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Synthesis, Structure, and Reactions of (Acylimino)triaryl-λ^5-bismuthanes: First Comparative Study of the (Acylimino)pnictorane Series

Yoshihiro Matano,*,† Hazumi Nomura,† Hitomi Suzuki,†,‡ Motoo Shiro,§ and Haruyuki Nakano¶

Contribution from the Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan, Rigaku Corporation, Akishima-shi, Tokyo 196-8666, Japan, and Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

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Abstract: The synthesis, structure, and reactions of (acylimino)triaryl-λ^5-bismuthanes and a comparative study of the structure and reactivity of a series of (acylimino)pnictoranes are reported. Treatment of *ortho*-substituted triarylbismuth dichlorides **1** (Ar_3BiCl_2; Ar = 2-MeC_6H_4, 2-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$) with amides **2** (H_2NCOR; R = CF_3, CCl_3, 3,5-$(CF_3)_2C_6H_3$) in the presence of 2.2 equiv of KO-*t*-Bu in dichloromethane afforded (acylimino)triaryl-λ^5-bismuthanes **3** ($Ar_3Bi{=}NCOR$) in yields of 77−96%. The *ortho*-substituted aryl ligands and the electron-withdrawing N-substituents afford kinetic and thermodynamic stabilization, respectively, to the reactive Bi═N bond. The structures and properties of a series of (acylimino)pnictoranes ($Ar_3M{=}NCOR$ and $H_3M{=}NCOCF_3$; M = P, As, Sb, Bi) are compared by IR and ^{13}C and ^{15}N NMR, X-ray crystallography, and ab initio molecular orbital calculations. It was found that the contribution of the $M^+{-}N{=}C{-}O^-$ canonical form becomes more prominent and the single-bond character of the M═N bond increases progressively as the pnictogen atom becomes heavier. The Bi═N bond of (acylimino)-λ^5-bismuthanes **3** possesses a highly polarized single-bond character, probably due to the differences in orbital size and electronegativity between the bismuth and nitrogen atoms. Thermal decomposition of (aroylimino)triaryl-λ^5-bismuthane **3f** (*o*-$Tol_3Bi{=}NCOAr$; Ar = 3,5-$(CF_3)_2C_6H_3$) produces a gel in dry conditions or aniline **12** ($ArNH_2$) in slightly wet conditions with a good recovery of tris(2-methylphenyl)bismuthane (**4a**). It is likely that the aryl isocyanate **13** (ArNCO) is produced during the thermolysis via a concerted C → N migration of the Ar group with an elimination of the triarylbismuthonio group as bismuthane **4a**. (Acylimino)triaryl-λ^5-bismuthanes **3** oxidize 1,1,2,2-tetraphenylethanediol, benzenethiol, methanol, and ethanol to benzophenone, diphenyl disulfide, methyl formate, and acetaldehyde, respectively, in two different reaction pathways depending on the structure of the substrates. Compound **3d** (*o*-$Tol_3Bi{=}NCOCCl_3$) transfers the nitrenoid moiety to triphenylphosphane, triphenylarsane, and tris(2-methylphenyl)stibane to give the corresponding (acylimino)pnictoranes ($Ar_3M{=}NCOCl_3$; M = P, As, Sb) and **4a**, suggesting that **3d** is thermodynamically much less stable than their lighter pnictogen counterparts. The copper-catalyzed decomposition of **3** (*o*-$Tol_3Bi{=}NCOR$) afforded *N*-acyl-*o*-toluidines **18** (*o*-TolNHCOR) via a Bi → N migration of the tolyl group. The observed reactivities of (acylimino)triaryl-λ^5-bismuthanes **3** demonstrate a good leaving ability of the bismuthonio group.

Introduction

Iminopnictoranes ($R_3M{=}NR'$; M = P, As, Sb, Bi)[1] are a class of compounds that include a formal double bond between the pnictogen(V) and nitrogen atoms and are structurally related to ylides ($R_3M{=}CR'R''$) and oxides ($R_3M{=}O$). The chemistry of iminopnictoranes has received considerable interest because of their importance for both organic and inorganic reactions as they form bonds to nitrogen.[2] Since the discovery of the Staudinger reaction,[3] numerous applications for organic synthesis have been reported for iminophosphoranes ($R_3P{=}NR'$), which can convert the C═O group in various carbonyl compounds to the C═NR′ group (aza-Wittig reaction) by abstracting carbonyl oxygen atoms as phosphane oxides

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* Corresponding author. E-mail: matano@kuchem.kyoto-u.ac.jp.

† Kyoto University.

‡ Present address: Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662-0891, Japan.

§ Rigaku Corp.

¶ The University of Tokyo.

(1) Unless otherwise noted, the bonds between the pnictogen and nitrogen atoms in iminopnictoranes are represented as M═N, irrespective of the actual nature of the bonds.

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($R_3P{=}O$).[2a−h] Iminophosphoranes also undergo metathesis with metal−oxo complexes to afford the corresponding metal−imido complexes.[2l,4] Although the number of examples is rather limited, iminoarsoranes ($R_3As{=}NR'$)[5] and imino-λ^5-stibanes ($R_3Sb{=}NR'$)[6] have been used as alternative nitrene sources for aza-Wittig type reactions. On the other hand, little is thus far known about the synthetic utility of imino-λ^5-bismuthanes ($R_3Bi{=}NR'$).[7]

The bonding properties of the M═N bond in iminopnictoranes have been a subject of considerable interest. The M═N bond of iminopnictoranes is often described as a hybrid with the ionic canonical form $M^+{-}N^-$ but with its bonding characteristics such as bond order, polarization, and energy being strongly dependent on a relevant pnictogen atom. Until now, much attention has been paid to iminophosphoranes, in which the observed P═N bond lengths[8] are significantly shorter than an ideal value for the P−N single bond length.[9] This bond shortening has been explained by the $p\pi{-}d\pi$ orbital interaction,[10,11] the $n{-}\sigma^*$ negative hyperconjugation,[12,13] and the electrostatic interaction[12,13] between phosphorus and nitrogen atoms. Among them, the $p\pi{-}d\pi$ orbital interaction has become a classical concept for representing the P═N bond,[14] but its contribution, if any, to the shortened P═N bond is now believed to be very small.[12,13] Recent theoretical studies on a parent iminophosphorane ($H_3P{=}NH$)[12,13] have concluded that the contribution of an ionic canonical form $P^+{-}N^-$ would be more important than that of a neutral canonical form P═N with $n{-}\sigma^*$ negative hyperconjugation.[15] By contrast, very little information is available about the bonding properties of the M═N bonds in other iminopnictoranes. In 1997, Koketsu and co-workers calculated the geometry and energy of a series of imaginary iminopnictoranes, $H_3M{=}NH$ (M = P, As, Sb, Bi), by ab initio molecular orbital calculations.[12] They concluded that it is hard for $n{-}\sigma^*$ negative hyperconjugation in iminopnictoranes with heavier pnictogen atoms to take place, resulting in smaller double-bond character. To the best of our knowledge, however, no attempt has been made to compare the structure and reactivity of iminopnictoranes on the basis of *experimental* results. This may largely be due to a lack of information regarding the final family members, imino-λ^5-bismuthanes ($R_3Bi{=}NR'$). Thus, to systematically understand the nature of the M═N bond in iminopnictoranes, it is necessary to elucidate the chemistry of imino-λ^5-bismuthanes so as to complete the iminopnictoranes family list.

Since the first report by Wittig and Hellwinkel in 1964,[16] imino-λ^5-bismuthanes have been prepared by oxidative nitrene transfer from Chloramine-T or (tosylimino)phenyl-λ^3-iodinane to triarylbismuthanes[7,16] and by a Kirsanov-type reaction[17] of triarylbismuth dihalides with sulfonamides.[18,19] Therefore, all known imino-λ^5-bismuthanes are of the type $Ar_3Bi{=}NSO_2R$ and are thermally stabilized by an electron-withdrawing sulfonyl group on the imido nitrogen. This means that information of the structure and reactivity of imino-λ^5-bismuthanes is limited to thermally stabilized *N*-sulfonyl derivatives.

Recently, it has been found that bismuthonium ylides ($R_3Bi{=}CR'R''$), isoelectronic analogues of imino-λ^5-bismuthanes, exhibit a wide range of reactivity depending on the structure of the alkylidene moiety[20] and that observed modes of reaction differ considerably from those of their lighter pnictogen counterparts. For instance, monocarbonyl ylides of the type $Ph_3M{=}CHCOR$ (M = P, As, Sb) undergo Wittig-type olefination with a variety of carbonyl compounds,[2a,j,20g] whereas the corresponding bismuthonium ylides ($Ph_3Bi{=}CHCOR$) undergo Corey−Chaycovsky-type epoxidation, ring expansion, or acyl transposition, depending on the structure of the carbonyl compounds.[20g,21] These findings have led us to investigate the properties and reactivities of imino-λ^5-bismuthanes bearing an N-substituent other than the sulfonyl group. Thus, we first set out to prepare (acylimino)triaryl-λ^5-bismuthanes of the type $Ar_3Bi{=}NCOR$ because the acyl group is commonly used as an N-substituent for lighter iminopnictoranes and it was expected to reflect the intrinsic properties of the Bi═N bond.

In this paper, we first describe the synthesis of (acylimino)triaryl-λ^5-bismuthanes, then provide a structural comparison with other (acylimino)pnictoranes of lighter family members, and

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Scheme 1

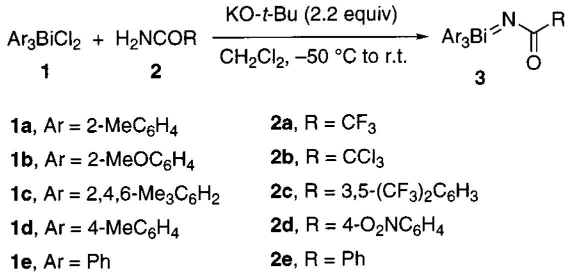


Table 1. Synthesis of (Acylimino)triaryl-λ^5-bismuthanes

entry	**1**	**2**	(acylimino)triaryl-λ^5-bismuthane (**3**)[a]	yield (%)
1	**1a**	**2a**	*o*-$Tol_3Bi{=}NCOCF_3$ (**3a**)	93
2	**1b**	**2a**	*o*-$Ans_3Bi{=}NCOCF_3$ (**3b**)	91
3	**1c**	**2a**	$Mes_3Bi{=}NCOCF_3$ (**3c**)	86
4	**1a**	**2b**	*o*-$Tol_3Bi{=}NCOCCl_3$ (**3d**)	77
5	**1b**	**2b**	*o*-$Ans_3Bi{=}NCOCCl_3$ (**3e**)	96
6	**1a**	**2c**	*o*-$Tol_3Bi{=}NCOC_6H_3$-3,5-$(CF_3)_2$ (**3f**)	95
7	**1b**	**2c**	*o*-$Ans_3Bi{=}NCOC_6H_3$-3,5-$(CF_3)_2$ (**3g**)	94
8	**1a**	**2d**	*o*-$Tol_3Bi{=}NCOC_6H_4$-4-NO_2 (**3h**)	*b, c*
9	**1a**	**2e**	*o*-$Tol_3Bi{=}NCOPh$ (**3i**)	*b, c*
10	**1d**	**2a**	*p*-$Tol_3Bi{=}NCOCF_3$ (**3j**)	*b, d*
11	**1e**	**2a**	$Ph_3Bi{=}NCOCF_3$ (**3k**)	*b, d*

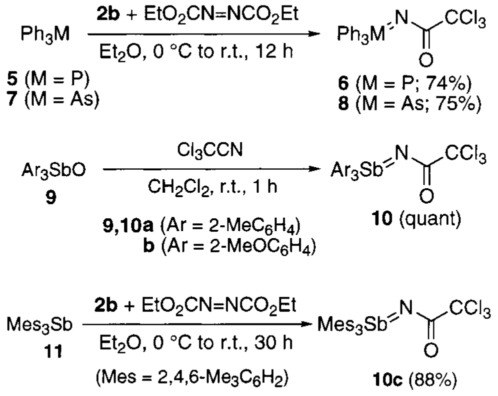
[a] *o*-Tol = 2-MeC_6H_4; *o*-Ans = 2-$MeOC_6H_4$; Mes = 2,4,6-$Me_3C_6H_2$; *p*-Tol = 4-MeC_6H_4. [b] Not isolated. [c] Decomposed thermally at room temperature. [d] Hydrolyzed in air.

finally discuss the reactivity of (acylimino)triaryl-λ^5-bismuthanes.[22] The single-bond character of the M=N bond as well as the contribution of the $M^+{-}N{=}C{-}O^-$ canonical form becomes more prominent as the pnictogen atom becomes heavier. The unique reactivities of (acylimino)triaryl-λ^5-bismuthanes observed demonstrate their potential utility in organic synthesis.

