A New Route to Iminoarsanes

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Dehydrohalogenation of (2,4,6-tri-*tert*-butylphenylamino)chloro[tris(trimethylsilyl)hydrazino]arsane **(3)** or [*tert*-butyl(trimethylsilyl)amino]chloro(2,4,6-tri-*tert*-butylphenylamino)arsane **(4)** with DBU yields novel stable compounds containing an As–N double bond, (2,4,6-tri-*tert*-butylphenylimino)[tris(trimethylsilylhydrazino]arsane) **(5)** and [*tert*-butyl(trimethylsilyl)amino]-(2,4,6-tri-*tert*-butylphenylimino)arsane **(6)**. The structure of **5** was confirmed by an X-ray structure determination.

Introduction

In contrast to the well-known iminophosphanes[1] little is known about the corresponding compounds containing an As−N double bond.[2−4] The first compound in which an As−N double bond was clearly proven by X-ray structural analysis was (2,4,6-tri-*tert*-butylphenylamino)(2,4,6-tri-*tert*-butylphenylimino)arsane prepared by Lappert et al. in 1986.[5] It is an example for an aminoiminoarsane, in which the As−N (p-p)π-bond is stabilized by both steric and electronic effects. Ten years later Roesky et al. described the synthesis and X-ray structural characterization of *As,N*-bis[2,4,6-tris(trifluoromethyl)phenyl]iminoarsane,[6] an iminoarsane which is only kinetically stabilized by its bulky organyl groups. Herein we report the preparation of hydrazino- and aminoiminoarsanes using a new method to generate the As−N (p-p)π-bond.

Results and Discussion

Synthesis

The Lappert and Roesky methods for the synthesis of iminoarsanes are based on generation of the As−N (p-p)π-bond by alkali metal chloride elimination from *N*-metalated aminochloroarsanes, produced by substituting an H-atom of the amino group with lithium or potassium amide. Our method of synthesis is distinct from these syntheses as it uses the principle of direct base-induced dehydrohalogenation of aminochloroarsanes to iminoarsanes. Bisaminochloroarsanes suitable for the dehydrohalogenation to aminoiminoarsanes were obtained by successively substituting two chlorine atoms of $AsCl_3$ by treatment with lithium organyl amides. The introduction of two amino groups in a stepwise sequence with isolation of the primary formed aminodichloroarsane allows the synthesis of bisaminochloroarsanes and corresponding aminoiminoarsanes with differently substituted N atoms (Scheme 1).

Treatment of $AsCl_3$ with lithium tris(trimethylsilyl)hydrazide or lithium trimethylsilyl(*tert*-butyl)amide, yielded the hydrazinodichloroarsane **1** or the aminodichloroarsane **2**, respectively. These compounds react with lithium (2,4,6-tri-*tert*-butylphenyl)amide to give the hydrazinoaminochloroarsane **3** and the bisaminochloroarsane **4**. All precursors were isolated in good yield and have not yet been described, except for compound **1**.[4b] Compounds **3** and **4** were dehydrohalogenated by reaction with 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) to give the hydrazinoiminoarsane **5** and the aminoiminoarsane **6** in good yields. Compound **6** is a red-orange amorphous solid and compound **5** is a red crystalline solid from which crystals suitable for X-ray structural analysis could be isolated. Under dry, oxygen-free argon both these novel compounds are stable indefinitely.

X-ray Crystal Structure of 5

A suitable crystal for data collection was obtained from toluene at room temperature. The molecular structure is shown in Figure 1 and selected bond lengths and angles are given in the legend. The As−N double bond of compound **5** has an (*E*)-configuration and a bond length of 170.8(3) pm. This bond length is comparable to those found for the aminoiminoarsane [171.4(7) pm] synthesized by Lappert et al.[5] and the iminoarsane [170.7(2) pm] prepared by Roesky et al.[6] The As1−N2 distance [182.2(2) pm] is shorter than the calculated value (187 pm) for an As−N single bond.[7] Therefore it is likely that there is some conjugation of the hydrazino nitrogen (N2) lone pair with the As−N (p-p)π-bond system, which one would expect because of the sp^2-hybridization of the planar coordinated N2 atom (sum of angles at N2 = 360°). The N2−N3 distance of 148.0(3) pm lies within the range expected for N−N single bonds (147 pm).[8] The nitrogen (N3) lone pair is not available for conjugation effects because of the perpendicular arrangement of the nitrogen lone pairs at N2 and N3. The plane formed by the phenyl ring occupies a vertical position to the central π-system. For that reason there is no conjugation between the two π-systems.

