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Synthesis and Structural Comparison of Triaryl(sulfonylimino)pnictoranes

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Triarylphosphanes **1** (Ar_3P; Ar = Ph, 4-MeC_6H_4), triphenylarsane (**2**), and triarylstibanes **3** (Ar_3Sb; Ar = 2-MeC_6H_4, 2-$MeOC_6H_4$) reacted with trifluoromethanesulfonamide (**7a**) in the presence of equimolar diethyl azodicarboxylate to afford the corresponding triaryl(sulfonylimino)pnictoranes [$Ar_3M{=}NSO_2CF_3$; **8** (M = P), **9** (M = As), **10** (M = Sb)]. The Kirsanov-type reaction of triarylantimony dichlorides **5** (Ar_3SbCl_2; Ar = 2-MeC_6H_4, 2-$MeOC_6H_4$) and triarylbismuth dichlorides **6** (Ar_3BiCl_2; Ar = 2-MeC_6H_4, 2-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$) with sulfonamides **7** (H_2NSO_2R; R = CF_3, 4-MeC_6H_4, Me) in the presence of 2 equiv of potassium *tert*-butoxide yielded triaryl(sulfonylimino)-λ^5-stibanes **10** and -bismuthanes **11**, respectively. The *ortho*-substitution in aryl ligands of **10** and **11** has been found to bring about considerable kinetic stabilization of the reactive Sb=N and Bi=N bonds. A structural comparison was made for a series of triaryl(sulfonylimino)pnictoranes **8**–**11** by IR spectroscopy and X-ray crystallography. In the IR spectra of **9**–**11**, SO_2 asymmetric stretching absorptions (ν_{SO2}) were observed at lower wavenumbers as compared to those of phosphorus counterparts **8**. The difference in frequency ($\Delta\nu_{SO2}$) from **8** increased progressively as the pnictogen element being utilized moved down the group 15 column on the periodic table. X-ray crystallographic analyses of eight of the triaryl(sulfonylimino)pnictoranes prepared confirmed the increasing single-bond character of the M=N bond, with the contribution from the canonical structure $M^+{-}N{=}S(O){-}O^-$ increasing in importance in the order P < As < Sb < Bi. Among all triaryl(sulfonylimino)pnictoranes examined, only imino-λ^5-bismuthanes **11** oxidized alcohols to carbonyl compounds.

Introduction

In recent decades, the chemistry of iminopnictoranes ($R_3M{=}NR'$; M = P, As, Sb, Bi)[1] has received considerable attention due to the role of these compounds in reactions that form a bond with nitrogen as well as the chemical analogy with ylides ($R_3M{=}CR'R''$) and oxides ($R_3M{=}O$).[2] For instance, the aza-Wittig reaction based on imino λ^5-phosphanes has found a wide range of applications in organic synthesis.[3] Although the examples are yet limited in number, the synthetic application of imino-λ^5-arsanes,[4] -stibanes,[4k,5] and -bismuthanes[4k,6] has also been a subject of recent studies.

A salient structural feature of the iminopnictoranes is the nature of the M=N bonds. The vast majority of related studies have been devoted to exploring the multiplicity of the P=N bond in imino-λ^5-phosphanes on the basis of experimental[7,8] and theoretical studies.[8c,9] Recent theoretical studies on an imaginary imino-λ^5-phosphane ($H_3P{=}NH$) have led to the conclusion that the electrostatic interaction, as well as the n−σ^* negative hyperconjugation,[10] between the phosphorus and nitrogen atoms is responsible for the P=N bond shortening of imino-λ^5-phosphane.[11] To gain a systematic understanding of the nature of M=N bonds, however, it would be more productive to compare the structure and

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reactivity of a series of iminopnictoranes bearing a common substituent on the nitrogen atom.

In 1997, Koketsu et al. reported a comparative study of the structure and reactivity of a series of imaginary iminopnictoranes ($H_3M{=}NH$; M = P, As, Sb, Bi) on the basis of ab initio molecular orbital calculations.[12] Recently, we have also carried out the first comparative study of the structure and reactivity of a series of *existing* (acylimino)triarylpnictoranes ($Ar_3M{=}NCOR$), for which the structural property of the *N*-acyl group has been found to be strongly indicative of the intrinsic properties of the $M{=}N$ bonds.[13] These studies have revealed that the single-bond character of the $M{=}N$ bond in iminopnictoranes increases as the atomic weight of the pnictogen atom increases. However, the effects of other *N*-substituents on the $M{=}N$ bonding nature have not yet been systematically examined, probably because of a lack of well-characterized examples among known iminopnictoranes, especially those derived from antimony and bismuth.

We have recently succeeded in determining the crystal structures of the monomeric imino-λ^5-stibanes that bear a trifluoromethylsulfonyl group on the nitrogen atom.[14] This success led us to compare the structural properties of an *N*-sulfonyliminopnictorane series, as we expected that the *N*-sulfonyl groups would, like *N*-acyl groups, also reflect the properties of the conjugated $M{=}N$ bond and bring some thermal stability to intrinsically thermolabile $Bi{=}N$ bonds. We report herein the results of synthesis and a structural comparison of a series of triaryl(sulfonylimino)pnictoranes. These results demonstrate that both the single-bond character of the $M{=}N$ bond and the contribution from canonical form $M^+{-}N{=}S(O){-}O^-$ increase progressively as the pnictogen element becomes heavier.

Experimental Section

General. All reactions with air-sensitive compounds were carried out under an argon atmosphere. Melting points were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 or a JEOL FX400 spectrometer using $CDCl_3$ as a solvent unless otherwise noted. Chemical shifts are reported as the relative value versus tetramethylsilane. ^{19}F NMR data were measured on a JEOL JNM-LA500 spectrometer in $CDCl_3$ using neat trifluoroacetic acid as an external standard. IR spectra were observed as KBr pellets on a Shimadzu FTIR-8100S or 8200A spectrometer. FABMS spectra were measured on a JEOL JMS-HS100 spectrometer using *m*-nitrophenyl octyl ether as a matrix. Elemental analyses were performed at Microanalytical Laboratory of Kyoto University. CH_2Cl_2 and Et_2O were distilled from calcium hydride and sodium benzophenone ketyl, respectively, before use. Pentane, hexane, $CHCl_3$, and $CDCl_3$ were distilled from CaH_2 and stored over 4 Å molecular sieves.

Triarylstibanes **3a**,**b** were prepared from $SbCl_3$ and the corresponding Grignard reagents.[15] Triarylantimony dichlorides **5** were prepared from **3a**,**b** and sulfuryl chloride. Triarylbismuth dichlorides **6**[13] were obtained by the reaction of the corresponding triarylbismuthanes with sulfuryl chloride according to Barton's procedure.[16] Other reagents were used as commercially received.

Triarylstibanes, 3a: ^{1}H NMR δ 2.48 (s, 9H), 6.98−7.05 (m, 6H), 7.24−7.29 (m, 6H). **3b**: ^{1}H NMR δ 3.76 (s, 9H), 6.82 (dt, 3H, $J = 1.0$, 7.1 Hz), 6.85−6.90 (m, 6H), 7.31 (ddd, 3H, $J = 7.2$, 7.1, 2.0 Hz).

Triarylantimony Dichlorides, 5a: mp 234−236 °C; ^{1}H NMR δ 2.69 (s, 9H), 7.35−7.39 (m, 6H), 7.44−7.48 (m, 3H), 7.90 (d,

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3H, $J = 7.6$ Hz). Anal. Calcd for $C_{21}H_{21}Cl_2Sb$: C, 54.12; H, 4.54. Found: C, 54.03; H, 4.56. **5b**: mp 231−238 °C; ^{1}H NMR δ 3.82 (s, 9H), 7.04−7.18 (m, 6H), 7.46−7.55 (m, 3H), 7.88 (dd, 3H, $J = 7.7$, 1.5 Hz). Anal. Calcd for $C_{21}H_{21}Cl_2O_3Sb$: C, 49.07; H, 4.12. Found: C, 48.54; H, 3.97.