Results and Discussion

Synthesis. As depicted in Scheme 1, treatment of *ortho*-substituted triarylbismuth dichlorides **1a**−**c** with α,α,α-trihaloacetamides **2a,b** in the presence of 2.2 equiv of KO-*t*-Bu in CH_2Cl_2 gave [(trihaloacetyl)imino]triaryl-λ^5-bismuthanes **3a**−**e** as air-stable solids in 77−96% yields (Table 1, entries 1−5). A similar reaction of tris(4-methylphenyl)bismuth dichloride (**1d**) or triphenylbismuth dichloride (**1e**) with **2a** gave the expected (acylimino)-λ^5-bismuthanes **3j,k**, but the product was so sensitive to moisture that it decomposed during attempted recrystallization under air to give an insoluble substance and **2a** (entries 10,11). The insoluble solid obtained from **1d** showed a sharp IR absorption at 625 cm^{-1}, which may be assigned as an asymmetric Bi−O−Bi stretching mode.[23] Its FABMS spectrum in 3-nitrobenzyl alcohol matrix showed a strong peak at *m*/*z* 634 in accord with a $[(4\text{-}MeC_6H_4)_3BiOCH_2C_6H_4\text{-}3\text{-}NO_2]^+$ ion. When treated with aqueous HCl, the substance was converted to dichloride **1d**. These results indicate that the insoluble solid is a polymeric triarylbismuthane oxide, $(Ar_3Bi{=}O)_n$,[23,24] probably derived from hydrolysis of the initially formed imino-λ^5-bismuthane.[25] The *ortho*-substituents in **3a**−**e**, therefore, afford significant kinetic stabilization[26] to the moisture-sensitive Bi=N bond in imino-λ^5-bismuthanes.[27]

Scheme 2



Dichlorides **1a,b** also reacted with 3,5-bis(trifluoromethyl)benzamide (**2c**) to yield the corresponding (aroylimino)-λ^5-bismuthanes **3f,g** as moderately stable solids (entries 6,7). The reaction between **1a** and *p*-nitrobenzamide (**2d**) gave the desired imino-λ^5-bismuthane **3h**, but the product gradually decomposed during recrystallization (entry 8). (Benzoylimino)-λ^5-bismuthane **3i** prepared from **1a** and benzamide (**2e**) decomposed more rapidly at room temperature to afford a mixture of tris(2-methylphenyl)bismuthane (**4a**), amide **2e**, aniline, and others (entry 9). The formation of aniline suggests the probable involvement of phenyl isocyanate as an intermediate during the thermal decomposition of **3i** (vide infra). These results revealed the ability of electron-withdrawing acyl groups to enhance the thermal stability of (acylimino)triaryl-λ^5-bismuthanes.

Compounds **3a**−**g** are colorless or pale yellow solids and soluble in CH_2Cl_2, $CHCl_3$, and benzene but are insoluble in hexane. Compounds **3a**−**e** can be stored in the solid state for over 1 month in a refrigerator, whereas **3f,g** decompose over the course of 1 day, even in a refrigerator (at 4 °C).

To compare the structure of **3** with those of lighter pnictogen counterparts, an iminophosphorane **6**,[28] an iminoarsorane **8**,[29] and imino-λ^5-stibanes **10a**−**c** were prepared by the oxidative condensation[30] of triphenylphosphane (**5**), triphenylarsane (**7**), and tris(2,4,6-trimethylphenyl)stibane (**11**) with **2b** in the presence of diethyl azodicarboxylate and by treating triarylstibane oxides **9a,b** with trichloroacetonitrile in CH_2Cl_2 (Scheme 2). Despite the presence of *ortho*-substituent groups, compounds **10a,b** are extremely moisture sensitive and readily decompose to give the corresponding oxides **9a,b** under ambient conditions. Thus, **10a,b** were characterized by ^1H NMR, FABMS, and IR analyses as well as by chemical transformations to other Sb(V)

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[26] Kinetic stabilization afforded by *ortho*-substituted aryl groups has been applied for stabilizing 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.; Matsumoto, T.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1665−1684.

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Table 2. IR and ^{13}C and ^{15}N Spectral Data for (Acylimino)triarylpnictoranes and **2b**

compd	$\nu_{C=O}{}^a$ ($\Delta\nu_{C=O}{}^b$)	^{13}C^c	^{15}N^d
o-Ans$_3$Bi=NCOCCl$_3$ (**3e**)	1561 (137)	172.2	225.3
Mes$_3$Sb=NCOCCl$_3$ (**10c**)	1583 (115)	171.5	184.3
Ph$_3$As=NCOCCl$_3$ (**8**)	1611 (87)	173.0	149.3
Ph$_3$P=NCOCCl$_3$ (**6**)	1638 (60)	170.1	117.6 ($\lvert J_{PN}\rvert$ = 41.35 Hz)
H$_2$NCOCCl$_3$ (**2b**)	1698	163.8	95.3

^{a} IR absorption of the C=O group on KBr pellets, reported in cm^{-1}. ^{b} Difference in frequency from $\nu_{C=O}$ of the parent amide **2b** (1698 cm^{-1}). ^{c} ^{13}C Chemical shifts of the carbonyl carbon atom, referenced to CDCl$_3$ (77 ppm). ^{d} ^{15}N Chemical shifts of the nitrogen atom of the ^{15}N-labeled derivatives. Recorded at 50.55 MHz in CDCl$_3$ (ca. 0.01 M), referenced to NH$_3$(l).

compounds.[31] Compound **10c** is much more stable toward atmospheric moisture than **10a,b**.

Structural Comparison of (Acylimino)pnictoranes. The structures of a series of (acylimino)pnictoranes were studied by means of IR and ^{13}C and ^{15}N NMR, as well as by X-ray analysis and ab initio molecular orbital calculations.

(a) IR and ^{13}C and ^{15}N NMR Spectra. The C=O stretching frequencies ($\nu_{C=O}$) and ^{13}C$_{C=O}$ and ^{15}N chemical shifts of [(trichloroacetyl)imino]triarylpnictoranes **3e**, **6**, **8**, and **10c** are summarized in Table 2. The C=O absorptions of these iminopnictoranes were observed at lower frequencies compared to that of amide **2b**. The differences in frequency ($\Delta\nu_{C=O}$) from **2b** increase progressively from iminophosphorane **6**, iminoarsorane **8**, imino-λ^5-stibane **10c**, to imino-λ^5-bismuthane **3e**, indicating that the double-bond character of the C=O bond decreases as the pnictogen atom becomes heavier. There are only slight differences among the ^{13}C$_{C=O}$ chemical shifts of **3e**, **6**, **8**, and **10c**. By contrast, the ^{15}N peaks shift significantly downfield as the pnictogen atom becomes heavier: the ^{15}N peaks of **2b**-^{15}*N*, **6**-^{15}*N*, **8**-^{15}*N*, **10c**-^{15}*N*, and **3e**-^{15}*N* were observed at δ 95.3, 117.6, 149.3, 184.3, and 225.3, respectively, relative to NH$_3$(l).[32] The ^{15}N chemical shift and coupling constant (J_{PN}) of **6** are close to those previously reported for Ph$_3$P=NCOAr[33] (Ar = *p*-substituted phenyl). The nitrogen nucleus is known to be deshielded when the bonding electrons are in the orbitals of high s character and/or when multiple bonding to nitrogen is present or enhanced.[34] Thus, the low-field appearance of the ^{15}N peak of **3e**-^{15}*N* suggests that the Bi$^+$−N=C−O$^-$ character makes a greater contribution than that of Bi$^+$−N$^-$−C=O.

(b) X-ray Crystallographic Analyses. The crystal structures of [(trichloroacetyl)imino]triarylpnictoranes **3e**, **6**, **8**, and **10c** were compared by X-ray crystallography. ORTEP diagrams are provided in Figures 1−4, crystallographic data are summarized in Table 3, and selected bond lengths and angles are listed in Table 4. These iminopnictoranes (Ar$_3$M=NCOCCl$_3$) exist in a monomeric form, and there is no intermolecular interaction between the pnictogen center and the neighboring molecules. The pnictogen atom possesses a distorted tetrahedral geometry with average C−M−C and N−M−C bond angles of 107.9−110.7 and 108.0−110.9°, respectively.

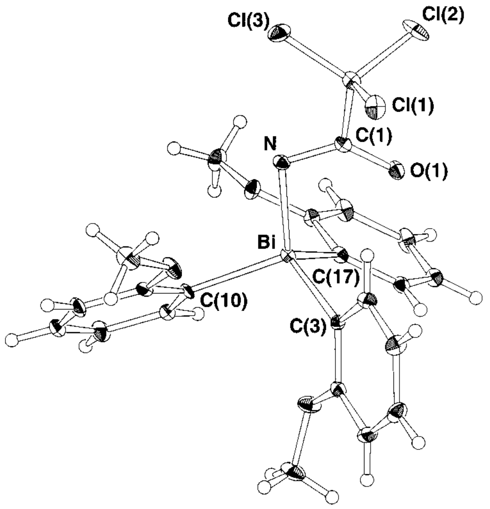

Figure 1. ORTEP diagram for **3e** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Bi−C(3), 2.198(4); Bi−C(10), 2.204(4); Bi−C(17), 2.196(4); C(3)−Bi−C(10), 109.4(1); C(3)−Bi−C(17), 109.3(1); C(10)−Bi−C(17), 106.2(1); N−Bi−C(3), 106.9(1); N−Bi−C(10), 108.8(1); N−Bi−C(17), 116.1(1).

