The Influence of the Neutral Coligand on the Spectroscopic Properties and Crystal Structures of Lithium Tri(*tert*-butyl)silylarsanides of the Type [(L)LiAs(H)Si*t*Bu$_3$] (L = DME, THF)

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Keywords: Arsanes / Arsanides / Lithium / Lithiation / Pnicogens

The reaction of [(dme)LiAsH$_2$] with F$_3$CSO$_3$Si*t*Bu$_3$ yields tri(*tert*-butyl)silylarsane (**1**). The reaction of **1** with *n*-butyllithium in 1,2-dimethoxyethane gives [(dme)LiAs(H)Si*t*Bu$_3$]$_2$ (**2**), whereas the lithiation of **1** in THF leads to the formation of the one-dimensional polymer [(THF)LiAs(H)Si*t*Bu$_3$]$_\infty$ (**3**). The Li–As bond lengths of both of these compounds show a similar value of approximately 260 pm. However, the smaller coordination number of the lithium atom in **3** leads to a short Li–O distance of 190 pm, whereas in **2**, which has a tetracoordinate lithium atom, an average bond length of 199 pm is observed.

Introduction

Silylphosphanes and their lithiated derivatives have aroused the interest of many research groups over several decades[1–5] because these compounds are valuable synthons for a wide variety of novel compounds such as phosphaalkenes and phosphaalkynes.[6] However, the homologous silylated arsanes, as well as their lithium derivatives, have been investigated far less extensively, although the synthesis and the structure of DME complexes of LiAsH$_2$ have been published[7,8] and have led to a moderate development of arsanide chemistry. The huge preference for phosphorus chemistry stems from the NMR-sensitive ^{31}P nucleus, which allows a spectroscopic follow-up of reactions prior to isolation of new compounds. Furthermore, the comparable van der Waals radii of phosphorus (1.85 Å) and arsenic (1.9 Å) due to the contraction of the d-block elements suggest a similar chemical behaviour of homologous compounds, whereas nitrogen (1.55 Å) and antimony (2.2 Å) differ more drastically. In addition, the structures of silylated amines also show planar-coordinated and sp^2-hybridized nitrogen atoms, whereas the heavy pnicogen atoms in silylated phosphanes, arsanes and stibanes display a pyramidal environment and avoid hybridisation.[5]

After the first synthesis of [LiAs(SiMe$_3$)$_2$] by Becker and co-workers 25 years ago,[9] the crystal structures of the DME[10] and THF adducts[11] were reported. The growing interest in these compounds, for example as precursors for element III/V semiconductors, finally led to the publication of slightly modified and improved preparation procedures.[12,13] Modifications of the substitution pattern of tris(triorganylsilyl)arsanes were also investigated.[14] Whereas the reaction of E(SiMe$_3$)$_3$ with an alkyllithium yields [LiE(SiMe$_3$)$_2$] (E = P, As, Sb), the monosubstituted trimethylsilylated phosphanes undergo redistribution reactions with the formation of a mixture of LiPH$_2$, [LiP(H)-SiMe$_3$] and [LiP(SiMe$_3$)$_2$].[15] In order to prevent these redistribution reactions larger groups such as Si*i*Pr$_3$ and Si*t*Bu$_3$ have to be employed, and even the bulkiness of the triisopropylsilyl substituents enforces an almost planar environment at the pnicogen atoms in E(Si*i*Pr$_3$)$_3$ (E = P, As, Sb).[16]

The synthesis of H$_2$AsSi*i*Pr$_3$ succeeded smoothly by the reaction of [(dme)LiAsH$_2$][7] with chlorotriisopropylsilane.[17] Metallation reactions led to the formation of triisopropylsilylarsanediides, which can be part of a cluster[18] or trapped between two metal fragments.[17] Monometallated triisopropylsilylarsanes have been published for the alkaline-earth metals;[19] however, there are no detailed investigations on the key compounds [(L)$_n$LiAs(H)SiR$_3$] with bulky trialkylsilyl substituents. There are only sporadic investigations on lithiated easily accessible primary arsanes, even though reports on [LiAs(H)R] were published as far back as 1964/65 (R = *t*Bu)[20] and 1977 (R = Ph).[21] The helical structure of [(THF)$_2$LiAs(H)Ph]$_\infty$ was determined more than two decades later.[22]

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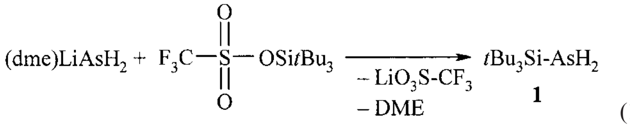
DOI: 10.1002/ejic.200500349