Synthesis of Triaryl(sulfonylimino)-λ^5-phosphanes 8, -arsane 9, and -stibanes 10 by Redox Condensation[17] (Method A). Diethyl azodicarboxylate (40% in toluene; 0.5 mL, ∼1.1 mmol) was added to a mixture of triarylphosphane **1** (1.0 mmol), amide **7a** (1.0 mmol), and Et_2O (10 mL) at 0 °C. The resulting mixture was allowed to gradually warm to room temperature with stirring. After 12 h, the solvent was removed under reduced pressure to leave a solid that was then washed with Et_2O and recrystallized from CH_2Cl_2/hexane to yield triaryl(sulfonylimino)-λ^5-phosphane **8**. Imino-λ^5-arsane **9** and imino-λ^5-stibanes **10** were similarly prepared from **2** and **3**, respectively.

Triphenyl[(trifluoromethanesulfonyl)imino]-λ^5-phosphane, 8a: mp 165−167 °C (lit.,[18] 168−169 °C); ^{1}H NMR δ 7.53−7.57 (m, 6H), 7.67 (t, 3H, $J = 7.4$ Hz), 7.77 (dd, 6H, $^3J_{PH} = 13.4$ Hz, $^3J_{HH} = 8.2$ Hz); IR ν 1590, 1485, 1437, 1320 (SO_2, as), 1246, 1211, 1171, 1157, 1113, 1096, 1028, 999, 795, 752, 741, 723, 693, 613, 581, 558, 544, 531, 511, 502, 434 cm^{-1}.

Tris(4-methylphenyl)[(trifluoromethanesulfonyl)imino]-λ^5-phosphane, 8b: mp 209−210 °C; ^{1}H NMR δ 2.43 (s, 9H), 7.32 (dd, 6H, $^3J_{HH} = 8.3$ Hz, $^4J_{PH} = 3.7$ Hz), 7.62 (dd, 6H, $^3J_{PH} = 13.1$ Hz, $^3J_{HH} = 8.3$ Hz); $^{13}C\{^1H\}$ NMR δ 21.7, 123.1 (d, $^1J_{PC} = 108$ Hz), 129.7 (d, $^2J_{PC} = 13.7$ Hz), 133.0 (d, $^3J_{PC} = 11.4$ Hz), 144.3 (d, $^4J_{PC} = 2.8$ Hz); IR ν 1601, 1563, 1501, 1449, 1402, 1381, 1316 (SO_2, as), 1283, 1233, 1204, 1190, 1175, 1165, 1113, 1094, 1040, 1022, 845, 810, 783, 750, 710, 668, 660, 625, 604, 575, 554, 534, 517, 511, 504, 459, 451 cm^{-1}. Anal. Calcd for $C_{22}H_{21}F_3NO_2PS$: C, 58.53; H, 4.69; N, 3.10. Found: C, 58.53; H, 4.77; N, 3.12.

Triphenyl[(trifluoromethanesulfonyl)imino]-λ^5-arsane, 9: mp 183−185 °C; ^{1}H NMR δ 7.56−7.60 (m, 6H), 7.68 (t, 3H, $J = 7.4$ Hz), 7.77 (d, 6H, $J = 7.8$ Hz); IR ν 1578, 1483, 1443, 1306 (SO_2, as), 1213, 1192, 1175, 1163, 1140, 1086, 1019, 997, 758, 749, 741, 706, 687, 623, 610, 573, 521, 478, 463, 419 cm^{-1}. Anal. Calcd for $C_{19}H_{15}AsF_3NO_2S$: C, 50.34; H, 3.34; N, 3.09. Found: C, 50.12; H, 3.45; N, 3.13.

Tris(2-methylphenyl)[(trifluoromethanesulfonyl)imino]-λ^5-stibane, 10a: mp 168−170 °C; ^{1}H NMR δ 2.48 (s, 9H), 7.38−7.42 (m, 6H), 7.53−7.57 (m, 3H), 7.74 (d, 3H, $J = 7.6$ Hz); $^{13}C\{^1H\}$ NMR δ 23.9, 127.6, 127.9, 132.2, 133.3, 135.0, 144.0; IR ν 1578, 1472, 1456, 1393, 1287 (SO_2, as), 1211, 1181, 1159, 1140, 1022, 797, 766, 749, 700, 654, 644, 619, 567, 546, 519, 484, 434, 410 cm^{-1}. Anal. Calcd for $C_{22}H_{21}F_3NO_2SSb$: C, 48.73; H, 3.90; N, 2.58. Found: C, 48.22; H, 3.90; N, 2.40.

Tris(2-methoxyphenyl)[(trifluoromethanesulfonyl)imino]-λ^5-stibane, 10b: mp 165−168 °C; ^{1}H NMR δ 3.68 (s, 9H), 6.99 (d, 3H, $J = 8.3$ Hz), 7.10−7.19 (m, 3H), 7.52−7.61 (m, 3H), 7.73 (d, 3H, $J = 7.6$ Hz); IR ν 1582, 1476, 1460, 1435, 1279 (SO_2, as), 1246, 1208, 1175, 1127, 1053, 1013, 874, 851, 791, 756, 669, 615, 569, 517, 484, 438, 426, 403 cm^{-1}. Anal. Calcd for $C_{22}H_{21}F_3NO_5SSb$: C, 44.77; H, 3.59; N, 2.37. Found: C, 44.54; H, 3.59; N, 2.38.

Synthesis of Triaryl(sulfonylimino)-λ^5-stibanes 10 and -bismuthanes 11 by the Kirsanov-Type Reaction[19] (Method B). KO-*t*-Bu (998 mg, 8.89 mmol) was added to a mixture of triarylbismuth dichloride **6** (4.00 mmol), amide **7** (4.05 mmol), and CH_2Cl_2 (80 mL) at −50 °C. The mixture was allowed to gradually warm to room temperature with stirring. The insoluble solid was filtered off through Celite, and the filtrate was concentrated under reduced pressure to leave an oily residue, which was crystallized from CH_2Cl_2/hexane to give triaryl(sulfonylimino)-λ^5-bismuthane **11**. Compounds **10** were similarly obtained from triarylantimony dichlorides **5**.

Tris(2-methylphenyl)[(trifluoromethanesulfonyl)imino]-λ^5-bismuthane, 11a: mp 131−138 °C; ^{1}H NMR δ 2.49 (s, 9H), 7.45−7.54 (m, 9H), 7.90 (d, 3H, $J = 7.8$ Hz); $^{13}C\{^1H\}$ NMR δ 24.4, 129.2, 132.3, 133.1, 135.0, 143.4, 146.9; ^{19}F NMR δ 0.046; IR ν 1586, 1559, 1464, 1453, 1420, 1387, 1279 (SO_2, as), 1202, 1171, 1157, 1125, 992, 795, 762, 752, 642, 623, 610, 569, 515, 428 cm^{-1}; FABMS *m/z* 630 ([M + H]$^+$). Anal. Calcd for $C_{22}H_{21}BiF_3NO_2S$: C, 41.98; H, 3.36; N, 2.23. Found: C, 41.97; H, 3.26; N, 2.15.

Tris(2-methoxyphenyl)[(trifluoromethanesulfonyl)imino]-λ^5-bismuthane, 11b: mp 137−151 °C (decomp); ^{1}H NMR δ 3.69 (s, 9H), 7.10−7.25 (m, 6H), 7.48−7.56 (m, 3H), 8.01 (dd, 3H, $J = 7.6$, 1.3 Hz); $^{13}C\{^1H\}$ NMR δ 56.1, 112.0, 123.9, 133.2, 135.0, 136.9, 159.8; ^{19}F NMR δ −0.259; IR ν 1590, 1563, 1472, 1435, 1294, 1279, 1269 (SO_2, as), 1242, 1206, 1159, 1121, 1046, 1013, 994, 787, 766, 758, 637, 612, 567, 517, 477, 430 cm^{-1}; FABMS *m/z* 678 ([M + H]$^+$). Anal. Calcd for $C_{22}H_{21}BiF_3NO_5S$: C, 39.00; H, 3.12; N, 2.07. Found: C, 38.93; H, 3.07; N, 2.09.

[(Trifluoromethanesulfonyl)imino]tris(2,4,6-trimethylphenyl)-λ^5-bismuthane, 11c: mp 173−175 °C; ^{1}H NMR δ 2.29 (s, 9H), 2.58 (s, 18H), 7.08 (s, 6H); IR ν 1590, 1566, 1453, 1381, 1294, 1267 (SO_2, as), 1198, 1163, 1113, 1028, 972, 941, 853, 687, 631, 612, 581, 565, 538, 511, 492 cm^{-1}; FABMS *m/z* 714 ([M + H]$^+$).