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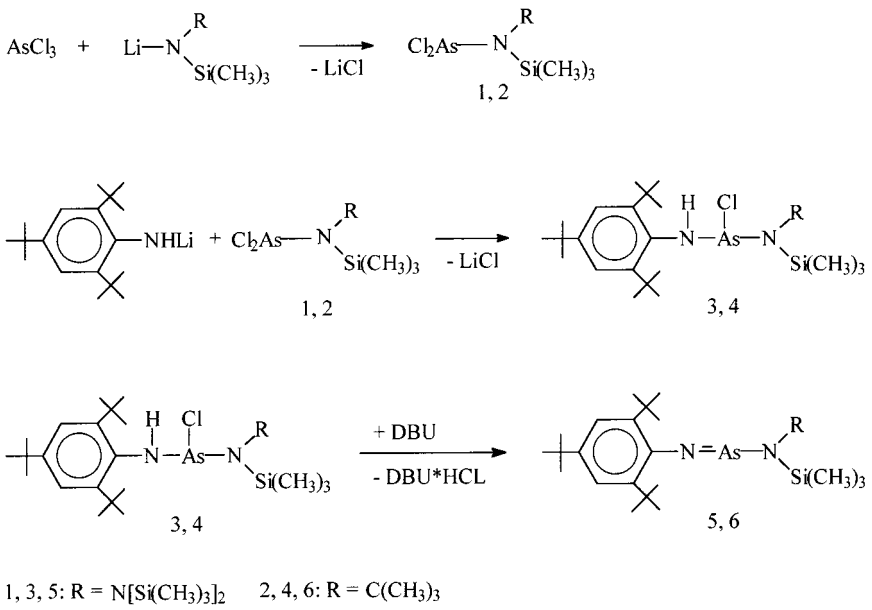

Scheme 1. Synthesis of aminoiminoarsanes

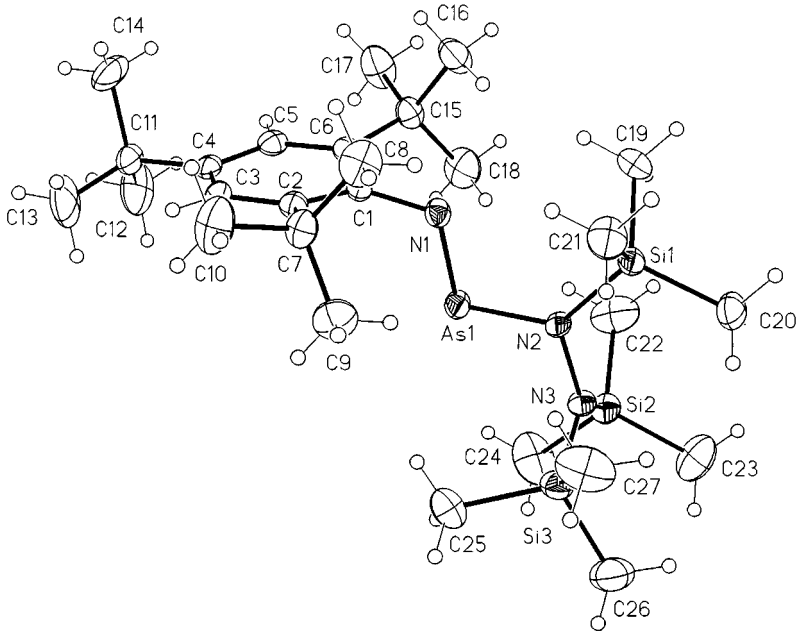

Figure 1. Moleculare structure of 5 (50% probabillity level, only one orientation of the disordered group is shown); selected bond lengths [pm], angles [°] and torsion angles [°]: As(1)−N(1) 170.8(3), As(1)−N(2) 182.3(2), N(2)−N(3) 147.9(4), N(1)−C(1) 144.5(4); As(1)−N(1)−C(1) 111.9(2), N(1)−As(1)−N(2) 104.0(1); C(1)−N(1)−As(1)−N(2) −178.5(2)

