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First Synthesis, Structure, and Reactivity of (Acylimino)triaryl-λ^5-bismuthanes Stabilized by *ortho*-Substituted Aryl Ligands

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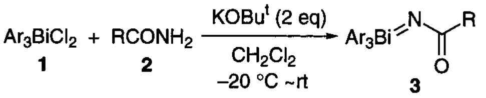
Summary: The reactive Bi(V)═N bond in (acylimino)-triaryl-λ^5-bismuthanes has been found to be stabilized effectively by ortho-substituted aryl ligands such as o-tolyl, o-anisyl, and mesityl groups. These imino-λ^5-bismuthanes, in which the bismuth center possesses a distorted tetrahedral geometry, behave as a nitrene precursor as well as an oxidizing agent, depending on the substrates and conditions.

Iminopnictoranes ($R_3M{=}NR'$; M = P, As, Sb, Bi) are a class of compounds bearing a formal double bond between the nitrogen and the pnictogen elements. They have been receiving considerable attention due to the chemical analogy to pnictogen ylides as well as for their potential utility in organic synthesis.[1] The properties and reactivity of the M═N bonds are known to vary considerably depending on the pnictogen atom. However, only little information is available concerning imino-λ^5-bismuthanes ($R_3Bi{=}NR'$). All known imino-λ^5-bismuthanes are thermally stabilized by a highly electronegative sulfonyl group on the nitrogen atom.[2−5] Modification of the *N*-substituent is expected to lead to different stability and reactivity of the Bi═N bond, but no imino-λ^5-bismuthanes bearing a functional group other than the sulfonyl have been reported to date. To obtain a better understanding of this class of bismuth(V) compounds, we have prepared a different type of imino-λ^5-bismuthanes and examined their fundamental properties. We report herein the first synthesis, the structure, and the reactivity of (acylimino)triaryl-λ^5-bismuthanes, which are stabilized by *ortho*-substituents on the aryl groups bonded to bismuth.

Scheme 1



1a; Ar = 2-MeC_6H_4
b; Ar = 2-$MeOC_6H_4$
c; Ar = 2,4,6-$Me_3C_6H_2$
d; Ar = 4-MeC_6H_4
e; Ar = 4-$MeOC_6H_4$

2a; R = CF_3
b; R = CCl_3
c; R = Ph
d; R = 4-$NO_2C_6H_4$
e; R = CMe_3

Table 1. Synthesis of (Acylimino)triaryl-λ^5-bismuthanes 3

entry	1	2	3 (isolated yield)
1	**1a**	**2a**	**3aa** (93%; Ar = 2-MeC_6H_4; R = CF_3)
2	**1a**	**2b**	**3ab** (77%; Ar = 2-MeC_6H_4; R = CCl_3)
3	**1b**	**2a**	**3ba** (90%; Ar = 2-$MeOC_6H_4$; R = CF_3)
4	**1b**	**2b**	**3bb** (96%; Ar = 2-$MeOC_6H_4$; R = CCl_3)
5	**1c**	**2a**	**3ca** (86%; Ar = 2,4,6-$Me_3C_6H_2$; R = CF_3)

The preparation of such compounds was effected as shown in Scheme 1. *ortho*-Substituted triarylbismuth dichlorides **1a**−**c** were reacted with trihaloacetamides **2a,b** in the presence of 2 equiv of potassium *tert*-butoxide (KO*t*-Bu) in dichloromethane to give (acylimino)triaryl-λ^5-bismuthanes **3aa**−**ca** as pale yellow solids (Table 1).[6] All attempts to isolate the *N*-aroyl counterparts formed from dichlorides **1a,b** and aromatic amides **2c,d** were unsuccessful. The crude products readily decomposed to the triarylbismuthane and the original amide **2c,d** during recrystallization. The KO*t*-Bu-promoted reaction of **1a** with pivalamide **2e** at room temperature resulted in formation of tris(2-methylphenyl)bismuthane **4** and recovery of **2e**. The similar reaction between the *para*-substituted triarylbismuth dichlorides **1d,e** and amide **2a** appeared to afford the expected imino-λ^5-bismuthanes, but they were quite sensitive to moisture and difficult to purify. These results show that the stability of (acylimino)triaryl-λ^5-

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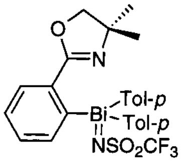
[1] Johnson, A. W. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993.

[2] Wittig, G.; Hellwinkel, D. *Chem. Ber.* **1964**, *97*, 789.