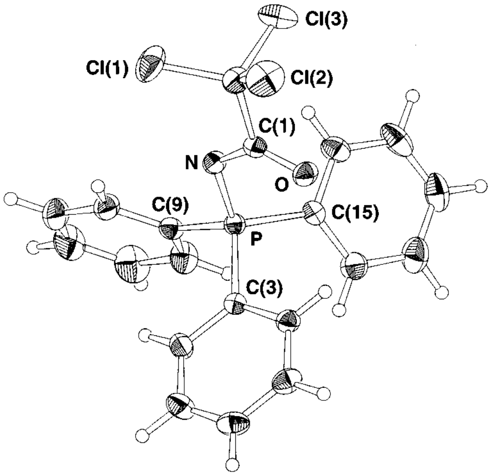

Figure 2. ORTEP diagram for **6** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): P−C(3), 1.800(2); P−C(9), 1.796(2); P−C(15), 1.799(2); C(3)−P−C(9), 106.9(1); C(3)−P−C(15), 108.1(1); C(9)−P−C(15), 108.8(1); N−P−C(3), 115.1(1); N−P−C(9), 105.2(1); N−P−C(15), 112.3(1).

The observed M=N bond lengths primarily reflect the orbital size of the respective pnictogen atom.[35] Therefore, the multiplicity of the M=N bond in iminopnictoranes is discussed by comparison with known M−N bond lengths of the corresponding tricoordinate pnictogen(III) amides. The Bi=N bond length of 2.125(3) Å in **3e** is comparable to that [2.13(1) Å] of (*p*-Tol)$_2$ArBi=NSO$_2$CF$_3$ [Ar = 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl][19] and is slightly shorter than known Bi−N bond lengths (2.165−2.20 Å) observed for bismuth(III) amides.[36] If we take into account a slight shortening (∼0.04 Å) of the Bi−X bond, which arises with the quaternization of the bismuth atom, the Bi=N bond of **3e** is considered to possess an appreciable single-bond character.[37] The P=N bond length of 1.620(2) Å in **6** is comparable to that [1.626(3) Å] of Ph$_3$P=NCOPh[38] and is much shorter than typical P−N bond lengths (1.68−1.75 Å) of phosphorus(III) amides[39] and an ideal P−N single bond

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[31] On treatment with an acid (HX), compounds **10a,b** were converted quantitatively to Ar$_3$SbX$_2$ (X = Cl or OAc).

[32] The chemical shift relative to NH$_3$(l) was calculated using the equation δ(NH$_3$) = δ(MeNO$_2$) + 380.23: Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Wiley: New York, 1979; Chapter 3.

[33] δ_N = 119.82−124.91, relative to NH$_3$(l); J_{PN} = 43.8−44.7 Hz: Chou, W.-N.; Pomerantz, M.; Witzcak, M. K. *J. Org. Chem.* **1990**, *55*, 716−721.

[34] See discussion in pp 7−9 and pp 58−67 in ref 32.

[35] 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. van der Waals radii: O, 1.4 Å; P, 1.9 Å; As, 2.0 Å; Sb, 2.2 Å; Bi, 2.4 Å.

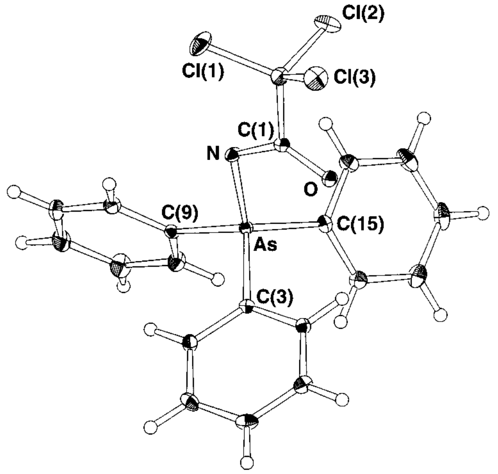

Figure 3. ORTEP diagram for **8** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): As−C(3), 1.913(2); As−C(9), 1.910(2); As−C(15), 1.909(2); C(3)−As−C(9), 107.18(7); C(3)−As−C(15), 108.01(8); C(9)−As−C(15), 110.18(8); N−As−C(3), 116.27(7); N−As−C(9), 103.16(7); N−As−C(15), 111.78(7).

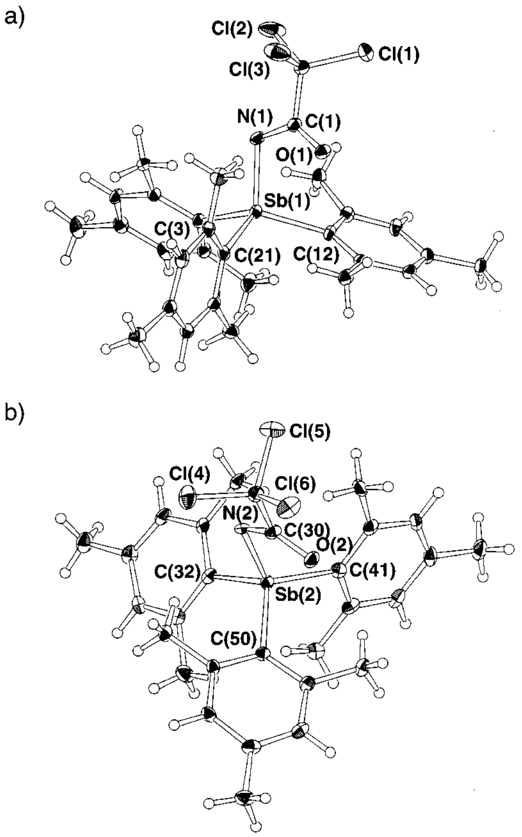

Figure 4. ORTEP diagrams for **10c** (30% probability ellipsoids). (a) Selected bond lengths (Å) and angles (deg): Sb(1)−C(3), 2.148(6); Sb(1)−C(12), 2.145(6); Sb(1)−C(21), 2.134(6); C(3)−Sb(1)−C(12), 115.2(2); C(3)−Sb(1)−C(21), 100.9(2); C(12)−Sb(1)−C(21), 115.9(2); N(1)−Sb(1)−C(3), 99.4(2); N(1)−Sb(1)−C(12), 105.0(2); N(1)−Sb(1)−C(21), 119.5(2). (b) Selected bond lengths (Å) and angles (deg): Sb(2)−C(32), 2.151(6); Sb(2)−C(41), 2.151(6); Sb(2)−C(50), 2.145(6); C(32)−Sb(2)−C(41), 102.3(2); C(32)−Sb(2)−C(50), 113.3(2); C(41)−Sb(2)−C(50), 115.0(2); N(2)−Sb(2)−C(32), 100.9(2); N(2)−Sb(2)−C(41), 119.6(2); N(2)−Sb(2)−C(50), 105.0(2).

length (1.80 Å) observed for potassium phosphoramidate.[9] On the basis of a previous discussion of the P−N bonding properties of phosphorus(III) amides,[39] it has been suggested that the back-bonding from the nitrogen atom to the phosphorus atom causes a P−N bond-shortening of 0.04−0.12 Å.[40] Therefore, the double-bond character of the P=N bond in **6** is much more significant than that of the Bi=N bond in **3e**. As is the case with aminophosphonium salts,[41] the positive charge on the phosphorus atom of **6** would be partially neutralized through the lone pair of electrons on the nitrogen. The As=N bond length of 1.783(2) Å in **8** is slightly longer than that [1.755(3) Å] of $Ph_3As{=}NSO_2Tol$[42] but shorter than typical As−N bond lengths (1.84−1.88 Å) of arsenic(III) amides.[39g,j,43] Imino-λ^5-stibane **10c** consists of two isolated molecules with similar geometry around the antimony center. The Sb=N bond lengths of 1.989(5)−1.992(5) Å in **10c** are slightly longer than those [1.958(4)−1.962(2) Å] of the *N*-sulfonyl derivatives, $Ar_3Sb{=}NSO_2CF_3$ (Ar = *o*-Tol, *o*-Ans)[44] but somewhat shorter than known Sb−N bond lengths (2.04−2.08 Å) of antimony(III) amides.[36e,39j,45]As expected, the bonding properties of the As=N and Sb=N bonds are between those of the Bi=N and P=N bonds.

Quite recently, Burford, Cameron, and co-workers compared the structures of the first homologous series of bis(amido)-diazadipnictetidines, $[DipNMN(H)Dip]_2$ (M = P, As, Sb, Bi; Dip = 2,6-diisopropylphenyl), with averaged M−N bond lengths

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[36] (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) Wirringra, U.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **1994**, *33*, 4607−4608. (d) Edwards, A. J.; Beswick, M. A.; Galsworthy, J. R.; Paver, M. A.; Raithby, P. R.; Rennie, M.-A.; Russell, C. A.; Verhorevoort, K. L.; Wright, D. S. *Inorg. Chim. Acta* **1996**, *248*, 9−14. (e) Burford, N.; Macdonald, C. L. B.; Robertson, K. N.; Cameron, T. S. *Inorg. Chem.* **1996**, *35*, 4013−4016. The values in parentheses are the averaged Bi−N bond lengths.

[37] The *ortho*-methoxy groups in **3e** were found to lean ca. 5° toward the bismuth center. This attractive interaction may cause a slight elongation of the Bi=N bond.

[38] Bar, I.; Bernstein, J. *Acta Crystallogr.* **1980**, *B36*, 1962−1964.

[39] Typical bond lengths are 1.68−1.69 Å for $P{-}N_{sp^2}$ and 1.74−1.75 Å for $P{-}N_{sp^3}$ bonds. For example, see: (a) Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1975**, 259−262. (b) Cobbledick, R. E.; Einstein, F. W. B. *Acta Crystallogr.* **1975**, *B31*, 2731−2733. (c) Rømming, C.; Songstad, J. *Acta Chem. Scand.* **1978**, *A32*, 689−699. (d) Thompson, M. L.; Haltiwanger, R. C.; Norman, A. D. *J. Chem. Soc., Chem. Commun.* **1979**, 647−648. (e) Scherer, O. J.; Andres, K.; Krüger, C.; Tsay, Y.-H.; Wolmerhäuser, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 571−572. (f) Thompson, M. L.; Tarassoli, A.; Haltiwanger, R. C.; Norman, A. D. *J. Am. Chem. Soc.* **1981**, *103*, 6770−6772. (g) Atwood, J. L.; Cowley, A. H.; Hunter, W. E.; Mehrotra, S. K. *Inorg. Chem.* **1982**, *21*, 1354−1356. (h) Chen, H.-J.; Haltiwanger, R. C.; Hill, T. G.; Thompson, M. L.; Coons, D. E.; Norman, A. D. *Inorg. Chem.* **1985**, *24*, 4725−4730. (i) Nieger, M.; Niecke, E.; Gärtner-Winkhaus, C. *Acta Crystallogr.* **1990**, *C46*, 2470−2472. (j) 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.

[40] It must be noted that the quaternization of phosphorus atom in the P(III) to P(V) conversion would cause the additional P−N bond shortening.

[41] (a) Cowley, A. H.; Kemp, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A. *J. Am. Chem. Soc.* **1983**, *105*, 7444−7445. (b) Chiche, L.; Christol, H. *J. Chem. Soc., Perkin Trans. 2* **1984**, 753−755. (c) Schomburg, D.; Bettermann, G.; Ernst, L.; Schmutzler, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 975−976. (d) Roesky, H. W.; Mainz, B.; Noltemeyer, M.; Sheldrick, G. M. *Z. Naturforsch. B* **1988**, *43*, 941−944.