Experimental Section

General Remarks: All investigations were carried out in the absence of air and moisture under dry, oxygen-free argon. − ^{1}H NMR: Varian EM 360 (60 MHz) or Bruker WH 90 (90 MHz), standards used: residual solvent or TMS. − ^{13}C NMR: Bruker WH 90 (22 MHz), standard used: solvent. − ^{29}Si NMR: Bruker AMX 300 (59.63 MHz), external standard TMS. − Mass spectra: Kratos MS 50. − IR spectra: Bruker FT IR IFS 113 V. − Microanalyses were performed by the microanalytical laboratory E. Pascher, Remagen-Bandorf. − Trimethylsilyl(*tert*-butyl)amine[9] and tris(trimethylsilyl)hydrazine[10] were prepared as reported in the literature.

Dichloro[tris(trimethylsilyl)hydrazino]arsane (1): Tris(trimethylsilyl)hydrazine (13 g, 52.4 mmol), dissolved in diethyl ether (120 mL), was treated with *n*BuLi (34 mL of a 1.6 M solution in *n*-hexane, 52.4 mmol) at room temperature and stirred for 1 h. This solution was then added dropwise at −78°C to $AsCl_3$ (9.5 g, 52.4 mmol), dissolved in diethyl ether (40 mL). Stirring was continued for another hour whilst allowing the mixture to warm to room tempera-

ture. Thereafter the solvent was removed under reduced pressure, and the residue was extracted with *n*-hexane (40 mL). Lithium chloride was filtered off and cooling at −24°C over two days yielded **1**. Yield: 14.4 g (70%), colourless solid, M.p. 130°C (slow decomposition). − ^{1}H NMR (C_6D_6): δ = 0.13 [s, 18 H, N(Tms)$_2$], 0.41 [s, 9 H, NTms]. − ^{13}C NMR (C_6D_6): δ = 2.51 [s, N(Tms)$_2$], 2.70 [s, NTms]. − MS (EI): *m*/*z* (%) = 392 (0.1) [M$^+$], 377 (3) [M$^+$ − CH_3], 357 (10) [M$^+$ − Cl], 247 (100) [M$^+$ − $AsCl_2$], 73 (95) [Tms$^+$] and other fragments.

[*tert*-Butyl(trimethylsilyl)amino]dichloroarsane (2): Trimethylsilyl(*tert*-butyl)amine (7.25 g, 50 mmol), dissolved in diethyl ether (20 mL), was mixed with *n*BuLi (31.5 mL of a 1.6 M solution in *n*-hexane, 50 mmol) at 0°C. Following 1 h stirring at room temperature the solution of the lithium salt was added dropwise to $AsCl_3$ (9.1 g, 50 mmol), dissolved in diethyl ether (20 mL), at −78°C during 30 mins. The mixture was then warmed slowly to room temperature, lithium chloride was filtered off and the solvent was removed under reduced pressure. Distillation of the remaining yellow-brown oil yielded **2**. Yield: 11.79 g (81%), Bp. 78°C/1 mbar. − ^{1}H NMR ($CDCl_3$): δ = 0.43 [s, 9 H, Tms], 1.53 [s, 9 H, *t*Bu]. − ^{13}C NMR ($CDCl_3$): δ = 6.05 [s, Si(*C*H$_3$)$_3$], 33.86 [s, C(*C*H$_3$)$_3$], 61.92 [s, *C*(CH$_3$)$_3$]. − MS (EI): *m*/*z* (%) = 289 (1) [M$^+$], 274 (33) [M$^+$ − CH_3], 254 (5) [M$^+$ − Cl], 218 (15) [M$^+$ − CH_3 − isobutene], 198 (21) [M$^+$ − Cl − isobutene], 166 (100) [M$^+$ − TmsCl − CH_3], 73 (80) [Tms$^+$], 57 (92) [*t*Bu$^+$] and other fragments.