[3] (a) Suzuki, H.; Nakaya, C.; Matano, Y.; Ogawa, T. *Chem. Lett.* **1991**, 105. (b) Suzuki, H.; Ikegami, T. *J. Chem. Res., Synop.* **1996**, 24.

[4] Pasenok, S. V.; Kirij, N. V.; Yagupolskii, Y. L.; Naumann, D.; Tyrra, W. *J. Fluorine Chem.* **1993**, *63*, 179.

[5] Compound **A** was structurally characterized by X-ray diffraction analysis, where the bismuth center adopts a distorted trigonal bipyramidal geometry with a Bi═N bond length of 2.13(1) Å. The oxazoline group at the *ortho* position intramolecularly coordinates to the bismuth. Ikegami, T.; Suzuki, H. *Organometallics* **1998**, *17*, 1013.



A

[6] A typical procedure is as follows: to a mixture of tris(2-methylphenyl)bismuth dichloride **1a** (2.21 g, 4.00 mmol), trifluoroacetamide **2a** (458 mg, 4.05 mmol), and dichloromethane (80 mL) was added KO*t*-Bu (998 mg, 8.89 mmol) at −50 °C. The resulting mixture was allowed to warm gradually to 10 °C with vigorous stirring. The insoluble solid was filtered through Celite, and the filtrate was concentrated under reduced pressure to leave an oily residue, which was crystallized from dichloromethane/hexane to give [(trifluoroacetyl)-imino]tris(2-methylphenyl)-λ^5-bismuthane (**3aa**) as a pale yellow solid (2.205 g, 93%): mp 108−116 °C (decomp); ^1H NMR (200 MHz, $CDCl_3$) δ 2.46 (s, 9H), 7.32−7.49 (m, 9H), 7.68−7.73 (m, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) δ 9.92 (vs neat CF_3CO_2H); IR (KBr) ν 1561 (C═O) cm^{-1}; 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. Compounds **3ab**−**ca** also gave satisfactory spectral and analytical data. See Supporting Information.

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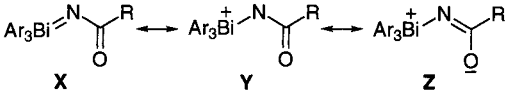
bismuthanes is strongly dependent on both steric and electronic environments around the Bi=N bond; the *ortho*-substituted aryl groups result in kinetic stabilization,[7] and the electron-withdrawing *N*-acyl group enhances the thermal stability.[8]

Compounds **3** can be stored in the solid state over a month in a refrigerator. They were characterized by NMR and IR spectroscopies as well as by elemental analysis.[6] Their IR spectra showed the characteristic C=O stretching band at rather low frequency (1561−1593 cm^{-1}) as compared to the parent amides **2a,b** or a phosphorus counterpart $Ph_3P{=}NCOCF_3$,[9] suggesting the important contribution of canonical form **Z** to the stabilization of the acylimino-λ^5-bismuthanes **3**.



To obtain further structural information, the crystal structure of **3bb** was elucidated by X-ray diffraction analysis.[10] Figure 1 shows the ORTEP diagram together with selected bond lengths and angles. The bismuth center possesses a distorted tetrahedral geometry with an average Bi−C bond length of 2.20 Å and an average C−Bi−C bond angle of 108.3°. The large N−Bi−C(17) bond angle of 116.1(1)° may be attributed to the electronic repulsion between the aromatic moiety and the carbonyl oxygen, the latter coordinating weakly to the bismuth center with a Bi−O(1) bond distance of 2.877(3) Å. Due to this intramolecular coordination, three atoms on the N−C(1) bond are almost in the same plane with a small Bi−N−C(1)−O(1) torsion angle of 4.2(5)°. The observed Bi−N bond length, 2.125(3) Å, lies close to the shorter end of the range of known Bi−N single bond distances [2.101(7)−2.28(2) Å].[11] Thus, the Bi=N bond possesses little double-bond character,[12] and the canonical structure **Z** best represents the actual bonding in **3bb**, as had been inferred from the IR data.