[42] Mai, H.-J.; Weller, F.; Dehnicke, K.; Maichle-Mössmer, C.; Strähle, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 851−855.

[43] Typical bond lengths are 1.84−1.85 Å for $As{-}N_{sp^2}$ and 1.87−1.88 Å for $As{-}N_{sp^3}$ bonds. For example, see: (a) Weiss, J.; Eisenhuth, W. *Z. Anorg. Allg. Chem.* **1967**, *350*, 9−17. (b) Rømming, C.; Songstad, J. *Acta Chem. Scand.* **1980**, *A34*, 365−373.

[44] Matano, Y.; Nomura, H.; Suzuki, H. *Inorg. Chem.* **2000**, *39*, 1340−1341.

[45] (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.; Rennie, M.-A.; Raithby, P. R.; Russell, C. A.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1994**, 2963−2966. The values in parentheses are the averaged Sb−N bond lengths.

Table 3. Crystallographic Data for (Acylimino)triarylpnictoranes

	6	**8**	**10c**	**3e**
empirical formula	$C_{20}H_{15}Cl_3NOP$	$C_{20}H_{15}AsCl_3NO$	$C_{58}H_{66}Cl_6N_2O_2Sb_2$	$C_{23}H_{21}BiCl_3NO_4$
fw	422.68	466.63	1279.39	690.76
cryst dimens (mm)	0.34 × 0.20 × 0.18	0.20 × 0.20 × 0.20	0.10 × 0.10 × 0.10	0.25 × 0.08 × 0.05
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
a (Å)	9.469(3)	9.4395(4)	16.6407(7)	8.776(2)
b (Å)	19.063(4)	19.098(1)	13.1648(6)	17.577(4)
c (Å)	10.976(4)	10.8085(6)	26.062(1)	15.875(4)
β (deg)	94.90(3)	95.312(2)	92.144(2)	96.10(2)
V (Å^3)	1973(1)	1940.1(2)	5705.5(4)	2434.9(10)
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Z	4	4	4	4
D_{calcd} (g cm^{-3})	1.422	1.597	1.489	1.884
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 70)
μ(Mo Kα) (cm^{-1})	5.54	21.74	12.69	141.85
temp (°C)	25	−150	−150	−130
$2\theta_{max}$ (deg)	55.0	54.9	55.0	55.2
no. of reflcns measd				
total	4800	18 746	52 765	4787
unique	4735	4420	13 003	4786
no. of observns	4735	4420	13 003	4342
no. of reflcns	$I > 0.00\sigma(I)$	all, $2\theta < 54.86°$	all, $2\theta < 54.97°$	$I > 2.00\sigma(I)$
no. of variables	235	235	631	290
R1, R_w	0.043, 0.132	0.025, 0.054	0.049, 0.137	0.025, 0.034
goodness of fit	1.11	1.00	0.95	1.11

Table 4. Selected Bond Lengths and Bond Angles of $Ar_3M{=}NCOCCl_3$

compd	M−N	N−C	C−O	M−C[a]	M···O	C−M−C[a]	N−M−C[a]	M−N−C	N−C−O
6 (M = P)	1.620(2)	1.333(3)	1.220(3)	1.798	2.912(2)	107.9	110.9	117.7(2)	129.9(2)
8 (M = As)	1.783(2)	1.323(2)	1.234(2)	1.911	2.837(1)	108.5	110.4	110.0(1)	130.7(2)
10c (M = Sb)	1.989(5)	1.329(8)	1.265(7)	2.142	2.901(4)	110.7	108.0	108.2(4)	129.4(6)
	1.992(5)	1.330(8)	1.244(7)	2.149	2.872(4)	110.2	108.5	106.3(4)	130.8(6)
3e (M = Bi)	2.125(3)	1.314(5)	1.255(5)	2.199	2.877(3)	108.3	110.6	104.0(3)	130.9(4)

[a] Average values. See captions under Figures 1−4.

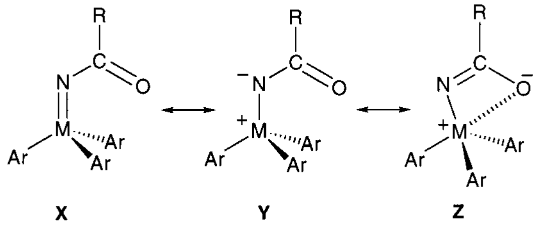
Table 5. M═N/M−N Bond-Length Ratios

M	M═N[a]	M−N[b]	M═N/M−N
P	1.620	1.709	0.948
As	1.783	1.867	0.955
Sb	1.991[c]	2.043	0.975
Bi	2.125	2.165	0.982

[a] The M═N bond lengths of **3e**, **6**, **8**, and **10c**. [b] The average M−N bond lengths of $[DipNMN(H)Dip]_2$, taken from refs 36c and 39j. [c] Average value.

of 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.[36c,39j] These values are within the range of typical M−N bond lengths of the respective pnictogen(III) amides (vide supra). To evaluate the multiplicity of the M═N bonds of a homologous series of (acylimino)triarylpnictoranes, the ratios of the M═N bond lengths of **6**, **8**, **11c**, and **3e** vs the averaged M−N bond lengths of $[DipNMN(H)Dip]_2$ were calculated. As shown in Table 5, the M═N/M−N bond-length ratios increase in the order P (0.948) < As (0.955) < Sb (0.975) < Bi (0.982).[46] This clearly suggests that the single-bond character of the M═N bond increases progressively as the pnictogen atom becomes heavier and is the most significant for **3e** of all the (acylimino)triarylpnictoranes examined. The difference in multiplicity of the M═N bonds may reasonably be attributed to the differences in orbital size and electronegativity among pnictogen atoms. Thus, the larger orbital radii and the smaller electronegativities of the heavier pnictogen atoms result in weaker conjugative interactions with nitrogen atoms.

Scheme 3



A structural feature around the *N*-acyl group is also noteworthy. The observed N−C bond lengths [1.314(5)−1.333(3) Å] are shorter than the typical N−C single bond length (1.38 Å), whereas the observed C═O bond lengths [1.220(3)−1.265(7) Å] are longer than the typical C═O double bond length (1.21 Å).[47] The M, N, C, and O atoms are almost on the same plane for all iminopnictoranes, with torsion angles of −4.8(3) to 4.2(5)°, indicating an extensive delocalization of the anionic charge of the nitrogen through the carbonyl group. It is likely that the canonical structures **Y** and **Z** contribute significantly to the actual bonding of (acylimino)pnictoranes (Scheme 3). Among them, **3e** bears the shortest N−C bond [1.314(5) Å] and the longest C═O bond [1.255(5) Å].[48] These data is indicative of the largest double-bond character of the N−C bond and the largest single-bond character of the C═O bond of **3e**. Thus, the contribution of the canonical structure **Z** would be

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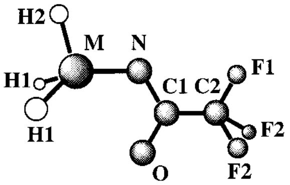
[46] One of the reviewers gave us valuable comments regarding the evaluation of the multiplicity of the M═N bonds. If we use an "ideal" P−N single bond length of 1.800 Å (ref 9), the P═N/P−N bond-length ratio is calculated to be 0.900.

[47] March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; Table 1.5, p 21. The values for the sp^2 carbon, nitrogen, and oxygen atoms are used.

[48] The difference in the C═O bond of the two molecules of **10c** might be caused by the different configuration of the aryl groups and the trichloroacetyl group.

Table 6. Calculated Parameters of $H_3M{=}NCOCF_3$ (M = P, As, Sb, Bi)[a]



M	M=N[b]	M=N/ M−N[c]	BO[d]	N−C1	C1=O	M−N−C1	M···O	M[e]	N[e]	O[e]	M−H1	M−H2
P	1.656 (1.601)	0.929	1.289	1.363	1.246	105.6	2.634	1.136	−1.000	−0.641	1.418	1.410
As	1.781 (1.715)	0.937	1.170	1.357	1.253	102.5	2.606	1.296	−0.979	−0.665	1.506	1.502
Sb	2.014 (1.899)	0.962	1.036	1.338	1.279	94.7	2.433	1.672	−0.929	−0.728	1.685	1.697
Bi	2.081 (1.977)	0.959	0.943	1.342	1.271	96.3	2.566	1.545	−0.876	−0.714	1.738	1.750

[a] At MP2 level. All bond lengths in angstroms and bond angles in degrees. [b] Values in parentheses are those of $H_3M{=}NH$, taken from ref 12. [c] Bond-length ratio of M=N in $H_3M{=}NCOCF_3$ vs M−N in $H_2M{-}NHCOCF_3$ (1.783 Å for M = P, 1.900 Å for M = As, 2.093 Å for M = Sb, 2.170 Å for M = Bi), calculated at the same level. [d] Mayer−Mulliken natural bond order (NBO) of M=N at the MP2 level. [e] Natural charges on M, N, and O atoms.

most significant for (acylimino)-λ^5-bismuthane **3e**, as inferred from the IR observations. All intramolecular M···O distances are within the sum of their van der Waals radii,[35] and the M−N−C bond angle decreases in the order P−N−C [117.7(2)°] > As−N−C [110.0(1)°] > Sb−N−C [106.3(4)−108.2(4)°] > Bi−N−C [104.0(3)°]. It is apparent that the electrostatic interaction between the positively charged pnictogen atom ($M^{\delta+}$) and the negatively charged carbonyl oxygen atom ($O^{\delta-}$) becomes increasingly important as the pnictogen becomes heavier.

(c) Ab initio Molecular Orbital Calculations. To obtain a greater insight into the nature of the M=N bond of (acylimino)pnictoranes, ab initio molecular orbital calculations were carried out for a series of [(trifluoroacetyl)imino]pnictoranes, $H_3M{=}NCOCF_3$ (M = P, As, Sb, Bi), by replacing all aryl groups on pnictogen atoms with hydrogen. These imaginary compounds are considered to be suitable models for discussing the structures and properties of some (acylimino)triarylpnictoranes that have been well characterized by X-ray crystallography. The calculations were performed at a level of second-order Møller−Plesset perturbation theory with a relativistic effective core potential and a valence double-ζ plus a polarization-quality basis set, which is the same as that used for the calculation of the geometries of $H_3M{=}NH$ (M = P, As, Sb, Bi)[12] and $H_3M{=}CH_2$.[49] Selected geometrical data for $H_3M{=}NCOCF_3$ are listed in Table 6.[50] In all compounds examined, the pnictogen center possesses a distorted tetrahedral geometry, and the M, N, C, and O atoms are on the same plane.

The calculated M=N bond lengths of $H_3M{=}NCOCF_3$ are slightly longer than those of the parent $H_3M{=}NH$,[12] suggesting that replacement of the *N*-hydrogen atom by a trifluoroacetyl group increases the single-bond character of the M=N bond. This phenomenon is probably due to the high electron-withdrawing ability of the trifluoroacetyl group. To compare the multiplicity of the M=N bond, the M−N bond lengths of $H_2M{-}NHCOCF_3$ (M = P, As, Sb, Bi) were also calculated. As shown in Table 6, the bond-length ratio of Bi=N/Bi−N (0.959) is close to that of Sb=N/Sb−N (0.962) and much larger than those of P=N/P−N (0.929) and As=N/As−N (0.937). Additionally, the calculated M=N bond order decreases progressively in the order P=N (1.289) > As=N (1.170) > Sb=N (1.036) > Bi=N (0.943). These results indicate that the single-bond character of the M=N bond becomes more prominent as the pnictogen atom becomes heavier.