(2,4,6-Tri-*tert*-butylphenylamino)chloro[tris(trimethylsilyl)hydrazino]arsane (3): 2,4,6-Tri-*tert*-butylphenylamine (1.25 g, 4.8 mmol), dissolved in diethyl ether (10 mL), was treated with *n*BuLi (3 mL of a 1.6 M solution in *n*-hexane) at room temperature. After stirring for 30 mins. the solution of the lithium salt was added dropwise to dichloro[tris(trimethylsilyl)hydrazino]arsane **(1)** (1.88 g, 4.8 mmol), dissolved in diethyl ether (50 mL). Stirring was continued for 30 mins. and the solvent was removed under reduced pressure. The residue was extracted with *n*-hexane (10 mL) and lithium chloride was filtered off. Crystallization from the filtrate at −78°C yielded **3**. Yield: 1.5 g (50%), light rose solid, M.p. 81−83°C. − ^{1}H NMR (C_6D_6): δ = 0.26 [s, 9 H, N(Tms)$_2$], 0.34 [s, 9 H, N(Tms)$_2$], 0.42 [s, 9 H, AsNTms], 1.28 [s, 9 H, *p*-*t*Bu], 1.56 [s, 18 H, *o*-*t*Bu], 5.82 [s, 1 H, NH], 7.49 [s, 2 H, Aryl]. − ^{13}C NMR (C_6D_6): δ = 3.80 [s, N{Si(*C*H$_3$)$_3$}$_2$], 3.86 [s, N{Si(*C*H$_3$)$_3$}$_2$], 3.98 [s, AsNSi(*C*H$_3$)$_3$], 30.48 [s, *p*-*C*(CH$_3$)$_3$], 31.71 [s, *p*-C(*C*H$_3$)$_3$], 34.55 [s, *o*-C(*C*H$_3$)$_3$], 36.71 [s, *o*-*C*(CH$_3$)$_3$], 124.08 [s, C3, C5], 138.13 [s, C4], 141.02 [s, C2, C6], 143.19 [s, C1]. − ^{29}Si NMR (C_6D_6): δ = 11.37 [N(Tms)$_2$], 12.37 [N(Tms)$_2$], 16.06 [NTms]. − MS (EI): *m*/*z* (%) = 617 (2) [M$^+$], 602 (0.4) [M$^+$ − CH_3], 581 (5) [M$^+$ − HCl], 509 (0.4) [M$^+$ − TmsCl], 357 (100) [M$^+$ − Mes*NH], 334 (54) [M$^+$ − HCl − N_2Tms_3], 247 (75) [$Tms_3N_2^+$], 73 (82) [Tms$^+$], 57 (20) [*t*Bu$^+$] and other fragments.