Results and Discussion

Synthesis and NMR Spectroscopy

Whereas the metallation of tri(*tert*-butyl)silylphosphane has already been reported,[23] there are no reports on the homologous arsane. The metathesis reaction of [(dme)Li-AsH_2] with $tBu_3SiO_3SCF_3$ in DME yields tri(*tert*-butyl)silylarsane (**1**) and lithium trifluoromethanesulfonate in large quantities according to Equation (1). This primary arsane shows no tendency to undergo dismutation or redistribution reactions. The AsH_2 moiety is clearly detected by the symmetric and asymmetric stretching vibrations at 2100 and 2091 cm^{-1} in the IR spectrum.



$$(dme)LiAsH_2 + F_3C{-}\overset{O}{\underset{O}{S}}{-}OSitBu_3 \xrightarrow[-\,LiO_3S\text{-}CF_3\ \ -\,DME]{} \underset{\mathbf{1}}{tBu_3Si\text{-}AsH_2} \quad (1)$$

The stoichiometric metallation of $H_2AsSitBu_3$ with alkyllithium leads to the monolithiated arsanides according to Equation (2). The solvent determines which solvate is formed during the metallation reaction. These complexes are very sensitive to moisture and air.

$$H_2As\text{-}SitBu_3 + \boldsymbol{n}BuLi \xrightarrow[-\,nBuH]{L} [(L)LiAs(H)SitBu_3] \quad L = DME\ (\mathbf{2}),\ THF\ (\mathbf{3}) \quad (2)$$

The deprotonation (lithiation) shifts the As–H stretching vibrations to lower energies. These frequencies, as well as the NMR parameters, are listed in Table 1. Several general trends can be deduced from the NMR spectroscopic parameters dependent on the pnicogen atom and the substitution of hydrogen by a lithium atom (higher negative charge on the pnicogen atom). The heavier pnicogen atom causes the E–H vibration to lie at lower wavenumbers and the ^1H NMR resonance at higher field. Furthermore, the $^{29}Si\{^1H\}$ NMR shift is observed at lower field for the arsenic derivatives. Similar trends are observed for the substitution of an H atom by a lithium atom: the trialkylsilylphosphanides and -arsanides show lower E–H stretching energies, a high-field shift of the proton in the NMR spectra, and a low-field shift for the silicon nuclei. The substitution of the triisopropylsilyl groups by the bulkier tri(*tert*-butyl)silyl substituents leads to larger δ values of the silicon nucleus.

Molecular Structures

The tetracoordinate pnicogen atoms in the lithium tri(*tert*-butyl)silylarsanides discussed above are bonded to a silicon, a hydrogen and two lithium atoms. The structure of the DME adduct is shown in Figure 1. The central structural motif is a four-membered Li_2As_2 cycle with an alkali metal in a distorted tetrahedral environment.

Table 1. Spectroscopic properties of $H_2AsSitBu_3$ (**1**) and the lithium tri(*tert*-butyl)silylarsanides of the type [(L)LiAs(H)SiR$_3$] [L = DME (**2**), THF (**3**)]. For comparison reasons the values of the homologous phosphorus derivatives $H_2PSitBu_3$ (**A**) and [(dme)LiP(H)SitBu$_3$]$_2$ (**B**) are also included.

	A	**B**	**1**	**2**	**3**
$\tilde{\nu}$	2295 2395	2261	2091 2100	2065	2042
$\delta(EH)$	0.94[a]	–2.11[b]	1.15	–2.83	–2.48
$\delta(SiCMe)$	1.09	1.10	1.10	1.42	1.47
$\delta(SiC)$	23.1	23.6	23.4	24.1	23.9
$\delta(SiCMe)$	30.7	31.5	30.6	32.2	32.0
$\delta(Si)$	24.1	33.6	31.2	39.2	38.2
Ref.	[24]	[23]			

[a] $^1J_{P,H}$ = 185.6 Hz; $\delta_{^{31}P}$ = –263.8 ppm. [b] $^1J_{P,H}$ = 165.9 Hz; $\delta_{^{31}P}$ = –322.2 ppm.