The large negative charge on the oxygen atom is indicative of the effective delocalization of the negative charge from nitrogen through the adjacent carbonyl group. The calculated natural charges on M, N, and O atoms, the N−C bond lengths, and the C=O bond lengths indicate that the contribution of the $M^+{-}N{=}C{-}O^-$ canonical structure becomes more significant in the order P < As < Bi ≤ Sb.[51] The inverted order of $H_3Sb{=}NCOCF_3$ and $H_3Bi{=}NCOCF_3$ is not accordance with the experimentally observed order P < As < Sb < Bi. This discrepancy may arise from the absence of a crystal environment and/or relativistic effects not included in the effective core potential.[52]

It should be noted that the heavier iminopnictoranes (M = Sb, Bi) possess much shorter M···O distances and smaller M−N−C1 bond angles compared to the lighter iminopnictoranes (M = P, As). Also noteworthy is that M−H2 bond lengths are longer than the M−H1 bond lengths in the heavier iminopnictoranes. These data suggest that the intramolecular coordination from the oxygen atom to the pnictogen center becomes important in $H_3Sb{=}NCOCF_3$ and $H_3Bi{=}NCOCF_3$.[53]

Reaction of (Acylimino)triaryl-λ^5-bismuthanes. The chemical behavior of (acylimino)triaryl-λ^5-bismuthanes **3** was investigated and compared with those of lighter (acylimino)triarylpnictoranes.

(a) Thermal Decomposition. The thermal stability of imino-λ^5-bismuthanes is strongly dependent on the N-substituents. When heated in absolutely dry and deaerated benzene-d_6 at 60 °C for 1 week in a sealed NMR tube, **3a** was recovered mostly unchanged.[54] By contrast, **3f** decomposed within 15 h under the same conditions to give bismuthane **4a** quantitatively (eq 1). The ^1H NMR spectrum of the reaction mixture showed broad, ill-resolved peak patterns, excepting those peaks attributable to **4a**. Exposure to air produced a gel that was insoluble in organic solvents such as CH_2Cl_2, $CHCl_3$, benzene, and DMSO.

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(49) Naito, T.; Nagase, S.; Yamataka, H. *J. Am. Chem. Soc.* **1994**, *116*, 10080−10088.

(50) All geometrical parameters are summarized in Supporting Information.

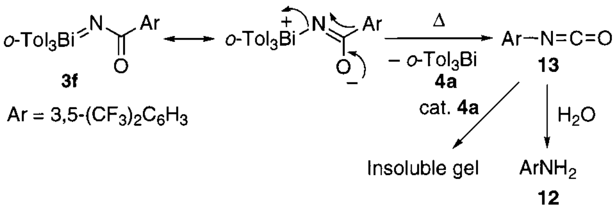
(51) A similar trend, P < As < Bi ≤ Sb, was observed for another basis set (the Stevens−Basch−Krauss−Jasien−Cundari relativistic ECP plus valence double-ζ polarization basis set) and/or calculation method (density functional theory with the B3LYP hybrid functional).

(52) It is known that the orbital size and energy of pnictogen atoms do not vary in a linear manner due to the relativistic effect and the d-orbital contraction. See: Nagase, S. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; Wiley: Chichester, U.K., 1994; Chapter 1, pp 1−24.

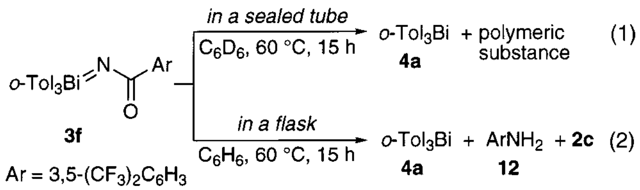
(53) The n orbital of the oxygen atom may interact with the σ^* orbitals of the Sb−H2 and Bi−H2 bonds to lengthen these bonds and shorten the Sb···O and Bi···O distances.

(54) In a previous communication (ref 22), we reported that **3a** decomposed by heating for 48 h at 60 °C in benzene to give bismuthane **4a** in a 61% yield together with **2a**. Later, it was found that the decomposition was caused by adventitious moisture present in the reaction system.

Scheme 4



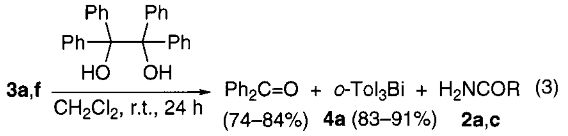
Interestingly, when the thermolysis of **3f** was carried out in benzene in a flask, 3,5-bis(trifluoromethyl)aniline (**12**) and amide **2c** were obtained with a good recovery of **4a** (eq 2). The formation of **12** strongly suggested the intermediary formation of 3,5-bis(trifluoromethyl)phenyl isocyanate (**13**) during thermolysis.

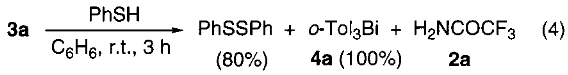


There are two possible pathways that may lead to **13** from **3f**, a concerted pathway via 1,2-migration and a stepwise pathway via free nitrene. When the thermolysis of **3f** was carried out in the presence of an excess (5−20 equiv) of a trapping agent or a hydrogen source such as cyclohexene, styrene, cyclohexane, or 9,10-dihydroanthracene, **12** and **2c** were obtained in a combined yield of 56−77%. Although the ratio **12**/**2c** varied slightly, the products trapped by the additive could not be detected by ^{1}H NMR in all cases examined. Thus, it is unlikely that a free nitrene species is involved as the primary intermediate. Although no direct evidence is available for the formation of **13**,[55] it is likely that the 3,5-bis(trifluoromethyl)phenyl group of **3f** migrates from the acyl carbon to the imido nitrogen concertedly with the elimination of a triarylbismuthonio group, leading to **13** and **4a** as the initial products (Scheme 4). The isocyanate **13** would readily be hydrolyzed by moisture in the solvent or from the atmosphere to give aniline **12**.[56] Previously, Furukawa and Oae reported a similar type of thermal decomposition of *N*-acylsulfilimines ($Ph_2S{=}NCOR$), where diphenyl sulfide and isocyanates (RNCO) are eliminated at much higher temperatures (ca. 200 °C).[57] The decomposition mode of (aroylimino)triaryl-λ^5-bismuthane **3f** contrasts to that of (benzoylimino)triphenylphosphorane ($Ph_3P{=}NCOPh$) and (benzoylimino)triphenylarsorane ($Ph_3As{=}NCOPh$), which thermally decompose to afford benzonitrile and the corresponding oxides ($Ph_3P{=}O$ and $Ph_3As{=}O$), presumably via enolate intermediates.[5a,58]

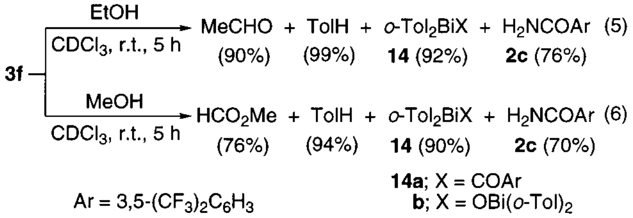
There exists a great difference in thermal stability between (sulfonylimino)-λ^5-bismuthane and (acylimino)-λ^5-bismuthane; (tosylimino)tris(2-methoxyphenyl)-λ^5-bismuthane [$(2\text{-}MeOC_6H_4)_3Bi{=}NSO_2C_6H_4\text{-}4\text{-}Me$][59] remained intact even after heating for 1 week at 60 °C in benzene-d_6.

(b) Oxidation. (Acylimino)triaryl-λ^5-bismuthanes **3** possess a mild oxidizing ability (eqs 3−6). 1,1,2,2-Tetraphenylethanediol was cleaved oxidatively by 1 equiv of **3a** or **3f** at room temperature to give benzophenone in 74−84% yields (eq 3). Benzenethiol was also oxidized by 0.5 equiv of **3a** to give diphenyl disulfide in 80% yield (eq 4). In these reactions, bismuthane **4a** was recovered in good yields.





Ethanol and methanol were oxidized by **3f** at room temperature. Treatment of **3f** with 5 equiv of ethanol in $CDCl_3$ for 5 h afforded acetaldehyde in 90% NMR yield (based on **3f**) together with toluene (99%), amide **2c** (76%), and bismuth(III) compounds **14** of the type *o*-Tol_2BiX (ca. 90% yield) (eq 5).[60] Methanol was oxidized to methyl formate (76% based on **3f**) with good recovery of toluene (94%), **2c** (70%), and **14** (ca. 90%) (eq 6). Formaldehyde, a putative initial product, could not be detected during the reaction, suggesting that the second oxidation step ($H_2CO \rightarrow HCO_2Me$) proceeded much more rapidly than the first ($CH_3OH \rightarrow H_2CO$). In this oxidation, the α-hydrogen is abstracted by the tolyl group. When the reaction was carried out using CD_3OH, deuterated toluene was formed (detected by GCMS).



Plausible reaction pathways for these oxidations are depicted in Scheme 5.[61] 1,1,2,2-Tetraphenylethanediol reacts with **3f** to form a cyclic intermediate **15**, which undergoes ligand cleavage to give benzophenone (path a). On the other hand, methanol and ethanol react with **3f** to form an acyclic intermediate **16**, which undergoes an intramolecular α-hydrogen abstraction by the adjacent tolyl group to form an aldehyde and *o*-$Tol_2BiNHCOAr$ **14a** (path b). The bismuth(III) amide **14a** is hygroscopic and slowly undergoes hydrolysis to generate amide **2c** and compound **14b**. The lighter pnictogen counterparts **6**, **8**, and **10a** did not oxidize these alcohols under the same reaction conditions, demonstrating a remarkable oxidizing ability of (acylimino)triaryl-λ^5-bismuthanes **3**.

(c) Other Reactions. Compound **3d** reacted with **5**, **7**, and tris(2-methylphenyl)stibane in benzene-d_6 at 60 °C to yield **6**, **8**, and **10a**, respectively, with a quantitative recovery of **4a** (eq 7). These results suggest that the (acylimino)triaryl-λ^5-bismuth-

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[55] This isocyanate **12** was found to polymerize in rigorously dried benzene-d_6 in the presence of a catalytic amount of **4a** to give a gel, which showed only broadened ^{1}H NMR signals.

[56] Amide **2c** may be formed by direct hydrolysis of **3f**.

[57] (a) Furukawa, N.; Nishio, T.; Fukumura, M.; Oae, S. *Chem. Lett.* **1978**, 209−210. (b) Furukawa, N.; Fukumura, M.; Nishio, T.; Oae, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3599−3605.

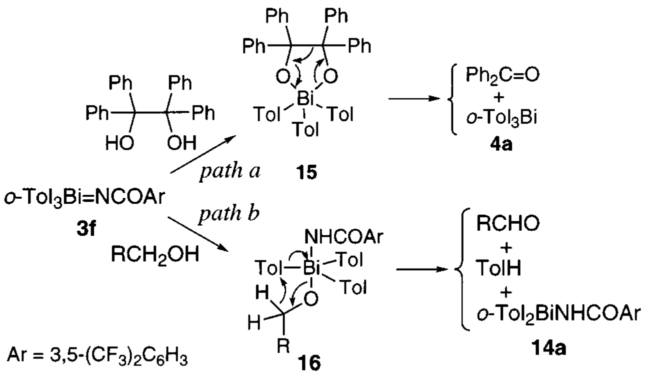
[58] Staudinger, H.; Hauser, E. *Helv. Chim. Acta* **1921**, *4*, 861−886.

