_3Bi(Ph_3AsO)_2](ClO_4)_2$ in both solvents show that the ν(PO) or ν(AsO) frequencies are very similar to those observed in the solid state. For either complex, no band due to free ligand was observed in solution. For the complexes $[Ph_3Bi(DMSO)]_2O(ClO_4)_2$ and $[Ph_3Bi(DMSO\text{-}d_6)]_2O(ClO_4)_2$, the ν(SO) frequency increased in dichloromethane by *ca.* 10 cm^{-1} and the relative intensity of this band was reduced by about 50%. The reduced intensity of the ν(SO) band suggests some dissociation of the complex. However, the presence of free DMSO or DMSO-d_6 cannot be ascertained from the solution spectra due the presence of strong perchlorate and phenyl bands in the 1100–1000-cm^{-1} region. The spectrum of $[Ph_3Bi(pyO)]_2O(ClO_4)_2$ in deuterated chloroform showed bands at 1250 and 1215 cm^{-1} which are indicative of the presence of free as well as coordinated pyO. However, no spectroscopic evidence was obtained for the presence of free Ph_3PO or Ph_3AsO in dichloromethane solutions of $[Ph_3Bi(Ph_3PO)]_2O(ClO_4)_2$ and $[Ph_3Bi(Ph_3AsO)]_2O(ClO_4)_2$. The ν(PO) frequency in solution was unchanged from the solid-state value but the ν(AsO) frequency was observed as a strong band showing maxima at 860 and 850 cm^{-1}. In view of these results no dissociation of the ligand L appears to occur in chloroform or dichloromethane,

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(31) In addition to the crystal structure determination of Ph_3BiCl_2,[3] the evidence for a trigonal-bipyramidal structure for a number of neutral Ph_3BiX_2 derivatives has been obtained in this laboratory by infrared and Raman spectroscopic studies in the solid state as well as in solution.

except for $[Ph_3Bi(DMSO)]_2O(ClO_4)_2$ and $[Ph_3Bi(pyO)]_2O(ClO_4)_2$.

Molar conductances for ~10^{-3} *M* solutions of these complexes in nitromethane and dichloromethane are shown in Table III. Λ_M values in nitromethane correspond to those for 1:2 electrolytes.[32] For a 10^{-3} *M* solution of a 1:1 electrolyte such as tetraethylammonium perchlorate, in dichloromethane, we observed a Λ_M value of 22.8 ohm^{-1} cm^2 mol^{-1} at 25°. Therefore, with the exceptions of $[Ph_3Bi(DMSO)]_2O(ClO_4)_2$ and $[Ph_3Bi(pyO)]_2O(ClO_4)_2$, these complexes also behave as 1:2 electrolytes in dichloromethane. Since the molar conductance of $[Ph_3Bi(OClO_3)]_2O$ in dichloromethane is ~1.4 ohm^{-1} cm^2 mol^{-1}, the lower Λ_M values for $[Ph_3Bi(DMSO)]_2O(ClO_4)_2$ and $[Ph_3Bi(pyO)]_2O(ClO_4)_2$ indicate the following equilibrium in solution

$$[Ph_3BiL]_2O(ClO_4)_2 \rightleftharpoons [Ph_3Bi(OClO_3)]_2O + 2L \tag{3}$$

In accordance with the proposed equilibrium there was a marked increase in the conductances upon adding free ligand to the dichloromethane solutions of $[Ph_3Bi(DMSO)]_2O(ClO_4)_2$ and $[Ph_3Bi(pyO)]_2O(ClO_4)_2$. The infrared data for the two complexes, in solution, are also consistent with the proposed dissociation. Conductance of $[Ph_3Bi(Ph_3AsO)_2](BF_4)_2$ in dichloromethane was found to decrease with time and this can be attributed to the decomposition of the complex into Ph_3BiF_2[2] and Ph_3AsOBF_3[6] as shown in eq 1.

