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Synthesis and Structure of the First Stable Iminoarsane

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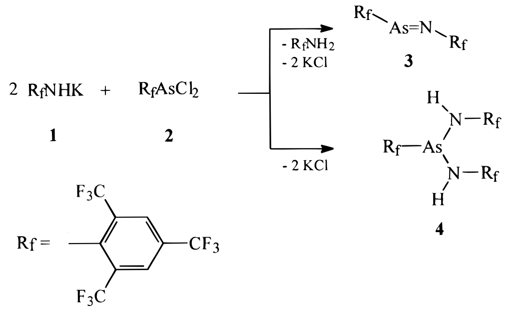
Introduction. Over the years, there has been considerable interest in compounds of group 15 elements having low coordination sites. Complexes of phosphorus, such as phosphoralkynes and -alkenes,[1] diphosphenes,[2] and iminophosphanes,[3] are of particular interest. Although the reactivity of these compounds has been known for a long time,[1−4] the chemistry of arsenic and its higher homologues has not been studied to any great extend, with the exception of the carbon−arsenic multiple bond systems.[5−8] After the early synthesis of arsabenzene,[7] recent research activities have focused on the preparation of compounds having arsenic silicon multiple bonds.[9] Lappert *et al.* reported the aminoiminoarsane (2,4,6-$Me_3C_6H_2NHAsNC_6H_2Me_3$-2,4,6).[10] Recently heteroallyl complexes of arsenic having a coordination number of two were synthesized and characterized by X-ray structural analysis.[11] Relatively few attempts, however, have been made obtaining complexes which include an As−N double bond.[12−14] Herein, we report on the synthesis and first X-ray structural characterization of a stable iminoarsane containing an arsenic−nitrogen double bond.

Results and Discussion. Treatment of (2,4,6-tris(trifluoromethyl)phenyl)dichlorophosphane with potassium 2,4,6-tris(trifluoromethyl)anilide, **1**, yielded the two thermally stable P,N-bis(2,4,6-tris(trifluoromethyl)phenyl)iminophosphane and *P*,*N*,*N′*-tris(2,4,6-tris(trifluoromethyl)phenyl)diaminophosphane.[15] Therefore we adopted this method to synthesise the analogous arsenic compounds. Reaction of **1** with (2,4,6-tris(trifluoromethyl)phenyl)dichloroarsane, **2**, resulted in compounds **3** and **4** (Scheme 1).

Scheme 1



Iminoarsane **3** is an orange solid with a melting point of 94 °C and is stable under inert gas atmosphere. Due to the steric requirements of the trifluoromethyl groups and the strong electron withdrawing effect of the 2,4,6-tris(trifluoromethyl)phenyl substituents, **3** is kinetically stabilized in comparison to less bulky substituted derivatives. The compound was characterized by elemental analysis, mass spectrometry, ^{1}H and ^{19}F NMR spectroscopy, and X-ray analysis.

Crystal Structure. The X-ray analysis shows the monomeric character of **3** in the solid state (Figure 1). The arsenic nitrogen bond distance (1.707(2) Å) indicates an arsenic−nitrogen double bond. The analogous bond lengths in the arsazene are 1.745(7) and 1.714(7) Å.[10] Pauling calculations predict distances of 1.73 Å for an arsenic nitrogen double and 1.95 Å for the corresponding single bond.[16] Both aryl substituents of **3** are in the (*E*) configuration. The angle of C(1)−N(1)−As(1) (125.6(2)°) is appropriate for a nearly ideally sp^2-hybridized imino nitrogen atom. The N(1)−As(1)−C(11) angle (96.3(1)°) indicates the perpendicular arrangement of the 2,4,6-tris(trifluoromethyl)phenyl substituent and the N(1)−As(1) bond direction.