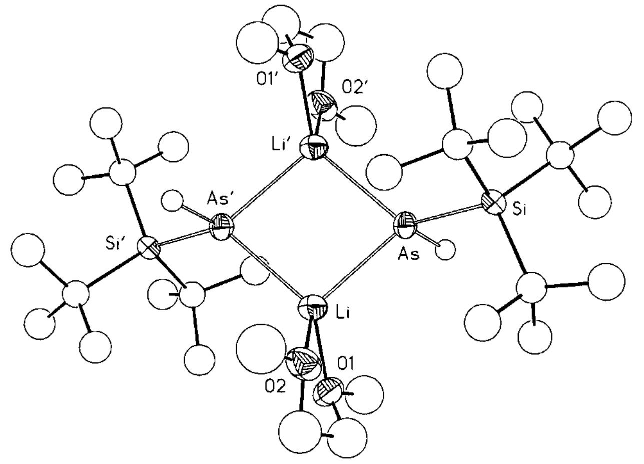


Figure 1. Molecular structure of **2**. The hydrogen atoms have been omitted for clarity, with the exception of the arsenic-bound H atom. Symmetry-related atoms (*x*, –*y* + 1, –*z* + 1) are marked with an apostrophe. Selected bond lengths [pm]: As–Li 260.9(3), As–Li′ 259.7(3), As–Si 231.49(5), As–H 154(2), Li–O1 201.0(4), Li–O2 197.2(4), Si–C1 194.6(2), Si–C5 194.9(2), Si–C9 195.3(2); angles [°]: Si–As–Li 122.61(8), Si–As–Li′ 123.90(8), Li–As–Li′ 85.2(1), Si–As–H 96(1), Li–As–H 111(1), Li′–As–H 120(1), As–Li–As′ 94.8(1).

The THF complex **3** crystallises as an infinite polymeric strand. Part of the chain is represented in Figure 2. Although the four-membered Li_2E_2 cycle (E = P, As), which can annelate into ladder-type structures, is the main structural feature, infinite chains of alternating lithium and pnicogen atoms have also been observed for [(dme)LiPH$_2$]$_\infty$[25,26] and [(THF)$_2$LiAs(H)Ph]$_\infty$.[22]

Selected structural parameters of the ether complexes of lithium tri(*tert*-butyl)silylarsanide are listed in Table 2 together with those of other phosphanides and arsanides of lithium. Bis(triisotriisopropylsilyl)phosphane[27] and tris(triisopropylsilyl)phosphane and -arsane[16] are included for comparison reasons as well. The anionic charge on the pnicogen atom leads to a shortening of the E–Si bond of approximately 6 pm due to an additional electrostatic attraction between the pnicogen and the silicon atoms. The Li–E distances are scattered widely between 247 and 262 pm for the phosphanides and between 258 and 273 pm for the arsanides. These values depend on the coordination

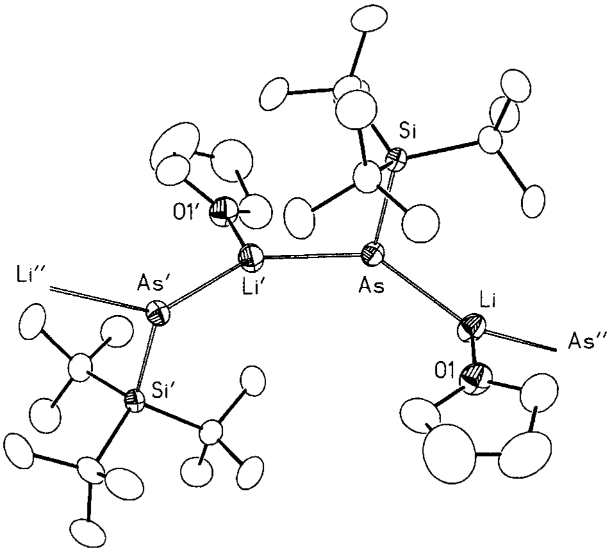


Figure 2. Structure model of **3**. All hydrogen atoms have been omitted for clarity. Symmetry-related atoms are marked with one (x + 1, y – 1/2, –z + 1/2) or two apostrophes (x + 1, y + 1/2, –z + 1/2). Selected bond lengths [pm]: As–Si 233.83(6), As–Li 258.1(4), As–Li′ 260.8(4), Li–O1 190.4(4), Si–C1 194.9(2), Si–C2 195.3(2), Si–C3 194.8(2); angles [°]: Si–As–Li 104.9(1), Si–As–Li′ 107.8(1), Li–As–Li′ 141.81(4), As–Li–As″ 128.4(1).

numbers of the alkali metal and the pnicogen atoms. Thus, the smallest Li–P bond lengths were observed for a phosphanide with a two-coordinate lithium atom and the shortest Li–As bonds were found for arsanides with three-coordinate alkali metals. Intramolecular steric repulsion leads to an enhancement of these bonds. The Li–O distances follow a similar pattern: triply coordinated lithium atoms show smaller distances, whereas a coordination number of four leads to an elongation of this bond. Furthermore, monodentate ethers display shorter Li–E bonds than the bidentate 1,2-dimethoxyethane ligand.