Tris(2-methylphenyl)(tosylimino)-λ^5-bismuthane, 11d: ^{1}H NMR δ 2.30 (s, 3H), 2.36 (s, 9H), 6.98 (d, 2H, $J = 8.0$ Hz), 7.35−7.48 (m, 9H), 7.57 (d, 2H, $J = 8.0$ Hz), 7.90−7.94 (m, 3H); $^{13}C\{^1H\}$ NMR δ 21.3, 24.3, 125.9, 128.5, 128.8, 131.7, 132.5, 135.4, 139.5, 143.6, 144.8, 146.7; IR ν 1599, 1586, 1493, 1468, 1451, 1383, 1275, 1229 (SO_2, as), 1204, 1161, 1117, 1076, 1024, 1007, 943, 820, 793, 756, 749, 735, 708, 664, 644, 625, 567, 546, 428 cm^{-1}; FABMS *m/z* 652 ([M + H]$^+$).

Tris(2-methoxyphenyl)(tosylimino)-λ^5-bismuthane, 11e: mp 179−182 °C (decomp); ^{1}H NMR δ 2.28 (s, 3H), 3.51 (s, 9H), 6.92−7.02 (m, 5H), 7.13−7.20 (m, 3H), 7.41−7.50 (m, 3H), 7.57 (d, 2H, $J = 8.1$ Hz), 8.04 (d, 3H, $J = 7.9$ Hz); $^{13}C\{^1H\}$ NMR δ 21.2, 55.7, 111.5, 123.6, 126.0, 128.2, 132.6, 135.7, 136.8, 138.7, 146.2, 160.0; IR ν 1580, 1568, 1472, 1451, 1435, 1298, 1277, 1248 (SO_2, as), 1229, 1183, 1165, 1119, 1075, 1049, 1019, 947, 853, 824, 789, 762, 712, 662, 567, 548, 477, 434 cm^{-1}; FABMS *m/z* 700 ([M + H]$^+$). Anal. Calcd for $C_{28}H_{28}BiNO_5S$: C, 48.07; H, 4.03; N, 2.00. Found: C, 48.35; H, 3.81; N, 2.06.

(Mesylimino)tris(2-methylphenyl)-λ^5-bismuthane, 11f: mp 158−175 °C (decomp); ^{1}H NMR δ 2.50 (s, 9H), 2.96 (s, 3H), 7.40−7.49 (m, 9H), 7.92−7.96 (m, 3H); $^{13}C\{^1H\}$ NMR δ 24.4, 44.3, 129.0, 131.8, 132.6, 135.2, 143.4, 147.0; IR ν 1584, 1559, 1466, 1451, 1310, 1275, 1227 (SO_2, as), 1204, 1163, 1088, 1003, 965, 953, 795, 783, 762, 750, 621, 527, 513, 428 cm^{-1}; FABMS *m/z* 576 ([M + H]$^+$). Anal. Calcd for $C_{22}H_{24}BiNO_2S$: C, 45.92; H, 4.20; N, 2.43. Found: C, 45.06; H, 3.92; N, 2.41.

(Mesylimino)tris(2-methoxyphenyl)-λ^5-bismuthane, 11g: mp 127−135 °C (decomp); ^{1}H NMR δ 2.92 (s, 3H), 3.65 (s, 9H), 7.07−7.22 (m, 6H), 7.44−7.52 (m, 3H), 8.04 (d, 3H, $J = 7.3$ Hz); $^{13}C\{^1H\}$ NMR δ 44.3, 55.9, 111.6, 123.8, 132.7, 135.6, 137.0, 160.0; IR ν 1588, 1566, 1474, 1433, 1312, 1298, 1279, 1254, 1246 (SO_2, as), 1215, 1184, 1167, 1117, 1084, 1046, 1019, 980, 862, 787, 764, 750, 646, 627, 565, 527, 515, 477, 430 cm^{-1}; FABMS *m/z* 624

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(17) Bittner, S.; Assaf, Y.; Krief, P.; Pomerantz, M.; Ziemnicka, B. T.; Smith, C. G. *J. Org. Chem.* **1985**, *50*, 1712−1718.

(18) Roy, A. K. *J. Am. Chem. Soc.* **1993**, *115*, 2598−2603.

(19) Kirsanov, A. V. *Zh. Obshch. Khim.* **1952**, *22*, 269−273.

([M + H]$^+$). Anal. Calcd for $C_{22}H_{24}BiNO_5S$: C, 42.38; H, 3.88; N, 2.25. Found: C, 42.45; H, 3.69; N, 2.06.

Although spectroscopic data clearly supported a high state of purity of **11c**,**d**, we were not successful in obtaining satisfactory analytical data of an accuracy within ±0.4%.

Oxidation of Alcohols by Triaryl(sulfonylimino)-λ^5-bismuthanes. A mixture of **11a** (15.7 mg, 25 μmol), ethanol (7.2 μL, 0.12 mmol), and $CDCl_3$ (0.5 mL) was heated at 40 °C, and the progress of the reaction was monitored by ^{1}H NMR using 9,10-dihydroanthracene (4.5 mg, 25 μmol) as an internal standard. After 36 h, acetaldehyde (67%), toluene (85%), and diarylbismuth amide **12a** (76%) were formed. 2-Propanol was similarly oxidized by **11e** to give acetone (75%), toluene (91%), and **12b** (73%). Compounds **8b**, **9**, and **10a** did not oxidize these alcohols under the same reaction conditions.

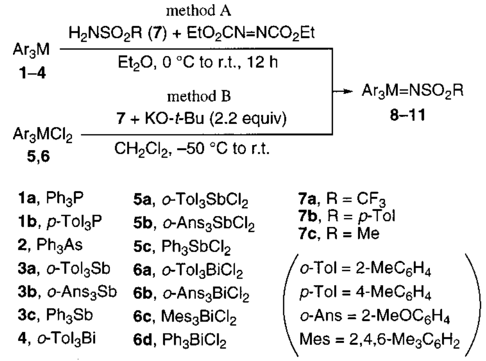
Bis(2-methylphenyl)bismuth trifluoromethanesulfonamide, 12a. ^{1}H NMR δ 2.47 (s, 6H), 4.51 (br-s, 1H, NH), 7.39−7.59 (m, 6H), 8.28 (d, 2H, J = 7.6 Hz); IR ν 3270, 1580, 1447, 1383, 1348 (SO_2, as), 1269, 1219, 1186, 1138, 955, 793, 747, 613, 561, 505, 432 cm^{-1}.

Bis(2-methylphenyl)bismuth tosylamide, 12b. ^{1}H NMR δ 2.39 (s, 3H), 2.40 (s, 6H), 4.37 (br-s, 1H, NH), 7.20 (d, 2H, J = 8.0 Hz), 7.32−7.41 (m, 4H), 7.45 (d, 2H, J = 7.2 Hz), 7.70 (d, 2H, J = 8.0 Hz), 8.15 (d, 2H, J = 7.2 Hz); IR ν 3290, 1599, 1578, 1495, 1447, 1398, 1310 (SO_2, as), 1302, 1286, 1204, 1142, 1088, 1020, 914, 810, 750, 741, 667, 563, 544, 432; FABMS m/z 470 ([M − Tol]$^+$).

Although spectroscopic data clearly supported a high state of purity of **12a**,**b**, we were not successful in obtaining satisfactory analytical data of an accuracy within ±0.4%.

X-ray Crystallographic Analysis of Triaryl(sulfonylimino)pnictoranes. Single crystals of **8a**, **8b**, **9**, **10a**, **10b**, **11a**, **11b**, and **11e** were grown from CH_2Cl_2/hexane or CH_2Cl_2/pentane at 4 °C. Data were recorded on a Rigaku AFC7S diffractometer, with graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation, using the $\omega-2\theta$ scan technique. The intensities of three representative reflections were measured after every 150 reflections. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. The structures were solved by the Patterson methods[20] (for **11a**) or direct methods[21] (for **8a**, **8b**, **9**, **10a**, **10b**, **11b**, and **11e**) and expanded using the Fourier techniques.[22] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[23] Anomalous dispersion effects were included in F_{calcd};[24] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[25] The values for the mass-attenuation coefficients are those of Creagh and Hubbel.[26] All calculations were performed using the teXsan[27] crystallographic software package of Molecular Structure Corporation. Further details of the crystal data are provided in Supporting Information.