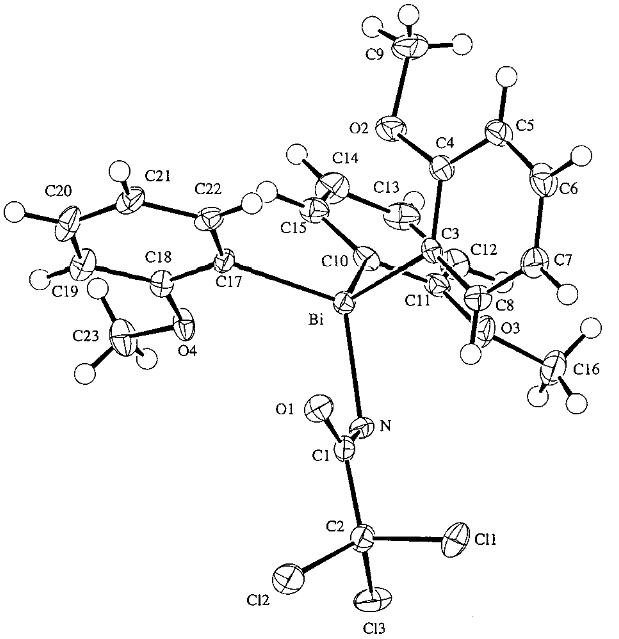


Figure 1. ORTEP diagram of **3bb**. Bond lengths (Å): Bi−N, 2.125(3); Bi−C(3), 2.198(4); Bi−C(10), 2.204(4); Bi−C(17), 2.196(4); N−C(1), 1.314(5); C(1)−O, 1.255(5). Bond angles (deg): N−Bi−C(3), 106.9(1); N−Bi−C(10), 108.8(1); N−Bi−C(17), 116.1(1); C(3)−Bi−C(10), 109.4(1); C(3)−Bi−C(17), 109.3(1); C(10)−Bi−C(17), 106.2(1); Bi−N−C(1), 104.0(3); N−C(1)−O, 130.9(4).

This is also in accord with the observed relatively short N−C bond length [1.314(5) Å] and somewhat longer C=O bond length [1.255(5) Å].[13] Three *ortho*-methoxyl groups surround the Bi=N bond through a weak interaction between the bismuth and oxygen atoms, protecting the reactive Bi=N bond both sterically and electronically.[8]

The reactivity of (acylimino)triaryl-λ^5-bismuthanes has been examined using **3aa** (Scheme 2).[14] When heated in benzene at 60 °C for 48 h, **3aa** decomposed completely to give bismuthane **4** (61% isolated yield) and **2a**.[15] This mode of decomposition is in marked contrast to that of the iminophosphorane $Ph_3P{=}NCOPh$, which decomposes at elevated temperatures to produce triphenylphosphine oxide and benzonitrile, presumably through an enolate structure.[16] In contrast to **3aa**, [(trifluoromethanesulfonyl)imino]tris(2-methylphenyl)-λ^5-bismuthane ($o\text{-}Tol_3Bi{=}NSO_2CF_3$)[17] remained mostly unchanged after a week-long heating in benzene-d_6 at 60 °C, showing that acylimino-λ^5-bismuthanes are much less stable thermally than the *N*-sulfonyl analogues.

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[7] 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. (b) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343. (c) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. *J. Am. Chem. Soc.* **1982**, *104*, 5820. (d) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855.

[8] *ortho*-Methoxy aryl groups have been shown to stabilize the cationic heteroatom thermodynamically. For example, see: (a) McEwen, W. E.; Lau, K. W. *J. Org. Chem.* **1982**, *47*, 3595. (b) Wada, M.; Kanzaki, M.; Fujiwara, M.; Kajihara, K.; Erabi, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1782. (c) Suzuki, H.; Ikegami, T.; Azuma, N. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1609. Thus, in compounds **3ba** and **3bb**, the *ortho*-methoxyl groups may also afford thermodynamic stabilization to the Bi=N bond.

[9] $\nu_{C=O}$ (**2a**): 1684 cm^{-1}. $\nu_{C=O}$ (**2b**): 1698 cm^{-1}. $\nu_{C=O}$ ($Ph_3P{=}NCOCF_3$): 1635 cm^{-1}, Cristau, H. J.; Manginot, E.; Torreilles, E. *Synthesis* **1991**, 382.

[10] $C_{23}H_{21}BiCl_3NO_4$, monoclinic, space group $P2_1/n$, $a = 8.776(2)$ Å, $b = 17.577(4)$ Å, $c = 15.875(4)$ Å, $\beta = 96.10(2)°$, $V = 2434.9(10)$ Å^3, $Z = 4$, $D_c = 1.884$ g cm^{-3}, $T = -130 \pm 1$ °C, 4787 independent and 4342 observed reflections ($I > 2.00\sigma(I)$) refined to $R = 2.5\%$, $R_w = 3.4\%$, GOF = 1.11. For further details, see Supporting Information.