The smallest angle is observed at the alkali metal atom in four-membered $\mathrm{Li_2E_2}$ ring systems. This fact is a consequence of repulsive forces between the large pnicogen atoms. If the four-membered cycle is opened to a one-dimensional strand, Li–E–Li′ angles of more than 140° are realized, whereas in polymeric $[\mathrm{(dme)LiPH_2}]_\infty$ a nearly linear Li–P–Li′ fragment is found. A linear E–Li–E′ moiety is never found because additional agostic interactions enhance the coordination number, especially of the low-coordinate alkali metal atoms.

Summary

Lithiated primary arsanes do not undergo redistribution reactions if large trialkylsilyl groups are bonded at the arsenic atom. The bidentate 1,2-dimethoxyethane ligand leads to a dimeric molecule whereas the smaller and monodentate tetrahydrofuran molecule favours the crystallisation of a one-dimensional coordination polymer. These compounds are valuable synthons for arsenide-transfer reactions and further deprotonation reactions (formation of arsanediides).

Experimental Section

General: All experiments and manipulations were carried out under an atmosphere of argon. Reactions were performed by using standard Schlenk techniques and in dried and thoroughly deoxygenated solvents. $[\mathrm{(dme)LiAsH_2}]$[7] as a DME solution and $\mathrm{F_3CSO_3Si}$-$t\mathrm{Bu_3}$[24] were prepared according to a literature procedure. The NMR spectroscopic data were obtained at room temperature from [D$_6$]benzene solutions. For the IR spectra the crystalline compounds were dissolved in Nujol and measured between CsBr windows.

$t\mathrm{Bu_3SiAsH_2}$ (1): A solution of $[\mathrm{(dme)LiAsH_2}]$ (80.0 mmol) in 100 mL of 1,2-dimethoxyethane was cooled to –50 °C. Then,

Table 2. Comparison of selected structural parameters of lithium trialkylsilylphosphanides and -arsanides of the type $[\mathrm{(L)}_n\mathrm{LiE(H)SiR_3}]$ (E = P, As) with $\mathrm{HP(Si}i\mathrm{Pr_3)_2}$[26] and $\mathrm{E(Si}i\mathrm{Pr_3)_3}$.[16]

	Li–E	E–Si	Li–O	LiELi′	ELiE′	Ref.
$\mathrm{HP(Si}i\mathrm{Pr_3)_2}$	–	226.5	–	–	–	[27]
$\mathrm{P(Si}i\mathrm{Pr_3)_3}$	–	226.5	–	–	–	[16]
$[\mathrm{(THF)_2LiP(H)Si}i\mathrm{Pr_3}]_2$	258.0	219.5	196.5	83.8	96.2	[28]
$[\mathrm{(dme)LiP(H)Si}t\mathrm{Bu_3}]_2$	253.1	221.3	200.8	81.6	98.4	[23]
$[\mathrm{(dme)LiP(SiMe_3)_2}]_2$	255.9	220.5	201.9	75.7	104.3	[26]
$[\mathrm{(THF)_2LiP(SiMe_3)_2}]_2$	262	219.5	198	80.0	100.0	[29]
$[\mathrm{LiP(SiPh_3)_2}]_2$	247.2	219.3	–	72.9	107.0	[30]
$[\mathrm{(dme)LiPH_2}]_\infty$	256.7	–	203.2	176.5	117.8	[25,26]
$\mathrm{As(Si}i\mathrm{Pr_3)_3}$	–	237.3	–	–	–	[16b]
2	260.3	231.5	199.1	85.2	94.8	
3	259.5	233.8	190.4	141.8	128.4	
$[\mathrm{(1,4\text{-}dioxane)_3LiAsPh_2}]$	266	–	194	–	–	[31]
$[\mathrm{(THF)_2LiAs(H)Si}i\mathrm{Pr_3}]_2$	263	229.7	195	86	94	[28]
$[\mathrm{(dme)LiAs(SiMe_3)_2}]_2$	259	230.7	210	81	99	[10]
$[\mathrm{(THF)_2LiAs(SiMe_3)_2}]_2$	269	228.6	196	81.8	98.2	[11]
$[\mathrm{(Et_2O)_2LiAsPh_2}]_2$	273.3	–	198.6	89.5	90.3	[31]
$[\mathrm{(THF)LiAs(}t\mathrm{Bu)As}t\mathrm{Bu_2}]_2$	258	–	189	79.4	100.6	[32]
$[\mathrm{LiAs\{CH(SiMe_3)_2\}_2}]_3$	260	–	–	102	138	[33]
$[\mathrm{(THF)_2LiAs(H)Ph}]_\infty$	270	–	194	143.4	116	[22]