The conjugation between the aryl substituents and the central As−N double bond should therefore be negligable. This in accordance with the fact that there is no broadening of the ^{19}F NMR signals of the *o*-CF_3 groups due to the nuclear quadrupole moment of ^{75}As as is observed in the spectrum of **4**. The C(1)−N(1) and the As(1)−C(11) distances of 1.388(4) and 1.999(3) Å, respectively, are typical for these atom combinations. The smallest arsenic−fluorine separation is 2.69 Å suggesting the absence of stabilizing As−F interactions.

Iminoarsane **3** opens new perspectives toward the synthesis of new arsenic nitrogen compounds, *e.g.* of heterocyclic complexes with As−N single bonds.

Experimental Section. Reactions were performed and worked up using standard Schlenk techniques, and products were handled under dry oxygen-free nitrogen. Solvents were dried, distilled, and stored using standard procedures. Literature methods were used for the preparation of 2,4,6-tris(trifluoromethylphenyl)aniline.[17] Infrared spectra were obtained using a Bio-Rad FTS7 spectrometer as Nujol films between KBr

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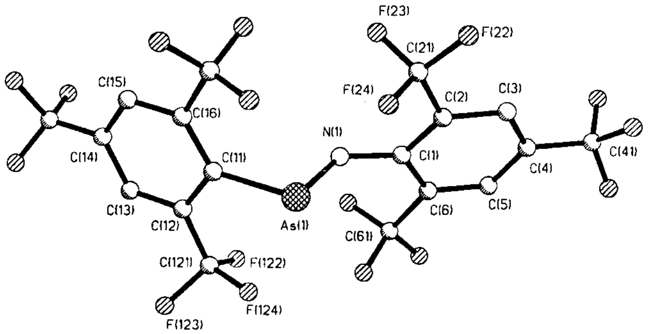

Figure 1. X-ray structure of **3**. Selected bond lengths (Å) and angles (deg): As(1)−N(1) = 1.707(2), N(1)−C(1) = 1.388(4), As(1)−C(11) = 1.999(3); C(1)−N(1)−As(1) = 125.6(2), N(1)−As(1)−C(11) = 96.3(1).

plates. NMR spectra were recorded on Bruker AM250, WP80SY, and MSL400 spectrometers (standards used: ^{1}H NMR, TMS; ^{19}F NMR, $CFCl_3$) and mass spectra on Finnigan MAT8230 and MAT95 and Varian CH5 spectrometers. Microanalyses were performed by the analytical laboratories of the University of Göttingen. Diffraction data were collected on a Siemens-Stoe AED four-circle diffractometer at 153 K with Mo Kα radiation and were solved by direct methods with SHELXS 86[18] and refined by full-matrix least-squares methods on F^2 (SHELXL 93[19]). Non-hydrogen atoms were refined anisotropically and hydrogen atoms inserted in calculated positions. Crystal data for complex (**3**) are summarized in Table 1 and atomic coordinates in Table 2 in the Supporting Information.

2,4,6-Tris(trifluoromethylphenyl)dichloroarsane, 2. A 68 mL (159 mmol) sample of Li-*n*-Bu (2.36 M in *n*-hexane) was added at −10 °C to a solution of 30.0 g (106 mmol) of 2,4,6-tris(trifluoromethyl)benzene in 50 mL of diethyl ether. The resulting suspension was added dropwise at −78 °C to a solution of 28.9 g (159 mmol) of $AsCl_3$ in diethyl ether. After slow warming to room temperature and 3 h of stirring, the reaction mixture was filtered and the solvents were removed from the filtrate *in vacuo* (10^{-2} bar). The crude product **2** was purified twice by distillation at 5×10^{-6} bar using a 10 cm Vigreux column to yield a colorless liquid. Crystals of **2** formed on standing. Yield: 13.6 g of **2** (30%), Bp: 36−39 °C. Anal. Calcd for $C_9H_2AsCl_2F_9$: C, 25.31; H, 0.47; Cl, 16.60; F, 40.05. Found: C, 25.6; H, 0.6; Cl, 16.8; F, 39.8. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 8.27 (s, 2 H, H-aryl). ^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ −53.5 (s, 6 F, *o*-CF_3), −64.2 (s, 3 F, *p*-CF_3). IR (Nujol): 3102 w, 1624 m, 1282 vs, 1197 vs, 1152 vs, 916 s, 857 s, 687 vs cm^{-1}. MS (EI), *m/e* (%): 426 $[M]^+$ (20), 391 $[M - Cl]^+$ (50), 262 $[C_9H_2F_8]^+$ (100).