Registry No. $[Ph_3Bi(OClO_3)]_2O$, 38496-61-6; Ph_3BiCl_2, 28719-54-2; $[Ph_3Bi(DMSO)_2](ClO_4)_2$, 38467-44-6; $[Ph_3Bi(DMSO\text{-}d_6)_2](ClO_4)_2$, 38467-45-7; $[Ph_3Bi(pyO)_2](ClO_4)_2$, 38467-46-8; $[Ph_3Bi(Ph_3PO)_2](ClO_4)_2$, 38467-47-9; $[Ph_3Bi(Ph_3PO)_2](PF_6)_2$, 38467-48-0; $[Ph_3Bi(Ph_3AsO)_2](ClO_4)_2$, 38467-49-1; $[Ph_3Bi(Ph_3AsO)_2](BF_4)_2$, 38467-50-4; $[Ph_3Bi(Ph_3AsO)_2](BF_4)_2 \cdot C_3H_6O$, 38467-51-5; $[Ph_3Bi(Ph_3AsO)_2](PF_6)_2$, 38467-52-6; $[Ph_3Bi(Ph_3AsO)_2](PF_6)_2 \cdot C_3H_6O$, 38467-53-7; $[Ph_3Bi(Ph_3AsO)_2](PF_6)_2 \cdot C_5H_{10}O$, 38566-47-1; $[2[Ph_3Bi(Ph_3AsO)_2](PF_6)_2 \cdot C_5H_8O_2$, 38531-33-8; $[Ph_3Bi(DMSO)]_2O(ClO_4)_2$, 38566-48-2; $[Ph_3Bi(DMSO\text{-}d_6)]_2O(ClO_4)_2$, 38531-34-9; $[Ph_3Bi(pyO)]_2O(ClO_4)_2$, 38566-49-3; $[Ph_3Bi(Ph_3PO)]_2O(ClO_4)_2$, 38566-44-8; $[Ph_3Bi(Ph_3AsO)]_2O(ClO_4)_2$, 38566-45-9; $[Ph_3Bi(Ph_3AsO)_2](NO_3)_2$, 38566-46-0.

Table III. Molar Conductances[a] for $Ph_3BiL_2X_2$ and $(Ph_3BiL)_2OX_2$ Complexes

Compd	Λ_M, ohm^{-1} cm^2 mol^{-1}	
	CH_3NO_2	CH_2Cl_2
$[Ph_3Bi(DMSO)_2](ClO_4)_2$	150	*b*
$[Ph_3Bi(pyO)_2](ClO_4)_2$	150	*b*
$[Ph_3Bi(Ph_3PO)_2](ClO_4)_2$	177	38
$[Ph_3Bi(Ph_3PO)_2](PF_6)_2$	184	44
$[Ph_3Bi(Ph_3AsO)_2](ClO_4)_2$	182	41
$[Ph_3Bi(Ph_3AsO)_2](BF_4)_2$	170	52
$[Ph_3Bi(Ph_3AsO)_2](PF_6)_2$	188	36
$[Ph_3Bi(DMSO)]_2O(ClO_4)_2$	162	12[c]
$[Ph_3Bi(pyO)]_2O(ClO_4)_2$	162	22[c]
$[Ph_3Bi(Ph_3PO)]_2O(ClO_4)_2$	163	41
$[Ph_3Bi(Ph_3AsO)]_2O(ClO_4)_2$	161	56

[a] At ~1 × 10^{-3} *M* and 25°. [b] Not sufficiently soluble. [c] Conductance increased upon adding free ligand.

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Notes

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Preparation and Chemistry of Sodium Bis(borane)dimethylarsenide(1−)

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Recent papers from this laboratory described studies of the reactions of B_2H_6 with $LiP(CH_3)_2$,[1] and with mono- and di-*N*-alkyl-substituted lithium amides, LiNHR and $LiNR_2$.[2] In addition we have described the reaction of amine hydrochlorides with $Na(CH_3)_2N(BH_3)_2$[3] and $Li(CH_3)_2P(BH_3)_2$[4] to form chain compounds with NBNB and NBPB backbones, respectively. This article represents an extension of this work to the formation and characterization of the arsenic–boron compound $Na(CH_3)_2As(BH_3)_2$ and its conversion to $(CH_3)_3N\text{-}BH_2\text{-}As(CH_3)_2\text{-}BH_3$.

Experimental Section

General Data. Standard high-vacuum and inert-atmosphere techniques[5] were employed for all manipulations. Boron-11 and proton nmr spectra were obtained using a Varian HA-100 spectrometer operating at 32.1 and 100 MHz, respectively. Boron chemical shifts are expressed in ppm relative to $(C_2H_5)_2O{\cdot}BF_3$. Infrared spectra were obtained with a Perkin-Elmer 337 spectrophotometer. Mass spectra were produced by a Hitachi-Perkin RMU-6E double-focusing spectrometer.

Pure dry solvents were stored over $LiAlH_4$ in evacuated bulbs and, when needed, were condensed directly into the reaction vessel. Dimethylarsine was prepared by the procedure of Feltham and Silverthorn,[6] modified slightly for vacuum-line application. Sodium dimethylarsenide was formed by the reaction of $(CH_3)_2AsH$ with finely divided sodium in benzene at 25°.[7]

For analysis arsenic was determined by the quantitative recovery of $(CH_3)_2AsH$ following acid hydrolysis. Boron, nitrogen, and hydrolytic hydrogen were determined by standard methods.

Preparation of $Na(CH_3)_2As(BH_3)_2$. In a typical reaction a 2.0-

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(7) The $(CH_3)_2AsH$–Na reaction outlined in ref 6 used tetrahydrofuran as the solvent. In this work we have found that benzene containing a trace of tetrahydrofuran is a more convenient reaction medium if actual isolation of $NaAs(CH_3)_2$ is desired.