Scheme 1



Results and Discussion

Synthesis. Triaryl(sulfonylimino)pnictoranes **8**−**11** were prepared by two different methods (Scheme 1 and Table 1). Triaryl(sulfonylimino)-λ^5-phosphanes **8**, -arsane **9**, and -stibanes **10** were prepared by the Bittner's redox condensation reaction (method A).[17] Treatment of triarylphosphanes **1a**,**b**, triphenylarsane (**2**), and triarylstibanes **3a**,**b** with trifluoromethanesulfonamide (**7a**) in the presence of an equimolar diethyl azodicarboxylate (DEADC) in Et_2O afforded the corresponding triaryl(sulfonylimino)-λ^5-phosphanes **8a**,**b**,[18] -arsane **9**, and -stibanes **10a**,**b**,[14] respectively (entries 1−5 in Table 1). With triphenylstibane (**3c**), however, triphenylstibane oxide[28] was obtained in place of the expected triphenyl(sulfonylimino)-λ^5-stibane **10c** (entry 6).[5a] Presumably, the resulting stibonium salt or imino-λ^5-stibane **10c** was readily hydrolyzed during the reaction. The DEADC-promoted redox condensation between tris(2-methylphenyl)bismuthane (**4**) and **7a** did not take place at room temperature even after 48 h, probably because of the low nucleophilicity of a lone electron pair of **4** (entry 7).

Alternatively, triaryl(sulfonylimino)-λ^5-stibanes **10a**,**b** were synthesized by a Kirsanov-type reaction (method B).[19] Triarylantimony dichlorides **5a**,**b** reacted with **7a** in the presence of 2.2 equiv of KO-*t*-Bu in CH_2Cl_2 to afford **10a**,**b** in 77−96% yields (entries 8,9). Triaryl(sulfonylimino)-λ^5-bismuthanes **11a**−**g** were similarly obtained in 23−98% yields from triarylbismuth dichlorides **6a**−**c** and amides **7a**−**c** (entries 11−17). However, triphenyl derivatives, $Ph_3Sb{=}NSO_2CF_3$[5a] (**10c**) and $Ph_3Bi{=}NSO_2CF_3$[6c] (**11h**), were readily hydrolyzed during workup in air to give triphenylstibane oxide together with trace amounts of μ-oxo-bridged antimony(V) compound $(Ph_3SbNHSO_2CF_3)_2O$[29] from the

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(20) PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1994.

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(22) DIRDIF-94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1994.

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(25) Creagh, D. C.; McAuley, W. J. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Vol. C, Table 4.2.6.8, pp 219−222.

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(28) Bordner, J.; Doak, G. O.; Everett, T. S. *J. Am. Chem. Soc.* **1986**, *108*, 4206−4213.

(29) This compound was structurally determined by X-ray crystallography. The bond parameters and crystal data are reported as a CIF file in the Supporting Information.

Table 1. Synthesis of Triaryl(sulfonylimino)pnictoranes

entry	Ar_3M or Ar_3MX_2	H_2NSO_2R	method[a]	iminopnictorane	yield/%
1	Ph_3P (**1a**)	**7a**	A	$Ph_3P{=}NSO_2CF_3$ (**8a**)	46
2	*p*-Tol_3P (**1b**)	**7a**	A	*p*-$Tol_3P{=}NSO_2CF_3$ (**8b**)	92
3	Ph_3As (**2**)	**7a**	A	$Ph_3As{=}NSO_2CF_3$ (**9**)	70
4	*o*-Tol_3Sb (**3a**)	**7a**	A	*o*-$Tol_3Sb{=}NSO_2CF_3$ (**10a**)	90
5	*o*-Ans_3Sb (**3b**)	**7a**	A	*o*-$Ans_3Sb{=}NSO_2CF_3$ (**10b**)	88
6	Ph_3Sb (**3c**)	**7a**	A	$Ph_3Sb{=}NSO_2CF_3$ (**10c**)	*b*
7	*o*-Tol_3Bi (**4**)	**7a**	A	no reaction	
8	*o*-Tol_3SbCl_2 (**5a**)	**7a**	B	**10a**	96
9	*o*-Ans_3SbCl_2 (**5b**)	**7a**	B	**10b**	77
10	Ph_3SbCl_2 (**5c**)	**7a**	B	**10c**	*b*
11	*o*-Tol_3BiCl_2 (**6a**)	**7a**	B	*o*-$Tol_3Bi{=}NSO_2CF_3$ (**11a**)	98
12	*o*-Ans_3BiCl_2 (**6b**)	**7a**	B	*o*-$Ans_3Bi{=}NSO_2CF_3$ (**11b**)	92
13	Mes_3BiCl_2 (**6c**)	**7a**	B	$Mes_3Bi{=}NSO_2CF_3$ (**11c**)	84
14	**6a**	**7b**	B	*o*-$Tol_3Bi{=}NSO_2$(*p*-Tol) (**11d**)	96
15	**6b**	**7b**	B	*o*-$Ans_3Bi{=}NSO_2$(*p*-Tol) (**11e**)	65
16	**6a**	**7c**	B	*o*-$Tol_3Bi{=}NSO_2Me$ (**11f**)	80
17	**6b**	**7c**	B	*o*-$Ans_3Bi{=}NSO_2Me$ (**11g**)	23
18	Ph_3BiCl_2 (**6d**)	**7a**	B	$Ph_3Bi{=}NSO_2CF_3$ (**11h**)	*b*

[a] **A**: **7** (1.0 equiv), $EtO_2CN{=}NCO_2Et$ (1.1 equiv), Et_2O, 0 °C to r.t., 12 h. **B**: **7** (1.0 equiv), KO-*t*-Bu (2.2 equiv), CH_2Cl_2, −50 °C to r.t. [b] Not isolated.

Table 2. SO_2 Asymmetric Stretching Bands of Triaryl(sulfonylimino)pnictoranes[a]

$Ar_3M{=}NSO_2CF_3$	$\nu(\Delta\nu^b)$	$Ar_3M{=}NSO_2$(*p*-Tol)	$\nu(\Delta\nu^b)$	$Ar_3M{=}NSO_2Me$	$\nu(\Delta\nu^b)$
o-$Tol_3Bi{=}NTf$ (**11a**)	1279 (41)	*o*-$Tol_3Bi{=}NTs$ (**11d**)	1229 (41)	*o*-$Tol_3Bi{=}NMs$ (**11g**)	1227 (28)
o-$Ans_3Bi{=}NTf$ (**11b**)	1269 (51)	*o*-$Ans_3Bi{=}NTs$ (**11e**)	1248 (22)	*o*-$Ans_3Bi{=}NMs$ (**11h**)	1246 (9)
$Mes_3Bi{=}NTf$ (**11c**)	1267 (53)				
o-$Tol_3Sb{=}NTf$ (**10a**)	1287 (33)	$Ph_3Sb{=}NTs^c$	1200 (70)		
o-$Ans_3Sb{=}NTf$ (**10b**)	1279 (41)				
$Ph_3As{=}NTf$ (**9**)	1306 (14)	$Ph_3As{=}NTs^d$	1250 (20)	$Ph_3As{=}NMs^d$	1255 (0)
p-$Tol_3P{=}NTf$ (**8b**)	1316 (4)				
$Ph_3P{=}NTf$ (**8a**)	1320 (0)	$Ph_3P{=}NTs^e$	1270 (0)	$Ph_3P{=}NMs^e$	1255 (0)

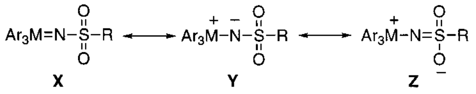
[a] Reported in cm^{-1}. Tf = SO_2CF_3. Ts = SO_2(*p*-Tol). Ms = SO_2Me. [b] Difference in frequency from the respective triphenyl(sulfonylimino)-λ^5-phosphanes (**8a**, $Ph_3P{=}NTs$, and $Ph_3P{=}NMs$). [c] Shah, J. J. *J. Tenn. Acad. Sci.* **1976**, *51*, 130−134. [d] Taken from ref 4g. [e] Taken from ref 17.

former and a polymeric triphenylbismuthane oxide[30] from the latter (entries 10 and 18). These results indicate that the *ortho*-substituted aryl ligands can provide the moisture-sensitive Sb═N and Bi═N bonds with some kinetic stabilization.[31] Triaryl(sulfonylimino)pnictoranes **8**−**11** were isolated as thermally stable solids that can be stored in a refrigerator (at 4 °C) for over a month.