***As,N*-Bis(2,4,6-tris(trifluoromethyl)phenyl)iminoarsane, 3.** At 0 °C, a solution of 2.00 g (6.8 mmol) of 2,4,6-tris(trifluoromethyl)aniline in 10 mL of THF was added to 0.67 g (16.8 mmol) of KH to yield potassium 2,4,6-tris(trifluoromethyl)anilide, **1**. After 2 h stirring, excess KH was removed by filtration. The solution was added dropwise to 1.45 g (3.4 mmol) **2** at 0 °C and stirred at room temperature for 12 h. All volatiles were removed *in vacuo*. The residue was washed with small amounts of ice-cold *n*-hexane to get **3** in solution. The solvent was removed *in vacuo*, and the crude product was purified by sublimation (5×10^{-6} bar, bath temperature 40 °C). Yield: 0.93 g **3** (42%), Mp: 94 °C. Anal. Calcd for $C_{18}H_4AsF_{18}N$: C, 33.20; H, 0.62; N, 2.15; F, 52.52. Found: C, 33.6; H, 0.6; N, 2.1; F, 52.5. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 7.82 (s, 2 H, H-aryl), 7.65 (s, 2 H, H-aryl). ^{19}F NMR (188 MHz, C_6D_6, 25 °C): δ −54.8 (sept, ^9J(F,F) = 4.2 Hz, 6 F, *o*-CF_3), −58.9 (sept, ^9J(F,F) = 4.2 Hz, 6 F, *o*-CF_3), −62.2 (s, 3 F, *p*-CF_3), −63.4 (s, 3 F, *p*-CF_3). IR (Nujol): 3098 w, 1631 m, 1278 vs, 1153 vs, 916 s cm^{-1}. MS (EI), *m/e* (%): 651 $[M]^+$ (30), 370 $[C_9H_2AsF_9N]^+$ (100), 238 $[C_9H_2F_6N]^+$ (90).

***As,N,N'*-Tris(2,4,6-tris(trifluoromethyl)phenyl)diaminoarsane, 4.** The residue of filtration and sublimation from the preparation of **3** was suspended in hot toluene and filtered off. After all volatiles were removed from the filtrate *in vacuo*, the colorless solid **4** was washed with a small amount of *n*-hexane. Yield: 1.55 g **4** (48%). Mp: 136 °C. Anal. Calcd for $C_{27}H_8AsF_{27}N_2$: C, 34.20; H, 0.85; N, 2.95; F, 54.10. Found: C, 34.4; H, 1.0; N, 3.0; F, 54.6. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 8.25 (s, 2 H, H-aryl), 7.96 (s, 4 H, H-aryl), 6.03 (br s, 2 H, NH). ^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ −55.8 (br s, 6 F, *o*-CF_3), −59.6 (s, 12 F, *o*-CF_3), −63.1 (s, 6 F, *p*-CF_3), −64.0 (s, 3 F, *p*-CF_3). IR (Nujol): 3449 m, 3429 m, 1634 s, 1272 vs, 1115 vs, 918 s, 681 s cm^{-1}. MS (EI), *m/e* (%): 948 $[M]^+$ (3), 652 $[C_{18}H_5AsF_{18}N]^+$ (40), 632 $[C_{18}H_4AsF_{17}N]^+$ (100).

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Supporting Information Available: Tables 1−5, listing the detailed crystallographic data, atomic coordinates for non-hydrogen atoms, bond lengths and angles, atomic coordinates for the hydrogen atoms, and anisotropic thermal parameters for the non-hydrogen atoms (6 pages). Ordering information is given on any current masthead page.

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