[11] (a) Clegg, W.; Compton, N. A.; Errington, R. J.; Norman, N. C.; Wishart, N. *Polyhedron* **1989**, *8*, 1579. (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. (c) Wirringra, U.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **1994**, *33*, 4607. (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. (e) Burford, N.; Macdonald, C. L. B.; Robertson, K. N.; Cameron, T. S. *Inorg. Chem.* **1996**, *35*, 4013.

[12] Koketsu et al. estimated the Bi=N/Bi−N bond length ratio between $H_3Bi{=}NH$ and $H_2Bi{-}NH_2$ to be 0.927 from ab initio calculations (MP2/DZ-d level). Koketsu, J.; Ninomiya, Y.; Suzuki, Y.; Koga, N. *Inorg. Chem.* **1997**, *36*, 694.

[13] Typical N−C_{sp2} and C_{sp2}=O bond lengths are 1.36 and 1.20 Å, respectively. See: March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; Table 1.5, p 21.

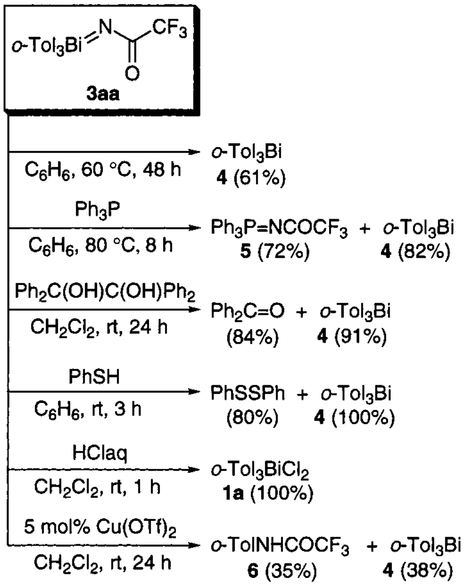
[14] All products were identified by comparison with the authentic specimens. Amide **2a** was an accompanying byproduct in the thermal decomposition, oxidation, and acidolysis. See Supporting Information.

[15] At present, we assume that **3aa** decomposes to generate a nitrene or nitrenoid species, which would abstract hydrogens from the solvent or the aryl ligands.

[16] (a) Staudinger, H.; Hauser, E. *Helv. Chim. Acta* **1921**, *4*, 861. (b) Horner, L.; Gross, A. *Justus Liebigs Ann. Chem.* **1955**, *591*, 117.

[17] This compound was obtained from the KO*t*-Bu-promoted reaction of **1a** and trifluoromethanesulfonamide. Matano, Y.; Nomura, H.; Suzuki, H. Unpublished results.

Scheme 2



When treated with an excess of triphenylphosphine in refluxing benzene, **3aa** transferred the nitrene unit to the phosphine to give the iminophosphorane **5**[9] and bismuthane **4**. Imide **3aa** also exhibited a mild oxidizing ability; benzpinacol and benzenethiol were oxidized to benzophenone and diphenyl disulfide, respectively, on treatment with an equimolar quantity of **3aa** at room temperature. The quantitative formation of **4** suggests the concerted elimination of the bismuthane from a pentavalent intermediate of the type *o*-Tol$_3$Bi(ER)$_2$ (E = O, S) during oxidation.[18] These findings demonstrate the good nucleofugal ability of the triarylbismuthonio moiety as a bismuthane. Treatment of **3aa** with an aqueous HCl solution in CH$_2$Cl$_2$ at room temperature yielded tris(2-methylphenyl)bismuth dichloride quantitatively. In the presence of a catalytic amount of copper(II) triflate, *N*-arylation proceeded smoothly to give *N*-tolylamide **6** with a moderate recovery of **4**. The yield of **6** was not affected by the presence or absence of excess styrene, ruling out the possible involvement of the nitrenoid species that would undergo aziridination. No C−N bond forming reaction was observed between **3aa** and benzaldehyde in boiling benzene.

Further studies on the chemistry of this class of bismuth(V) compounds are in progress.

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Supporting Information Available: Spectroscopic and analytical data for compounds **3**, experimental details of the reactions in Scheme 2, and X-ray diffraction data (ORTEP diagrams, crystal and data collection parameters, positional parameters, and bond distances and angles) for **3bb**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) For reviews on the ligand coupling of hypervalent compounds, see: (a) Barton, D. H. R.; Finet, J.-P. *Pure Appl. Chem.* **1987**, *59*, 937. (b) Finet, J.-P. *Chem. Rev.* **1989**, *89*, 1487. (c) Oae, S. *Pure Appl. Chem.* **1996**, *68*, 805, and references therein.