[*tert*-Butyl(trimethylsilyl)amino]chloro(2,4,6-tri-*tert*-butylphenylamino)arsane (4): 2,4,6-Tri-*tert*-butylphenylamine (3 g, 11.5 mmol), dissolved in diethyl ether (130 mL), was treated with *n*BuLi (9.3 mL of a 1.6 M solution in *n*-hexane) at room temperature. After stirring for 30 mins. the solution of the lithium salt was added dropwise at −78°C to [*tert*-butyl(trimethylsilyl)amino]dichloroarsane **(2)** (3.32 g, 11.5 mmol), dissolved in diethyl ether (20 mL). The mixture was warmed slowly to room temperature and stirring was continued for 1 h. The solvent was removed under reduced pressure and the residue was extracted with *n*-hexane (15 mL). Lithium chloride was filtered off and cooling of the filtrate at −78°C for three weeks yielded **4**. Yield: 3.6 g (60%), colourless solid, M.p. 90−92°C. − ^{1}H NMR (C_6D_6): δ = 0.47 [s, 9 H, Tms], 1.33 [s, 9 H, *p*-*t*Bu], 1.40 [s, 9 H, N−*t*Bu], 1.66 [s, 18 H, *o*-*t*Bu], 6.03 [s, 1 H, NH], 7.55 [s, 2 H, Aryl]. − ^{13}C NMR (C_6D_6): δ = 6.26 [s, Si(*C*H$_3$)$_3$], 30.41 [s, *p*-*C*(CH$_3$)$_3$], 31.58 [s, *p*-C(*C*H$_3$)$_3$], 33.78 [s, NC(*C*H$_3$)$_3$], 34.10 [s, *o*-C(*C*H$_3$)$_3$], 36.82 [s, *o*-*C*(CH$_3$)$_3$], 59.54 [s, N*C*(CH$_3$)$_3$], 124.05 [s, C3, C5], 138.20 [s, C4], 144.67 [s, C1], 145.03 [s, C2, C6]. − MS (EI): *m*/*z* (%) = 514 (6) [M$^+$], 479 (2) [M$^+$ − Cl], 260 (90) [Mes*NH$^+$], 254 (20) [M$^+$ − Mes*NH], 246 (100) [Mes*H$^+$], 198 (84) [TmsNHAsCl$^+$] and other fragments.

(2,4,6-Tri-*tert*-butylphenylimino)[tris(trimethylsilyl)hydrazino]-arsane (5): DBU (0.39 g, 2.55 mmol), dissolved in *n*-hexane (5 mL), was added dropwise to (2,4,6-tri-*tert*-butylphenylamino)chloro[tris-(trimethylsilyl)hydrazino]arsane **(3)** (1.5 g, 2.43 mmol), dissolved in *n*-hexane (10 mL), at room temperature. The solution immediately turned red. Stirring was continued for 1 h, DBU·HCl was filtered off and crystallization from the filtrate at −26°C yielded **5**. Yield: 1.08 g (77%), red crystalline solid, M.p. 164−170°C. − ^{1}H NMR (CCl_4/TMS): δ = 0.2 [s, 18 H, N(Tms)$_2$], 0.5 [s, 9 H, NTms], 1.34 [s, 9 H, *p*-*t*Bu], 1.44 [s, 18 H, *o*-*t*Bu], 7.27 [s, 2 H, Aryl]. − ^{13}C NMR (C_6D_6): δ = 2.67 [s, Si(*C*H$_3$)$_3$], 30.41 [s, *p*-*C*(CH$_3$)$_3$], 32.06 [s, *p*-C(*C*H$_3$)$_3$], 33.82 [s, *o*-C(*C*H$_3$)$_3$], 36.73 [s, *o*-*C*(CH$_3$)$_3$], 121.77 [s. C3, C5], 137.05 [s, C2, C6], 142.20 [s, C4], 149.29 [s, C1]. − ^{29}Si (C_6D_6): δ = 10.96 [N(Tms)$_2$], 15.68 [NTms]. − MS (EI): *m*/*z* (%) = 581 (52) [M$^+$], 566 (5) [M$^+$ − CH_3], 334 (100) [M$^+$ − N_2(Tms)$_3$], 247 (92) [(Tms)$_3N_2^+$], 73 (65) [Tms$^+$], 57 (28) [*t*Bu$^+$] and other fragments. − IR (KBr): ṽ = 2956 (vs), 2904 (s), 2856 (s), 1595 (m), 1478 (m), 1460 (m), 1413 (s), 1389 (m), 1360 (s), 1253 (vs), 1213(s), 1191 (m), 1146 (m), 1021 (m), 925 (vs), 880 (vs), 842 (vs), 768 (s), 747 (m), 681 (m), 655 (m), 640 (w), 610 (w), 572 (m) cm^{-1}. − $C_{27}H_{56}AsN_3Si_3$ (581.94): calcd. C 55.73 H 9.70 N 7.22; found C 56.22 H 9.81 N 7.01