Structural Comparison. The structures of triaryl(sulfonylimino)pnictoranes **8**−**11** were characterized by ^{1}H and ^{13}C NMR, IR, and FABMS spectroscopies as well as by X-ray crystallography. In the IR spectra, the SO_2 asymmetric stretching absorptions (ν_{SO2}) of sulfonylimino-λ^5-arsanes, -stibanes, and -bismuthanes were observed at lower frequencies than those of sulfonylimino-λ^5-phosphanes (Table 2).

In a series of the *N*-trifluoromethanesulfonyl derivatives, the differences in frequency ($\Delta\nu_{SO2}$) from **8a** increased progressively in the order **9** < **10a**,**b** < **11a**−**c**, suggesting that the single-bond character of the S═O bond becomes increasingly prominent as the pnictogen atom becomes heavier. A similar trend was also observed for the *N*-tosyl and *N*-mesyl derivatives derived from P, As, and Bi. Therefore, the contribution of a canonical form **Z** would be more significant than that of two others **X** and **Y** for heavy triaryl(sulfonyl)iminopnictoranes (Scheme 2). Both the SO_2 symmetric and S−N stretching bands overlapped with other absorptions and could not be located.

Scheme 2



A series of triaryl(sulfonylimino)pnictoranes, **8a**, **8b**, **9**, **10a**, **10b**, **11a**, **11b**, and **11e**, were characterized by X-ray crystallography and their structures compared. ORTEP diagrams are presented in Figures 1−8, selected bond parameters are listed in Table 3, and crystal data are summarized in Table 4.[32] All iminopnictoranes were found to exist in a monomeric form, and no intermolecular interaction between the pnictogen atom and neighboring molecules was apparently observed. Each pnictogen center possesses a distorted tetrahedral geometry, to which one of the sulfonyl oxygen atoms, O(1), coordinates weakly (vide infra). The *ortho*-substituents in compounds **10** and **11** were

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(30) (a) Goel, R. G.; Prasad, H. S. *J. Organomet. Chem.* **1972**, *36*, 323−332. (b) Goel, R. G.; Prasad, H. S. *J. Organomet. Chem.* **1973**, *50*, 129−134. (c) Suzuki, H.; Ikegami, T.; Matano, Y. *Tetrahedron Lett.* **1994**, *35*, 8197−8200. (d) Matano, Y.; Nomura, H. *J. Am. Chem. Soc.* **2001**, *123*, 6443−6444.

(31) Kinetic protection by *ortho*-substituted aryl groups has been employed for the stabilization of highly reactive functionalities. For example, see: (a) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587−4589. (b) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343−1344. (c) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. *J. Am. Chem. Soc.* **1982**, *104*, 5820−5821. (d) Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* **1997**, *277*, 78−80. (e) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1665−1684.

(32) After the previous communication (ref 14), the structures of imino-λ^5-stibanes **10a**,**b** were re-solved at a recommended level of calculation, and the bond parameters of these compounds reported herein are the revised ones.

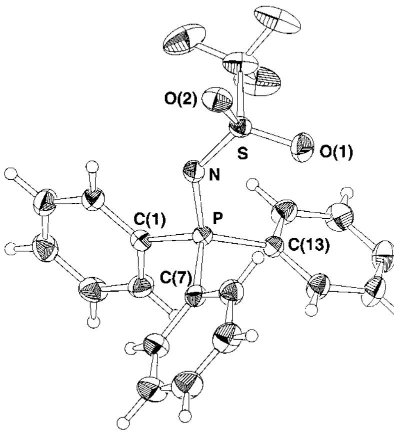

Figure 1. ORTEP diagram for **8a** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): P−C(1), 1.793(2); P−C(7), 1.793(2); P−C(13), 1.800(2); C(1)−P−C(7), 109.8(1); C(1)−P−C(13), 107.7(1); C(7)−P−C(13), 107.9(1); N−P−C(1), 105.3(1); N−P−C(7), 109.8(1); N−P−C(13), 116.2(1).

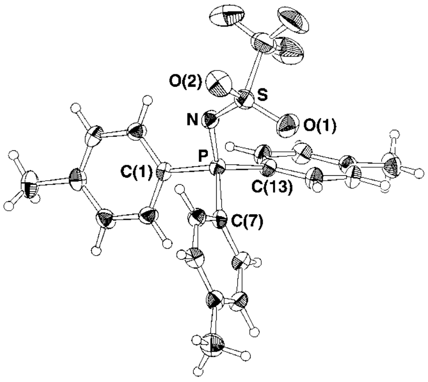

Figure 2. ORTEP diagram for **8b** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): P−C(1), 1.791(4); P−C(7), 1.796(4); P−C(13), 1.794(4); C(1)−P−C(7), 107.1(2); C(1)−P−C(13), 108.0(2); C(7)−P−C(13), 109.2(5); N−P−C(1), 104.6(2); N−P−C(7), 111.7(2); N−P−C(13), 115.7(2).

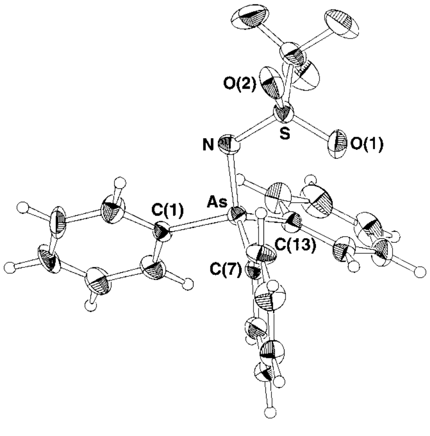

Figure 3. ORTEP diagram for **9** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): As−C(1), 1.898(8); As−C(7), 1.908(8); As−C(13), 1.920(8); C(1)−As−C(7), 108.2(3); C(1)−As−C(13), 108.0(4); C(7)−As−C(13), 109.6(4); N−As−C(1), 103.3(4); N−As−C(7), 111.4(4); N−As−C(13), 115.8(4).

found to interact with the pnictogen center sterically or electronically: In **10a** and **11a**, there is repulsive interaction between the *ortho*-methyl groups and the pnictogen center, whereas in **10b**, **11b**, and **11e** there is attractive interaction between the *ortho*-methoxy oxygen and pnictogen atoms.[33]

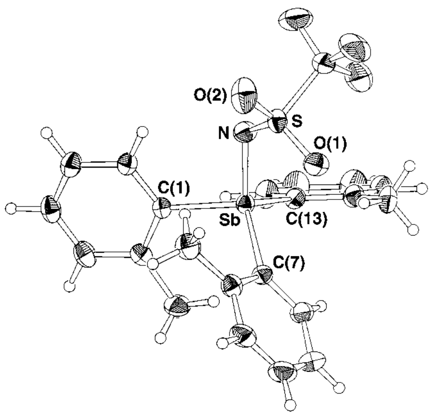

Figure 4. ORTEP diagram for **10a** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Sb−C(1), 2.101(4); Sb−C(7), 2.106(4); Sb−C(13), 2.114(4); C(1)−Sb−C(7), 108.8(2); C(1)−Sb−C(13), 106.3(2); C(7)−Sb−C(13), 113.5(2); N−Sb−C(1), 100.5(2); N−Sb−C(7), 117.0(2); N−Sb−C(13), 109.4(2).