[59] Matano, Y.; Nomura, H.; Suzuki, H. Manuscript in preparation.

[60] The X group in compound **14** was assigned as OBi(*o*-Tol)$_2$, $NHCOC_6H_3\text{-}3,5\text{-}(CF_3)_2$, or OR (R = Et or Me) by comparison with the authentic sample or by analysis of the ^{1}H NMR data. See the Experimental Section.

[61] Similar Bi(V)-alkoxo intermediates were proposed by Barton et al. for the oxidation of alcohols with organobismuth(V) compounds. See: (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.

Scheme 5



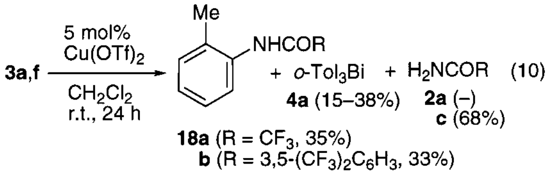
ane **3** is thermodynamically much less stable than their lighter pnictogen counterparts.

$$\mathbf{3d} \xrightarrow[\text{60 °C, 7–14 h}]{\mathbf{5},\ \mathbf{7},\ o\text{-}Tol_3Sb \atop C_6D_6,} \underset{\mathbf{6},\ \mathbf{8},\ \mathbf{10a}}{Ar_3M{=}NCOCCl_3} + \underset{\mathbf{4a}\ \text{(quant)}}{o\text{-}Tol_3Bi} \quad (7)$$

Treatment of **3a** with aqueous HCl in CH_2Cl_2 gave dichloride **1a** and amide **2a** quantitatively (eq 8). Similar acidolysis was observed for the reaction of **3b** with acetic acid, in which diacetate **17** was formed in 98% yield (eq 9). In the presence of a catalytic amount of copper(II) triflate, both **3a,f** underwent aryl migration to give the *N*-acyltoluidines **18a,b**, respectively, with a moderate recovery of **4a** and **2a,c** (eq 10). The yield of **18** was not affected by the presence or absence of styrene, ruling out the possible involvement of a nitrenoid species therein. Although **3a** did not react with benzaldehyde in boiling benzene, **3a,f** were found to react with dimethyl acetylenedicarboxylate (DMAD) to afford highly stabilized bismuthonium ylides.[62] This indicates that the (acylimino)triaryl-λ^5-bismuthanes **3** possess nucleophilicity and undergo the Michael addition to the acetylenic carbon of DMAD. In contrast, the lighter pnictogen counterparts **6**, **8**, and **10a** did not react with DMAD under the same reaction conditions (in $CDCl_3$, 50 °C, 15 h).

$$\mathbf{3a} \xrightarrow[CH_2Cl_2,\ \text{r.t., 1 h}]{HCl\,aq} \underset{\mathbf{1a}\ (100\%)}{o\text{-}Tol_3BiCl_2} + \underset{\mathbf{2a}}{H_2NCOCF_3} \quad (8)$$

$$\mathbf{3b} \xrightarrow[Et_2O,\ \text{r.t., 4 h}]{AcOH} \underset{\mathbf{17}\ (98\%)}{o\text{-}Ans_3Bi(OAc)_2} + \underset{\mathbf{2a}}{H_2NCOCF_3} \quad (9)$$



Summary

(Acylimino)triaryl-λ^5-bismuthanes have been prepared by the base-promoted reaction of triarylbismuth dichlorides with amides. The *ortho*-substituted aryl ligands have been found to afford kinetic stabilization to the reactive Bi=N bond. The thermal stabilities of (acylimino)triaryl-λ^5-bismuthanes are strongly dependent on the acyl group, with the less electron-withdrawing acyl groups making them more thermally labile. Experimental as well as theoretical comparisons of the structures have been made for a series of (acylimino)pnictoranes, which have revealed that the single-bond character of the M=N bond as well as the contribution of the canonical form $M^+{-}N{=}C{-}O^-$ becomes increasingly prominent as pnictogen atoms become heavier. This apparently is owing to the differences in orbital size and electronegativity among pnictogen atoms. (Acylimino)triaryl-λ^5-bismuthanes have been found to possess remarkable oxidizing and nitrene-transfer abilities and nucleophilicity, which appear to be largely attributable to the good leaving ability of the bismuthonio group as well as to the highly polarized character of the Bi=N bonding. The observed reactivities of (acylimino)triaryl-λ^5-bismuthanes differ considerably from those of the lighter pnictogen counterparts and demonstrate their potential utility in organic synthesis.

Experimental Section

General Methods. All reactions were carried out under an argon atmosphere unless otherwise noted. All melting points were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 or a JEOL FX400 spectrometer using $CDCl_3$ as the solvent unless otherwise noted. Chemical shifts are reported as the relative value vs tetramethylsilane. ^{15}N NMR spectra were measured on a JEOL α-500 spectrometer and the chemical shifts referenced to NH_3(l).[32] ^{19}F NMR spectra were measured on a JEOL JNM-LA500 spectrometer in $CDCl_3$ with neat CF_3COOH as an external standard. Unless otherwise noted, IR spectra were observed as KBr pellets on a Shimadzu FTIR-8100S spectrophotometer. EIMS, CIMS, and GCMS spectra were recorded on a Shimadzu QP5000 or QP2000 mass spectrometer. FABMS spectra were measured on a JEOL JMS-HS100 spectrometer using *m*-nitrophenyl octyl ether as a matrix. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University. Column chromatography was performed on silica gel (Wakogel C200). Dichloromethane (CH_2Cl_2) was distilled from CaH_2 before use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl before use. Hexane, pentane, and $CDCl_3$ were distilled from CaH_2 and stored over 4 Å molecular sieves. Benzenes (C_6H_6 and C_6D_6) were distilled from sodium and stored over 4 Å molecular sieves. Sealed NMR samples were prepared by using a vacuum line with rigorously dried and deaerated solvents. Triarylbismuth dichlorides **1** were prepared from the corresponding triarylbismuthanes and sulfuryl chloride according to Barton's procedure.[63] Triarylstibane oxides **9**[64] and tris(2,4,6-trimethylphenyl)stibane (**11**)[65] were prepared according to reported methods. Trichloroacetamide-^{15}N (**2b**-^{15}N) was prepared from trichloroacetyl chloride and $^{15}NH_3$, generated in situ from $^{15}NH_4Cl$ and KOH.[66] Other reagents used were of commercial grade.

Triarylbismuth Dichlorides. 1a: ^1H NMR δ 2.75 (s, 9H), 7.44−7.57 (m, 9H), 8.04 (d, 3H, J = 7.2 Hz). **1b**: ^1H NMR δ 3.87 (s, 9H), 7.19−7.27 (m, 6H), 7.45−7.54 (m, 3H), 8.13 (d, 3H, J = 8.2 Hz). **1c**: ^1H NMR δ 2.31 (s, 9H), 2.72 (s, 18H), 7.14 (s, 6H). **1d**: ^1H NMR δ 2.41 (s, 9H), 7.45 (d, 6H, J = 8.2 Hz), 8.37 (d, 6H, J = 8.2 Hz). **1e**: ^1H NMR δ 7.52−7.56 (m, 3H), 7.64−7.69 (m, 6H), 8.53 (d, 6H, J = 7.6 Hz).

Triarylstibane Oxides. 9a: mp 261−265 °C (dec); ^1H NMR δ 2.14 (s, 9H), 7.03−7.21 (m, 9H), 7.89 (d, 3H, J = 7.4 Hz). Anal. Calcd for $C_{21}H_{21}OSb$: C, 61.35; H, 5.15. Found: C, 61.48; H, 5.17. **9b**: ^1H NMR δ 3.24 (s, 9H), 6.71 (d, 3H, J = 8.1 Hz), 6.85−6.93 (m, 3H), 7.18−7.25 (m, 3H), 7.83 (dd, 3H, J = 7.3, 1.6 Hz).

Tris(2,4,6-trimethylphenyl)stibane (11): ^1H NMR δ 2.29 (s, 9H), 2.33 (s, 18H), 6.86 (s, 6H).

Synthesis of (Acylimino)triaryl-λ^5-bismuthanes 3. General Procedure. KO-*t*-Bu (998 mg, 8.89 mmol) was added to a mixture of

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[62] Matano, Y.; Nomura, H.; Suzuki, H. *J. Organomet. Chem.* **2000**, *611*, 89−99.

[63] Barton, D. H. R.; Bhatnagar, N. Y.; Finet, J.-P.; Motherwell, W. B. *Tetrahedron* **1986**, *42*, 3111−3122.

[64] Westhoff, T.; Huber, F.; Rüther, R.; Preut, H. *J. Organomet. Chem.* **1988**, *352*, 107−113.

[65] Ates, M.; Breunig, H. J.; Soltani-Neshan, A.; Tegeler, M. *Z. Naturforsch. B* **1986**, *41*, 321−326.

[66] Clusius, K.; Effenberger, E. *Helv. Chim. Acta* **1955**, *38*, 1834−1843.

triarylbismuth dichloride **1** (4.00 mmol), amide **2** (4.05 mmol), and CH_2Cl_2 (80 mL) at −50 °C. The resulting mixture was allowed to warm gradually to room temperature with stirring. The insoluble solid was filtered out through Celite and the filtrate concentrated under reduced pressure to leave an oily residue that was then crystallized from CH_2Cl_2/hexane to give (acylimino)triaryl-λ^5-bismuthane **3**. Compounds **3f,g** were isolated as solids in a high state of purity but gradually decomposed upon standing even at 4 °C. Due to thermal instability (**3h,i**) or moisture sensitivity (**3j,k**), compounds **3h−k** could not be isolated, but the formation of these compounds in a high yield was confirmed by ^{1}H NMR and FABMS.

[(Trifluoroacetyl)imino]tris(2-methylphenyl)-λ^5-bismuthane (3a): mp 108−116 °C (dec); ^{1}H NMR δ 2.46 (s, 9H), 7.32−7.49 (m, 9H), 7.68−7.73 (m, 3H); ^{19}F NMR δ 9.92; IR $\nu_{C=O}$ 1561; FABMS *m/z* 594 ([M + H]$^+$). Anal. Calcd for $C_{23}H_{21}BiF_3NO$: C, 46.55; H, 3.57; N, 2.36. Found: C, 46.59; H, 3.47; N, 2.09.

[(Trifluoroacetyl)imino]tris(2-methoxyphenyl)-λ^5-bismuthane (3b): mp 136−143 °C (dec); ^{1}H NMR δ 3.64 (s, 9H), 7.05−7.17 (m, 6H), 7.41−7.50 (m, 3H), 7.83−7.87 (m, 3H); ^{19}F NMR δ 10.14; IR $\nu_{C=O}$ 1566; FABMS *m/z* 642 ([M + H]$^+$). Anal. Calcd for $C_{23}H_{21}BiF_3NO_4$: C, 43.07; H, 3.30; N, 2.18. Found: C, 42.86; H, 3.33; N, 1.91.