[*tert*-Butyl(trimethylsilyl)amino](2,4,6-tri-*tert*-butylphenylimino)arsane (6): [*tert*-Butyl(trimethylsilyl)amino]chloro(2,4,6-tri-*tert*-butylphenylamino)arsane **(4)** (1.6 g, 3.1 mmol), dissolved in *n*-hexane (10 mL), was treated with DBU (0.5 g, 3.3 mmol), dissolved in *n*-hexane (3 mL). The solution immediately turned red. Stirring was continued for 1 h, DBU·HCL was filtered off and cooling of the filtrate at −26°C yielded **6**. Yield: 1.1 g (75%), red solid, M.p. 87−90°C. − ^{1}H NMR (CCl_4/TMS): δ = 0.39 [s, 9 H, Tms], 1.32 [s, 9 H, *p*-*t*Bu], 1.37 [s, 18 H, *o*-*t*Bu], 1.80 [s, 9 H, N−*t*Bu], 7.24 [s, 2 H, Aryl]. − ^{13}C NMR (C_6D_6): δ = 5.93 [s, Si(*C*H$_3$)$_3$], 30.48 [s, *p*-*C*(CH$_3$)$_3$], 32.10 [s, *p*-C(*C*H$_3$)$_3$], 33.31 [s, *o*-C(*C*H$_3$)$_3$], 33.47 [s, NC(*C*H$_3$)$_3$], 36.63 [s, *o*-*C*(CH$_3$)$_3$], 60.97 [s, N*C*(CH$_3$)$_3$], 121.63 [s, C3, C5], 138.23 [s, C2, C6] 142.17 [s, C4], 150.16 [s, C1]. − ^{29}Si NMR (C_6D_6): δ = 5.99. − MS (EI): *m*/*z* (%) = 478 (30) [M$^+$], 463 (6) [M$^+$ − CH_3], 421 (12) [M$^+$ − *t*Bu], 334 (100) [M$^+$ − N(Tms)*t*Bu], 278 (50) [M$^+$ − N(Tms)*t*Bu − isobutene], 73 (90) [Tms$^+$], 57 (50) [*t*Bu$^+$] and other fragments. − IR (KBr): ṽ = 2963 (vs), 2903 (m), 2864 (m), 1621 (w), 1596 (w), 1479 (m), 1436 (m), 1409 (s), 1388 (m), 1360 (s), 1253 (s) 1234 (w), 1215 (s) 1179 (m), 1116 (s), 1034 (m), 958 (s), 917 (w), 847 (vs), 761 (m), 739 (m), 678 (s), 632 (m), 534 (w), 485 (m), 416 (w) cm^{-1}.

Crystal Data for 5: $C_{27}H_{56}AsN_3Si_3$, M = 581.9, monoclinic, space group $P2_1/n$ (No. 14), red crystals, dimensions 0.10 × 0.15 × 0.35 mm, a = 9.865(3), b = 34.578(2), c = 10.035(1) Å, β = 98.80(2)°, V = 3.383(1) Å^3, D_c = 1.14 Mg m^{-3}, Z = 4, μ (CuKα) = 2.5 mm^{-1}, T = 208(2) K, F(000) = 1256; 5328 reflection were collected on an Enraf−Nonius CAD4 diffractometer ($2\theta_{max}$ = 120°, $-11 \le h \le 0$, $0 \le k \le 38$, $-11 \le l \le 11$), 5008 symmetry independent reflections (R_{int} = 0.027) were used for the structure solution (direct methods)[11] and refinement (full matrix least-squares on F^2,[12] 302 parameters, 60 restraints), non-hydrogen atoms were refined anisotropically, H atoms localized by difference electron density and refined using a riding model; $wR2$ = 0.108 [R_1 = 0.039 for 3969 $I > 2\sigma(I)$]. An empirical absorption correction on the basis of

ψ-scans was applied (min./max. transmission 0.190/0.764). The *p*-*t*Bu-group is disordered.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Data Centre as supplementary publication no. CCDC-132004. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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