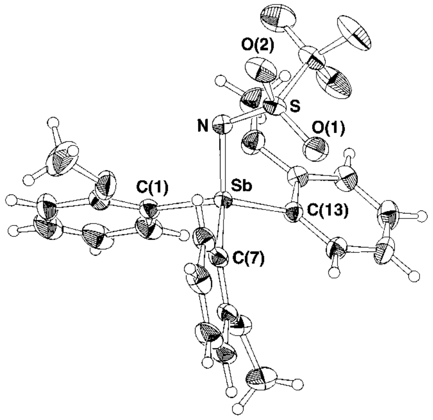

Figure 5. ORTEP diagram for **10b** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Sb−C(1), 2.098(2); Sb−C(7), 2.098(2); Sb−C(13), 2.090(2); C(1)−Sb−C(7), 106.66(9); C(1)−Sb−C(13), 110.45(10); C(7)−Sb−C(13), 113.16(9); N−Sb−C(1), 107.63(9); N−Sb−C(7), 107.24(9); N−Sb−C(13), 111.41(8).

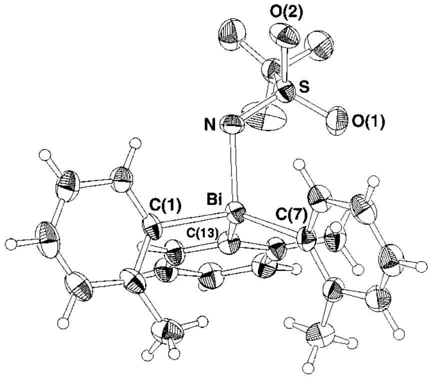

Figure 6. ORTEP diagram for **11a** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Bi−C(1), 2.224(7); Bi−C(7), 2.245(7); Bi−C(13), 2.224(7); C(1)−Bi−C(7), 111.9(3); C(1)−Bi−C(13), 106.3(3); C(7)−Bi−C(13), 122.0(3); N−Bi−C(1), 96.4(3); N−Bi−C(7), 107.3(3); N−Bi−C(13), 110.1(3).

The observed M═N bond lengths primarily reflect the orbital size of the respective pnictogen atoms[34] and are within the range of those of known iminopnictoranes.[2e,4k,7,13,14,35,36] The M═N bond lengths of the *N*-sulfonyl derivatives examined here are slightly shorter than those of *N*-trichloroacetyl

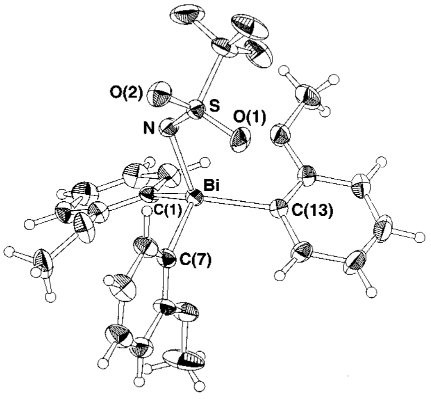

Figure 7. ORTEP diagram for **11b** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Bi−C(1), 2.212(8); Bi−C(7), 2.211(8); Bi−C(13), 2.192(9); C(1)−Bi−C(7), 112.4(3); C(1)−Bi−C(13), 115.0(3); C(7)−Bi−C(13), 107.0(3); N−Bi−C(1), 99.4(3); N−Bi−C(7), 104.7(4); N−Bi−C(13), 117.9(3).

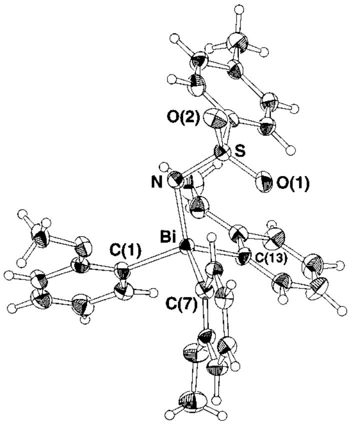

Figure 8. ORTEP diagram for **11e** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Bi−C(1), 2.197(10); Bi−C(7), 2.188(9); Bi−C(13), 2.211(10); C(1)−Bi−C(7), 110.0(4); C(1)−Bi−C(13), 106.5(4); C(7)−Bi−C(13), 106.0(4); N−Bi−C(1), 109.1(4); N−Bi−C(7), 106.1(4); N−Bi−C(13), 119.0(3).

derivatives, which constitute another homologous series of iminopnictoranes characterized by X-ray crystallography.[13] To estimate the multiplicity of the M═N bonds, the M═N bond lengths are compared to the reported M−N bond lengths of pnictogen(III) amides. The P═N bond lengths of 1.603(2)−1.609 (3) Å in **8a**,**b** are much shorter than typical P−N bond lengths (1.68−1.75 Å) observed for phosphorus(III) amides[37] and the ideal P−N single-bond length (1.80 Å) observed for potassium phosphoramidate.[38] Previous discussion of the bonding nature of the P−N bond of phosphorus(III) amides[37] has suggested that the back-bonding from the nitrogen to the phosphorus causes a P−N bond shortening of 0.04−0.12 Å.[39] Therefore, the P═N bonds of **8a**,**b** are considered to possess considerable double-bond character. The As═N bond length of 1.776(7) Å in **9** is shorter than typical As−N bond lengths (1.84−1.88 Å) of arsenic(III) amides.[37e,40] The Sb═N bond lengths of 1.952(4)−1.962(2) Å in imino-λ^5-stibanes **10a**,**b** are also shorter than known Sb−N bond lengths (2.01−2.08 Å) of antimony(III) amides.[41] The Bi═N bond lengths of 2.073(8)−2.117(6) Å in imino-λ^5-bismuthanes **11a**,**b**,**e** are slightly shorter than known Bi−N bond lengths (2.165−2.20 Å) of bismuth(III) amides.[41c,d,42] Recently, Burford and co-workers have compared the structures of a homologous series of bis(amido)-diazadipnictetidines, $[\mathrm{DipNMN(H)Dip}]_2$ (M = P, As, Sb, Bi; Dip = 2,6-diisopropylphenyl), from which the average M−N bond lengths are estimated to be 1.709 Å for P−N, 1.867 Å for As−N, 2.043 Å for Sb−N, and 2.165 Å for Bi−N.[42c,43] Table 5 summarizes the ratios of the M═N bond lengths of the triaryl[(trifluoromethylsulfonyl)imino]pnictoranes versus the M−N bond lengths observed for $[\mathrm{DipNMN(H)Dip}]_2$. The ratios increase steadily and approximate toward unity as the pnictogen atoms become heavier, leading us to conclude that the single-bond character of the M═N bond is more prominent with heavier pnictogen elements.

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(33) The *ortho*-methyl groups of **10a** and **11a** lean ∼3−5° away from the pnictogen center, whereas the *ortho*-methoxy groups of **10b**, **11b**, and **11e** lean ∼5−6° toward the pnictogen center.

(34) Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: Oxford, U.K., 1998. Covalent radii: N, 0.70 Å; P, 1.10 Å; As, 1.21 Å; Sb, 1.41 Å; Bi, 1.52 Å; O, 0.66 Å. van der Waals radii: P, 1.90 Å; As, 2.00 Å; Sb, 2.20 Å; Bi, 2.40 Å; O, 1.40 Å.

(35) Imino-λ^5-arsanes: (a) Roesky, H. W.; Witt, M.; Clegg, W.; Isenberg, W.; Noltemeyer, M.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 943−944. (b) Witt, M.; Roesky, H. W.; Noltemeyer, M.; Clegg, W.; Schmidt, M.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 974−975. (c) Bailey, K.; Gosney, I.; Gould, R. O.; Lloyd, D.; Taylor, P. *J. Chem. Res., Synop.* **1988**, 386−387. (d) Kokorev, G. I.; Litvinov, I. A.; Musin, R. Z.; Naumov, V. A. *Zh. Obshch. Khim.* **1991**, *61*, 2713−2721. (e) Mai, H.-J.; Weller, F.; Dehnicke, K.; Maichle-Mössmer, C.; Strähle, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 851−855. See also ref 7i.

(36) A dimeric imino-λ^5-stibane: Edwards, A. J.; Paver, M. A.; Pearson, P.; Raithby, P. R.; Rennie, M.-A.; Russell, C. A.; Wright, D. S. *J. Organomet. Chem.* **1995**, *503*, C29−C31.