[(Trifluoroacetyl)imino]tris(2,4,6-trimethylphenyl)-λ^5-bismuthane (3c): mp 133−134 °C; ^{1}H NMR δ 2.27 (s, 9H), 2.48 (s, 18H), 7.01 (s, 6H); IR $\nu_{C=O}$ 1576; FABMS *m/z* 678 ([M + H]$^+$). Anal. Calcd for $C_{29}H_{33}BiF_3NO$: C, 51.41; H, 4.91; N, 2.07. Found: C, 51.24; H, 4.90; N, 2.12.

[(Trichloroacetyl)imino]tris(2-methylphenyl)-λ^5-bismuthane (3d): mp 113−115 °C (dec); ^{1}H NMR δ 2.51 (s, 9H), 7.35 (t, 3H, *J* = 7.4 Hz), 7.41−7.49 (m, 6H); 7.67−7.69 (m, 3H); IR $\nu_{C=O}$ 1593; FABMS *m/z* 642 ([M + H]$^+$; ^{35}Cl × 3). Anal. Calcd for $C_{23}H_{21}BiCl_3NO$: C, 42.98; H, 3.29; N, 2.18. Found: C, 42.81; H, 3.21; N, 2.19.

[(Trichloroacetyl)imino]tris(2-methoxyphenyl)-λ^5-bismuthane (3e): mp 112−114 °C (dec); ^{1}H NMR δ 3.66 (s, 9H), 7.05−7.17 (m, 6H), 7.40−7.49 (m, 3H), 7.85−7.89 (m, 3H); ^{13}C NMR δ 56.1, 111.8, 123.6, 132.2, 135.4, 136.6, 160.4, 172.2 (C═O); IR $\nu_{C=O}$ 1561; FABMS *m/z* 690 ([M + H]$^+$; ^{35}Cl × 3). Anal. Calcd for $C_{23}H_{21}BiCl_3NO_4$: C, 39.99; H, 3.06; N, 2.03. Found: C, 39.81; H, 3.02; N, 2.11.

[(3,5-Bis(trifluoromethyl)benzoyl)imino]tris(2-methylphenyl)-λ^5-bismuthane (3f): ^{1}H NMR δ 2.51 (s, 9H), 7.31−7.49 (m, 9H), 7.73−7.81 (m, 3H), 7.88 (s, 1H), 8.62 (s, 2H); FABMS *m/z* 738 ([M + H]$^+$).

[(3,5-Bis(trifluoromethyl)benzoyl)imino]tris(2-methoxyphenyl)-λ^5-bismuthane (3g): ^{1}H NMR δ 3.62 (s, 9H), 7.05−7.17 (m, 6H), 7.40−7.49 (m, 3H), 7.85−7.93 (m, 4H), 8.65 (s, 2H); FABMS *m/z* 786 ([M + H]$^+$).

[(4-Nitrobenzoyl)imino]tris(2-methylphenyl)-λ^5-bismuthane (3h): ^{1}H NMR δ 2.51 (s, 9H), 7.30−7.49 (m, 9H), 7.75−7.78 (m, 3H), 8.19 (d, 2H, *J* = 9.1 Hz), 8.27 (d, 2H, *J* = 9.1 Hz); FABMS *m/z* 647 ([M + H]$^+$).

(Benzoylimino)tris(2-methylphenyl)-λ^5-bismuthane (3i): ^{1}H NMR δ 2.52 (s, 9H), 7.28−7.45 (m, 12H), 7.76−7.80 (m, 3H), 8.10−8.15 (m, 2H); FABMS *m/z* 602 ([M + H]$^+$).

[(Trifluoroacetyl)imino]tris(4-methylphenyl)-λ^5-bismuthane (3j): ^{1}H NMR δ 2.40 (s, 9H), 7.39 (d, 6H, *J* = 7.7 Hz), 7.71 (d, 6H, *J* = 7.7 Hz); FABMS *m/z* 594 ([M + H]$^+$).

[(Trifluoroacetyl)imino]triphenyl-λ^5-bismuthane (3k): ^{1}H NMR δ 7.60−7.71 (m, 9H), 7.84 (d, 6H, *J* = 7.0 Hz); FABMS *m/z* 552 ([M + H]$^+$).

Synthesis of Iminophosphorane 6 and Iminoarsorane 8. These compounds were prepared according to Bittner's method.[30] Diethyl azodicarboxylate (40% in toluene, 0.50 mL, ca. 1.1 mmol) was added to a mixture of triphenylphosphane (**5**) (262 mg, 1.00 mmol), **2b** (163 mg, 1.00 mmol), and Et_2O (10 mL) at 0 °C. The resulting mixture was stirred for 12 h, during which time the mixture was allowed to warm to room temperature. The volatiles were removed under reduced pressure to leave an oily residue that was then washed with Et_2O and THF and crystallized from CH_2Cl_2/hexane to yield iminophosphorane **6** as a colorless solid (314 mg, 74%). Iminoarsorane **8** was prepared similarly from arsane **7**.

[(Trichloroacetyl)imino]triphenylphosphorane (6): mp 184−186 °C (lit.[28] mp 183−184 °C); ^{1}H NMR δ 7.46−7.66 (m, 9H), 7.79 (dd, 6H, *J* = 12.5, 7.7 Hz); ^{13}C NMR δ 126.4 ($^1J_{PC}$ = 100.3 Hz), 128.9 ($^3J_{PC}$ = 12.4 Hz), 132.9 ($^4J_{PC}$ = 3.0 Hz), 133.1 ($^2J_{PC}$ = 10.2 Hz), 170.1 ($^2J_{PC}$ = 5.6 Hz, C═O); IR $\nu_{C=O}$ 1638; FABMS *m/z* 422 ([M + H]$^+$; ^{35}Cl × 3).

[(Trichloroacetyl)imino]triphenylarsorane (8): mp 218−219 °C (lit.[29] mp 216 °C); ^{1}H NMR δ 7.49−7.67 (m, 9H), 7.77 (d, 6H, *J* = 7.7 Hz); ^{13}C NMR δ 127.5, 129.7, 132.5, 132.6, 173.0 (C═O); IR $\nu_{C=O}$ 1611; FABMS *m/z* 466 ([M + H]$^+$; ^{35}Cl × 3).

Synthesis of Imino-λ^5-stibanes 10a−c. Method A. A mixture of triarylstibane oxides **9a,b** (0.63 mmol), trichloroacetonitrile (0.25 mL, 2.5 mmol), and CH_2Cl_2 (15 mL) was stirred at room temperature for 1 h. The resulting mixture was evaporated in vacuo to leave an oily residue that contained (acylimino)triaryl-λ^5-stibanes **10a,b** in a high state of purity. Compounds **10a,b** were extremely moisture sensitive and readily decomposed to give the corresponding oxides **9a,b** under ambient conditions.

Method B. Diethyl azodicarboxylate (40% in toluene, 1.5 mL, ca. 3.3 mmol) was added to a mixture of tris(2,4,6-trimethylphenyl)stibane (**11**) (1.438 g, 3.00 mmol), **2b** (487 mg, 3.00 mmol), and Et_2O (30 mL) at 0 °C. The resulting mixture was stirred for 30 h and worked up as described for the synthesis of **6** to give **10c** as a moderately moisture-sensitive solid.

[(Trichloroacetyl)imino]tris(2-methylphenyl)-λ^5-stibane (10a): ^{1}H NMR δ 2.46 (s, 9H), 7.28−7.38 (m, 6H), 7.44−7.52 (m, 3H), 7.57 (d, 3H, *J* = 7.7 Hz); ^{13}C NMR δ 23.6, 127.3, 128.9, 131.7, 132.3, 135.1, 144.0, 173.7 (C═O); IR (in CH_2Cl_2) $\nu_{C=O}$ 1582; FABMS *m/z* 556 ([M + H]$^+$; ^{35}Cl × 3, ^{123}Sb; ^{35}Cl × 2,^{37}Cl, ^{121}Sb).

[(Trichloroacetyl)imino]tris(2-methoxyphenyl)-λ^5-stibane (10b): ^{1}H NMR δ 3.62 (s, 9H), 6.94 (d, 3H, *J* = 8.2 Hz), 7.05−7.12 (m, 3H), 7.44−7.52 (m, 3H), 7.65 (d, 3H, *J* = 7.4 Hz); IR (in CH_2Cl_2) $\nu_{C=O}$ 1581; FABMS *m/z* 604 ([M + H]$^+$; ^{35}Cl × 3, ^{123}Sb; ^{35}Cl × 2, ^{37}Cl, ^{121}Sb).

[(Trichloroacetyl)imino]tris(2,4,6-trimethylphenyl)-λ^5-stibane (10c): ^{1}H NMR δ 2.27 (s, 9H), 2.49 (s, 18H), 6.91 (s, 6H); ^{13}C NMR δ 21.0, 23.3, 130.5, 133.0, 141.4, 143.6, 171.5 (C═O); IR $\nu_{C=O}$ 1583; FABMS *m/z* 640 ([M + H]$^+$; ^{35}Cl × 3, ^{123}Sb; ^{35}Cl × 2,^{37}Cl, ^{121}Sb).

^{15}N NMR Spectra of ^{15}N-Labeled (Acylimino)triarylpnictoranes. ^{15}N-labeled compounds **3e**-^{15}N, **6**-^{15}N, **8**-^{15}N, and **10c**-^{15}N were prepared according to the procedures described above using **2b**-^{15}N. Compound **2b**-^{15}N: ^{1}H NMR δ 5.72 (d, 1H, J_{HN} = 91.2 Hz), 6.57 (d, 1H, J_{HN} = 91.9 Hz); IR ν 3363 (m), 3312 (m), 3242 (m), 3179 (m), 1692 (s, C═O), 1613 (m), 1379 (m), 1349 (m), 1102 (m), 927 (w), 831 (s), 824 (s), 751 (m), 668 (w), 640 (m), 619 (m), 437 (w). The incorporation of the ^{15}N atom was confirmed by FABMS and ^{15}N NMR. Compound **3e**-^{15}N: FABMS *m/z* 691 ([M + H]$^+$; ^{35}Cl × 3). Compound **6**-^{15}N: FABMS *m/z* 423 ([M + H]$^+$; ^{35}Cl × 3). Compound **8**-^{15}N: FABMS *m/z* 467 ([M + H]$^+$; ^{35}Cl × 3). The ^{15}N NMR spectra of the samples (ca. 0.01 M in $CDCl_3$) were obtained at room temperature using gated, broad-band proton decoupling, a pulse angle of approximately 30°, and a postacquisition delay of 20 s. Nitromethane was used as an external standard. Chemical shifts relative to NH_3(l) were calculated using the equation $\delta(NH_3) = \delta(MeNO_2) + 380.23$,[32] and data are listed in Table 2.

Thermal Decomposition of (Acylimino)triaryl-λ^5-bismuthanes 3. (a) In a Sealed Tube. Compound **3f** (10.2 mg, 14 μmol) was placed in a sealable NMR tube that was thoroughly evacuated using a vacuum line. Benzene-d_6, dried over sodium, was vacuum transferred into the tube. After three freeze−pump−thaw cycles, the tube was evacuated and sealed. The thermal decomposition of **3f** was monitored at several intervals by ^{1}H NMR. After 15 h at 60 °C, the only peaks observed on the spectrum were those of tris(2-methylphenyl)bismuthane (**4a**). The yield of **4a** was quantitative. When **3a** was similarly reacted in a sealed tube under the same conditions, no decomposition was observed even after 1 week.