(37) Typical bond lengths are 1.68−1.69 Å for P−N$_{\mathrm{sp2}}$ and 1.74−1.75 Å for P−N$_{\mathrm{sp3}}$ bonds. For example, see: (a) Rømming, C.; Songstad, J. *Acta Chem. Scand.* **1978**, *A32*, 689−699. (b) Thompson, M. L.; Haltiwanger, R. C.; Norman, A. D. *J. Chem. Soc., Chem. Commun.* **1979**, 647−648. (c) Scherer, O. J.; Andres, K.; Krüger, C.; Tsay, Y.-H.; Wolmerhäuser, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 571−572. (d) Thompson, M. L.; Tarassoli, A.; Haltiwanger, R. C.; Norman, A. D. *J. Am. Chem. Soc.* **1981**, *103*, 6770−6772. (e) Atwood, J. L.; Cowley, A. H.; Hunter, W. E.; Mehrotra, S. K. *Inorg. Chem.* **1982**, *21*, 1354−1356. (f) Chen, H.-J.; Haltiwanger, R. C.; Hill, T. G.; Thompson, M. L.; Coons, D. E.; Norman, A. D. *Inorg. Chem.* **1985**, *24*, 4725−4730. (g) Cobbledick, R. E.; Einstein, F. W. B. *Acta Crystallogr.* **1975**, *B31*, 2731−2733.

(38) Cameron, T. S.; Chan, C.; Chute, W. J. *Acta Crystallogr.* **1980**, *B36*, 2391−2393. The anion of potassium phosphoramidate ($K[H_3NO_3P]$) is considered to contain an "ideal" P−N single bond [1.800(4) Å], where the nitrogen atom is sp^3 hybridized with no lone pair of electrons.

(39) The quaternization of the phosphorus atom through the P(III) to P(V) conversion causes additional P−N bond-shortening.

(40) Typical bond lengths are 1.84−1.85 Å for As−N$_{\mathrm{sp2}}$ and 1.87−1.88 Å for As−N$_{\mathrm{sp3}}$ bonds. For example, see: (a) Weiss, V. J.; Eisenhuth, W. *Z. Anorg. Allg. Chem.* **1967**, *350*, 9−17. (b) Rømming, C.; Songstad, J. *Acta Chem. Scand.* **1980**, *A34*, 365−373.

(41) (a) Edwards, A. J.; Paver, M. A.; Raithby, P. R.; Russell, C. A.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1993**, 2257−2258. (b) Edwards, A. J.; Paver, M. A.; Rannie, M.-A.; Raithby, P. R.; Russell, C. A.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1994**, 2963−2966. (c) Burford, N.; Macdonald, C. L. B.; Robertson, K. N.; Cameron, T. S. *Inorg. Chem.* **1996**, *35*, 4013−4016. (d) Mason, M. R.; Phulpagar, S. S.; Mashuta, M. S.; Richardson, J. F. *Inorg. Chem.* **2000**, *39*, 3931−3933. The values in parentheses are averaged.

(42) (a) Clegg, W.; Compton, N. A.; Errington, R. J.; Norman, N. C.; Wishart, N. *Polyhedron* **1989**, *8*, 1579−1580. (b) Clegg, W.; Compton, N. A.; Errington, R. J.; Fisher, G. A.; Green, M. E.; Hockless, D. C. R.; Norman, N. C. *Inorg. Chem.* **1991**, *30*, 4680−4682. (c) Wirringa, U.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **1994**, *33*, 4607−4608. The values in parentheses are averaged.

(43) Burford, N.; Cameron, T. S.; Lam, K.-C.; LeBlanc, D. J.; Macdonald, C. L. B.; Phillips, A. D.; Rheingold, A. L.; Stark, L.; Walsh, D. *Can. J. Chem.* **2001**, *79*, 342−348.

Table 3. Selected Bond Parameters of Triaryl(sulfonylimino)pnictoranes

	8a	**8b**	**9**	**10a**	**10b**	**11a**	**11b**	**11e**
				Bond Lengths (Å)				
M−N	1.603(2)	1.609(3)	1.776(7)	1.952(4)	1.962(2)	2.117(6)	2.096(7)	2.073(8)
N−S	1.536(2)	1.548(3)	1.557(7)	1.535(4)	1.535(2)	1.532(7)	1.516(7)	1.574(8)
S−O(1)	1.423(2)	1.427(3)	1.439(6)	1.445(4)	1.445(2)	1.433(7)	1.444(6)	1.463(9)
S−O(2)	1.426(2)	1.418(3)	1.422(6)	1.431(4)	1.436(2)	1.454(7)	1.450(7)	1.451(8)
M···O(1)	3.216(2)	3.137(3)	3.038(6)	3.259(4)	3.112(2)	3.285(7)	3.210(7)	3.067(8)
				Bond Angles (deg)				
M−N−S	131.7(1)	127.1(2)	118.9(4)	122.9(2)	117.3(1)	118.6(4)	117.6(4)	112.1(5)
N−S−O(1)	115.4(1)	115.7(2)	115.1(4)	116.0(2)	116.1(1)	117.2(4)	117.5(4)	113.8(5)
N−S−O(2)	111.7(1)	112.0(2)	111.8(4)	113.2(3)	112.3(1)	110.6(4)	112.6(4)	108.0(5)
				Torsion Angles (deg)				
M−N−S−O(1)	−4.2(3)	2.8(4)	−0.9(7)	10.3(4)	−9.6(2)	−16.9(7)	5.5(7)	−22.9(7)

Table 4. Crystal Data for Triaryl(sulfonylimino)pnictoranes

	8a	**8b**	**9**	**10a**	**10b**	**11a**	**11b**	**11e**
empirical formula	$C_{19}H_{15}F_3NO_2PS$	$C_{22}H_{21}F_3NO_2PS$	$C_{19}H_{15}AsF_3NO_2S$	$C_{22}H_{21}F_3NO_2SSb$	$C_{22}H_{21}F_3NO_5SSb$	$C_{22}H_{21}BiF_3NO_2S$	$C_{22}H_{21}BiF_3NO_5S$	$C_{28}H_{28}BiNO_5S$
fw	409.36	451.44	453.31	542.22	590.22	629.45	677.45	699.57
cryst dimensions (mm^3)	0.38 × 0.20 × 0.20	0.50 × 0.24 × 0.10	0.12 × 0.12 × 0.08	0.40 × 0.10 × 0.10	0.30 × 0.10 × 0.10	0.10 × 0.10 × 0.20	0.20 × 0.19 × 0.10	0.45 × 0.15 × 0.10
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
a (Å)	10.610(1)	10.419(2)	11.085(5)	11.285(2)	10.955(2)	10.507(1)	11.403(2)	8.757(4)
b (Å)	11.414(1)	21.244(2)	14.494(3)	15.234(3)	14.268(2)	12.553(1)	17.981(2)	14.985(8)
c (Å)	8.6814(5)	10.697(2)	24.257(2)	13.410(2)	9.055(3)	9.377(1)	11.777(2)	20.761(4)
α (deg)	92.255(8)				100.29(2)	92.361(9)		
β (deg)	100.704(7)	112.56(1)	98.94(2)	103.10(1)	110.43(2)	108.031(8)	94.63(1)	96.93(3)
γ (deg)	114.343(9)				107.50(1)	74.032(7)		
V ($Å^3$)	933.2(2)	2186.5(7)	3850(1)	2245.3(7)	1199.5(6)	1129.3(2)	2406.8(5)	2704(1)
space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Z	2	4	8	4	2	2	4	4
D_{calcd} (g cm^{-3})	1.457	1.371	1.564	1.604	1.634	1.851	1.869	1.718
radiation (λ, Å)	(Mo Kα, 0.71069)	(Mo Kα, 0.71069)	(Mo Kα, 0.71069)	(Mo Kα, 0.71069)	(Mo Kα, 0.71069)	(Mo Kα, 0.71069)	(Mo Kα, 0.71069)	(Mo Kα, 0.71069)
μ (Mo Kα) (cm^{-1})	3.02	2.65	19.16	13.62	12.91	79.26	74.55	66.22
temp (°C)	23 ± 1	23 ± 1	26 ± 1	25 ± 1	26 ± 1	22 ± 1	21 ± 1	23 ± 1
$2\theta_{max}$ (deg)	55.0	55.0	55.0	55.0	55.0	54.8	55.0	55.0
no. reflns measd								
total	4524	5282	4664	5406	5869	5433	5764	6869
unique	4519	5210	4634	5353	5521	5122	5701	6560
no. reflns	4290 (all, $2\theta <$ 55.00°)	5019 (all, $2\theta <$ 54.98°)	3437 ($I > 0.00\sigma(I)$, $2\theta <$ 55.02°)	5153 (all, $2\theta <$ 54.99°)	5521 (all, $2\theta <$ 54.99°)	5122 (all, $2\theta <$ 54.85°)	5701 (all, $2\theta <$ 54.98°)	6212 (all, $2\theta <$ 55.00°)
no. variables	244	271	244	272	299	272	298	325
R_1, R_w	0.043, 0.147	0.063, 0.216	0.057, 0.177	0.040, 0.140	0.027, 0.086	0.045, 0.135	0.048, 0.150	0.053, 0.176
GOF	1.06	1.04	0.81	0.85	1.01	1.10	0.90	1.12

Table 5. M═N/M−N Bond Length Ratios

M	M═N/Å	M−N/Å[a]	M═N/M−N
P (**8a**,**b**)	1.603−1.609	1.709	0.938−0.941
As (**9**)	1.776	1.867	0.951
Sb (**10a**,**b**)	1.952−1.962	2.043	0.955−0.960
Bi (**11a**,**b**)	2.096−2.117	2.165	0.968−0.978

[a] Averaged M−N bond lengths of $[DipNMN(H)Dip]_2$, taken from ref 42c and 43.

The bonding nature of the $M-N-SO_2$ linkage is also noteworthy. All observed N−S bond lengths are in the range 1.516(7)−1.574(8) Å. They are close to that [1.590(2) Å] of Chloramine-T[44] but much shorter than the ideal N−S single-bond length (1.76 Å) observed for sulfamic acid ($H_3N^+-SO_3^-$).[45] In contrast, the S═O bond lengths of 1.418(3)−1.463(9) Å are somewhat longer than the typical S═O double-bond length (1.40 Å).[46] Among *N*-trifluoromethylsulfonyl derivatives, **10a**,**b** and **11a**,**b** possess longer S═O and shorter N−S bonds compared to **8a**,**b** and **9**, indicating the increased contribution of canonical form **Z** to the heavier (sulfonylimino)pnictoranes, in accordance with the IR data (Scheme 2).

The M═N and S−N bond lengths are also dependent on the structure of the sulfonyl group. The *N*-trifluoromethylsulfonyl derivatives possess slightly longer M═N bonds compared to those of the *N*-tosyl derivatives; the M═N bonds of **8a** [1.603(2) Å], **9** [1.776(7) Å] and **11b** [2.096(7) Å] are all longer than those of Ph_3P═NTs [1.579(4) Å],[7c] Ph_3As═NTs [1.755(3) Å],[35e] and **11e** [2.073(8) Å]. In contrast, the

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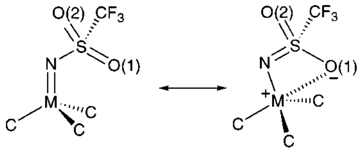
[44] Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 4057−4058.

[45] (a) Sass, R. L. *Acta Crystallogr.* **1960**, *13*, 320−324. (b) Osaki, K.; Tadokoro, H.; Nitta, I. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 524−528.

[46] Gillespie, R. J.; Robinson, E. A. *Can. J. Chem.* **1963**, *41*, 2074−2085.

Scheme 3



N—S bond lengths of **8a** [1.536(2) Å], **9** [1.557(7) Å], and **11b** [1.516(7) Å] are slightly shorter than those of Ph_3P═NTs [1.586(4) Å],[7c] Ph_3As═NTs [1.572(3) Å],[35e] and **11e** [1.574(8) Å]. These findings may be interpreted by the strong electron-withdrawing ability of the trifluoromethyl group on the sulfur atom, enhancing both the single-bond character of the M═N bond and the double-bond character of the N—S bond.[47]

All intramolecular M···O(1) distances are much longer than the sum of the covalent radii (1.76 Å for P—O; 1.87 Å for As—O; 2.07 Å for Sb—O; 2.18 Å for Bi—O) but are clearly shorter than the sum of the van der Waals radii (3.30 Å for P···O; 3.40 Å for As···O; 3.60 Å for Sb···O; 3.80 Å for Bi···O).[34] A comparison of the observed M···O(1) distances with these values allows us to conclude that the electrostatic interaction between the negatively charged sulfonyl oxygen O(1) and the positively charged pnictogen atoms would become more important in the order P < As < Sb < Bi (Scheme 3).

Reactions. To compare the oxidizing ability of **8b**, **9**, **10a**, **11a**, and **11d**, these compounds were treated with excess of an alcohol in $CDCl_3$. Imino-λ^5-bismuthanes **11a**,**d** oxidized ethanol to acetaldehyde and 2-propanol to acetone, respectively (eqs 1, 2). In these oxidations, toluene and bis(2-methylphenyl)bismuth amides **12a**,**b** were formed as byproducts, indicating that the α-hydrogen is abstracted from the substrate by the tolyl group originally attached to the bismuth atom.[48] The observed reactivity of **11a**,**d** stands in marked contrast to that of imino-λ^5-phosphane **8b**, -arsane **9**, and -stibane **10a**, which did not oxidize these alcohols under the employed conditions (in $CDCl_3$, 40 °C, 36−70 h).

$$\mathbf{11a} + \mathrm{EtOH} \xrightarrow[40\ ^\circ\mathrm{C},\ 36\ \mathrm{h}]{\mathrm{CDCl_3}} \underset{(67\%)}{\mathrm{MeCHO}} + \underset{(85\%)}{\mathrm{TolH}} + \underset{\mathbf{12a}\ (76\%)}{o\text{-}\mathrm{Tol_2BiNHSO_2CF_3}} \tag{1}$$

$$\mathbf{11d} + i\text{-}\mathrm{PrOH} \xrightarrow[\mathrm{reflux,\ 2\ h}]{\mathrm{CDCl_3}} \underset{(75\%)}{\mathrm{Me_2CO}} + \underset{(91\%)}{\mathrm{TolH}} + \underset{\mathbf{12b}\ (73\%)}{o\text{-}\mathrm{Tol_2BiNHSO_2}(p\text{-}\mathrm{Tol})} \tag{2}$$

Summary

A series of triaryl(sulfonylimino)pnictoranes $Ar_3M{=}NSO_2R$ (M = P, As, Sb, Bi) were prepared, and their structures were elucidated by X-ray crystallography. The *ortho*-substitution in aryl ligands has been found to provide kinetic stabilization to the reactive Sb═N and Bi═N bonds. The observed X-ray structures clearly show the increased single-bond character of the M═N bonds and the increased contribution of a canonical form M^+—N═S(O)—O^- as the central pnictogen element becomes heavier. Of several iminopnictoranes examined, only triaryl(sulfonylimino)-λ^5-bismuthane **11** could oxidize alcohols to carbonyl compounds.

Acknowledgment. This work was supported by Grants-in-Aid (1120224 and 12640516) from the Ministry of Education, Science, Sports and Culture of Japan. We thank Dr. Masamichi Ogasawara for ^{19}F NMR measurement.

Supporting Information Available: CIF files for the crystal structures of **8a**, **8b**, **9**, **10a**, **10b**, **11a**, **11b**, **11e** and $(Ph_3SbNHSO_2CF_3)_2O$. These materials are available free of charge via the Internet at http://pubs.acs.org.

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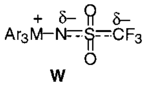
(47) Because of the inductive ($-I_\sigma$) effect of the trifluoromethyl group, the canonical structure **W** may contribute to some extent to the actual bonding state of the *N*-trifluoromethylsulfonyl derivatives.



$$Ar_3\overset{+}{M}{-}\overset{\delta-}{N}{\cdots}\underset{O}{\overset{O}{S}}{\cdots}\overset{\delta-}{CF_3}$$

W

(48) Bi(V)−alkoxo intermediates were proposed by Barton et al. in the oxidation of alcohols by organobismuth(V) compounds. (a) Barton, D. H. R.; Kitchin, J. P.; Lester, D. J.; Motherwell, W. B.; Papoula, M. T. B. *Tetrahedron* **1981**, *37* (Supplement 9), 73−79. (b) Barton, D. H. R.; Lester, D. J.; Motherwell, W. B.; Papoula, M. T. B. *J. Chem. Soc., Chem. Commun.* **1980**, 246−247.