(b) In a Flask. A flask containing a benzene solution (20 mL) of **3f** (0.8−1.0 mmol) was heated at 60 °C for 15 h. The mixture was then concentrated under reduced pressure to leave an oily residue that was examined by ^{1}H NMR. 3,5-Bis(trifluoromethyl)aniline (**12**) and 3,5-bis(trifluoromethyl)benzamide (**2c**) were formed in 22−75% and 15−76% yields, respectively, together with a good recovery of bismuthane **4a**. Aniline **12** was characterized by comparison with the authentic specimen. The residue was chromatographed on silica gel with hexane/

ethyl acetate as the eluent to afford **4a**: mp 132−136 °C (lit.[67] mp 130−131 °C); ^{1}H NMR δ 2.44 (s, 9H), 7.03−7.11 (m, 3H), 7.23−7.37 (m, 6H), 7.55 (dd, 3H, J = 7.3, 1.3 Hz). Aniline **12**: ^{1}H NMR δ 4.07 (br-s, 2H), 7.03 (s, 2H), 7.21 (s, 1H). When a benzene solution of **3a** was heated at 60 °C for 48 h under N_2 or Ar in a flask, **4a** was obtained in 61% yield together with amide **2a**. When the thermolysis of **3f** was carried out in the presence of an excess (5−20 equiv) of a trapping agent or a hydrogen source such as cyclohexene, styrene, cyclohexane, or 9,10-dihydroanthracene, **12** and **2c** were obtained in a combined yield of 56−77%. Products trapped by the additive could not be detected by ^{1}H NMR.

Oxidation of 1,1,2,2-Tetraphenylethanediol. A mixture of **3a** (121 mg, 0.204 mmol), 1,1,2,2-tetraphenylethanediol (78 mg, 0.21 mmol), and CH_2Cl_2 (10 mL) was stirred at room temperature for 24 h. Evaporation of the solvent under reduced pressure left an oily residue that was then chromatographed on silica gel (hexane/EtOAc) to give **4a** (89 mg, 91%), benzophenone (65.3 mg, 84%), and unchanged diol. The products were identified by comparison with the authentic specimens. The presence of **2a** in the residue was confirmed by ^{1}H NMR and MS. When **3f** was used instead of **3a**, benzophenone and **4a** were formed in 74% and 83% yield, respectively.

Oxidation of Benzenethiol. A mixture of **3a** (178 mg, 0.300 mmol), benzenethiol (62 μL, 0.60 mmol), and benzene (10 mL) was stirred at room temperature for 3 h. Concentration of the mixture under reduced pressure left an oily residue that was chromatographed on silica gel (hexane/EtOAc) to give **4a** (148 mg, 100%) and diphenyl disulfide (53 mg, 80%). The products were identified by comparison with the authentic specimens.

Oxidation of Ethanol and Methanol. A mixture of **3f** (13 mg, 18 μmol), ethanol (5 μL, 89 μmol), and $CDCl_3$ (0.50 mL) was allowed to stand in an NMR tube at room temperature. The progress of the reaction was monitored by ^{1}H NMR. After 5 h, acetaldehyde (90%), toluene (99%), amide **2c** (76%), and compounds **14** of the type *o*-Tol_2BiX (92%) were formed. Methanol was similarly oxidized by **3f** to afford methyl formate (76%), toluene (94%), **2c** (70%), and **14** (90%) after 5 h. The oxidation products (acetaldehyde and methyl formate) and toluene were identified by comparison with the authentic specimens. The spectral data for the major component (>70%) of **14** was identical to that of a bismuth compound obtained from the reaction of bis(2-methylphenyl)bismuth trifluoromethanesulfonate[68] with aqueous NaOH. On the basis of spectral data as well as by comparison with a previous result with $Mes_2BiOBiMes_2$,[69] we identified the major component of **14** as tetrakis(2-methylphenyl)dibismuth oxide (**14b**) (*o*-Tol_2BiOBi*o*-Tol_2): ^{1}H NMR 2.15 (s, 12H), 7.22−7.32 (m, 8H), 7.38−7.42 (m, 4H), 8.20 (d, 4H, J = 7.2 Hz). Two minor components were tentatively assigned as bis(2-methylphenyl)bismuth 3,5-bis(trifluoromethyl)benzamide and bis(2-methylphenyl)bismuth alkoxide, but only on the basis of the ^{1}H NMR spectra of the crude products, and attempts to prepare these samples independently failed. We speculate that the amide **14a** formed initially, *o*-$Tol_2BiNHCOAr$ (Ar = 3,5-$(CF_3)_2C_6H_3$), would have been hydrolyzed by moisture from the solvent or atmosphere to produce **14b** and amide **2c**.

Reaction of 3d with 5, 7, and Triarylstibane. A mixture of **3d** (10.6 mg, 16.5 μmol), **5** (11.6 mg, 44.2 μmol), and C_6D_6 (0.75 mL) was heated at 60 °C for 7 h. Iminophosphorane **6** was formed with a quantitative recovery of **4a**. Triphenylarsane (**7**) and tris(2-methylphenyl)stibane also reacted with **3d** under similar conditions to generate **8** and **10a**, respectively, together with **4a**.

Reaction of 3a with Aqueous HCl. To a CH_2Cl_2 solution (3 mL) of **3a** (118 mg, 0.199 mmol) was added aqueous HCl (ca. 12 N, 0.2 mL), and the resulting mixture was vigorously stirred at room temperature. After 1 h, the organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (5 mL × 2). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to leave an oily residue that was recrystallized from CH_2Cl_2/hexane to yield **1a** (111 mg, 100%): mp 182−185 °C (dec) (lit.[70] mp 172 °C).

Reaction of 3b with Acetic Acid. A mixture of **3b** (194 mg, 0.303 mmol), acetic acid (0.19 mL, 3.3 mmol), and Et_2O (10 mL) was stirred at room temperature for 4 h. The mixture was evaporated under reduced pressure to leave an oily residue that was then extracted with Et_2O (10 mL). The Et_2O extract was dried over $MgSO_4$ and evaporated under reduced pressure to leave an oily residue that was recrystallized from CH_2Cl_2/hexane to yield tris(2-methoxyphenyl)bismuth diacetate (**17**) as a crystalline solid (188 mg, 98%): mp 143−145 °C (dec) (lit.[71] mp 147 °C); ^{1}H NMR δ 1.67 (s, 6H), 3.86 (s, 9H), 7.15−7.23 (m, 6H), 7.37−7.45 (m, 3H), 8.20 (d, 3H, J = 7 Hz).

Copper(II) Trifluoromethanesulfonate-Catalyzed Aryl Migration of 3. A mixture of **3a** (147 mg, 0.247 mmol), $Cu(OTf)_2$ (4.9 mg, 0.014 mmol), and CH_2Cl_2 (10 mL) was stirred at room temperature for 24 h. Evaporation of the mixture under reduced pressure left an oily residue that was then chromatographed on silica gel (hexane/EtOAc) to give bismuthane **4a** (45 mg, 38%) and *N*-trifluoroacetyl-*o*-toluidine (**18a**) (17.7 mg, 35%): mp 79−81 °C (lit.[72] mp 81−82 °C); ^{1}H NMR δ 2.31 (s, 3H), 7.16−7.32 (m, 3H), 7.45−7.85 (br-s, 1H, NH), 7.78 (d, 1H, J = 6.6 Hz); CIMS *m*/*z* 204 ($[M + H]^+$), 134, 107. The yield of **18a** was not affected by the presence or absence of an excess amount of styrene. A similar treatment of **3f** with $Cu(OTf)_2$ afforded **18b** (33%), **2c** (68%), and **4a** (15%). *N*-[3,5-Bis(trifluoromethyl)benzoyl]-*o*-toluidine (**18b**): ^{1}H NMR δ 2.35 (s, 3H), 7.15−7.33 (m, 3H), 7.66−7.71 (br-s, 1H, NH), 7.77 (d, 1H, J = 8.6 Hz), 8.07 (s, 1H), 8.32 (s, 2H); EIMS *m*/*z* 347 (M^+), 328, 241, 213, 106.

Ab initio Molecular Orbital Calculations of Iminopnictorane Structures, $H_3M{=}NCOCF_3$ (M = P, As, Sb, Bi). The molecular structures of imaginary iminopnictoranes, $H_3M{=}NCOCF_3$ (M = P, As, Sb, Bi), were predicted by ab initio calculations. The geometry optimization and bond-order and charge-distribution analyses were made using the Gaussian 98 program system.[73] The basis set was at the valence double-ζ plus polarization function level with the relativistic effective core potential (ECP). For pnictogen atoms, the Los Alamos effective core potential plus the valence double-ζ basis functions[74] augmented with the d-polarization function were used, where the exponents of the d functions were 0.340 (P), 0.293 (As), 0.211 (Sb), and 0.185 (Bi). The functions for carbon, nitrogen, oxygen, fluorine, and hydrogen were the (9s5p/4s)/[3s2p/2s] valence double-ζ basis functions by Dunning and Hay.[75] In addition, the d-polarization functions were placed on carbon, nitrogen, and oxygen atoms, where the exponents of the d functions were 0.600 (C), 0.864 (N), and 1.154 (O). No polarization functions were placed on the hydrogen and fluorine atoms. The molecular structures were optimized at the second-order Møller−Plesset (MP2) perturbation theory level using the analytical gradient method. All the geometrical parameters were optimized without any symmetry constraints. The stationary structures were confirmed by vibrational analysis. The Mayer−Mulliken natural bond order of the M=N bond and the natural charges[76] on the pnictogen, nitrogen,

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and oxygen atoms were calculated. The bond order and the natural charges were computed at the MP2 level.

X-ray Crystallographic Analyses of 3e, 6, 8, and 10c. Single crystals of compounds **3e**, **6**, **8**, and **10c** were grown from CH_2Cl_2/hexane (**3e**, **6**, **8**) or Et_2O/pentane (**10c**) at 4 °C. Data were recorded on a Rigaku AFC7S diffractometer (**6**), a Rigaku RAXIS-IV imaging plate diffractometer (**3e**), or a Rigaku RAXIS-RAPID imaging plate diffractometer (**8**, **10c**), with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. The structures were solved by the direct method[77] and were expanded using Fourier techniques.[78] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom-scattering factors were taken from Cromer and Waber.[79] Anomalous dispersion effects were included in F_{calc};[80] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[81] The values for the mass-attenuation coefficients are those of Creagh and Hubbel.[82] All calculations were performed using a teXsan[83] crystallographic software package of the Molecular Structure Corp. Further details of the X-ray crystallography are provided in the Supporting Information.

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Note Added after ASAP: An incorrect formula was published on Page 4 in the version posted October 11, 2001. The corrected version was reposted October 16, 2001.

Supporting Information Available: Text providing full IR data for **3a−e**, **6**, **8**, and **10c**, tables of all the bond lengths and angles obtained by ab initio molecular orbital calculations on the structures of $H_3M{=}NCOCF_3$, and X-ray crystallographic data (tables and figures) for the structures of **3e**, **6**, **8**, and **10c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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