$F_3CSO_3SitBu_3$ (13.9 g, 40.0 mmol) dissolved in 25 mL of DME was added dropwise. After complete addition the reaction solution was heated to reflux for 5 h. Thereafter all volatile materials were removed in vacuo at room temp. and the residue redissolved in 100 mL of *n*-pentane. This solution was decanted from the precipitate. After removal of the solvent 8.84 g of tri(*tert*-butyl)silylarsane (**1**; 32.0 mmol, 80%) remained as a slightly yellow solid which was very sensitive towards moisture and air. M.p. 207 °C. ^{1}H NMR: δ = 1.10 (Si*t*Bu$_3$), 1.15 (AsH$_2$) ppm. ^{13}C{^{1}H} NMR: δ = 23.4 (SiC), 30.6 (SiCMe$_3$) ppm. ^{29}Si{^{1}H} NMR: δ = 31.20 (Si*t*Bu$_3$) ppm. IR: $\tilde{\nu}$ = 2292 cm^{-1} w, 2177 w, 2100 vs, 2091 vs, 1478 vs, 1441 w, 1423 w, 1390 vs, 1366 s, 1260 w, 1189 w, 1178 w, 1096 w, 1049 w, 1013 s, 956 m, 932 m, 913 w, 816 vs, 745 w, 695 vw, 648 m w, 624 s, 609 m, 587 m, 565 s, 495 vs, 450 s, 407 w, 378 w. $C_{12}H_{29}AsSi$ (276.37): calcd. C 52.15, H 10.58; found C 51.07, H 10.59.

[(dme)LiAs(H)Si*t*Bu$_3$] (2): Tri(*tert*-butyl)silylarsane (**1**; 0.42 g, 1.5 mmol) was dissolved in 10 mL of DME at –78 °C. Then, 1.5 mmol of *n*-butyllithium in hexane (0.6 ml of 2.5 M solution) was added dropwise. Whilst warming to room temp. the solution turned yellow. All volatile materials were removed at room temp. in vacuo and the residue was extracted with pentane. From this solution 0.44 g of **2** (0.6 mmol, 78%) precipitated at 0 °C in the shape of slightly blue prisms; decomp. above 135 °C. ^{1}H NMR: δ = –2.83 (LiAsH), 1.42 (Si*t*Bu$_3$), 3.11 (DME), 3.25 (DME) ppm. ^{7}Li{^{1}H} NMR: δ = 3.9 ppm. ^{13}C{^{1}H} NMR: δ = 24.1 (SiC), 32.2 (SiCMe$_3$), 58.5 (DME), 71.6 (DME) ppm. ^{29}Si{^{1}H} NMR: δ = 39.2 (Si*t*Bu$_3$) ppm. IR: $\tilde{\nu}$ = 2065 cm^{-1} vs, 1478 vs, 1444 m, 1407 vw, 1390 s, 1366 m, 1354 w, 1271 s, 1262 s, 1242 m, 1192 s, 1180 s, 1162 m, 1123 vs, 1107 vs, 1086 vs, 1046 s, 1032 s, 1014 vs, 956 w, 932 m, 869 s, 838 m, 814 vs, 644 m, 623 m, 592 s, 564 s, 539 m, 497 vs, 451 s, 410 m, 380 m, 354 w, 347 w, 343 w, 331 w, 325 w, 300 w. $C_{32}H_{76}As_2Li_2O_4Si_2$ (744.85): calcd. C 51.60, H 10.28; found C 51.03, H 10.28.

[(THF)LiAs(H)Si*t*Bu$_3$] (3): A 2.5 M solution of *n*-butyllithium in hexane (15 mL) was added dropwise to a solution of tri(*tert*-butyl)silylarsane (**1**; 0.58 g, 2.1 mmol) in 15 mL of THF at 0 °C. Whilst warming up to room temp. the solution turned greenish. Recrystallisation from benzene gave **3** (0.53 g, 1.5 mmol, 71%) as colourless prisms; decomp. above 127 °C. ^{1}H NMR: δ = –2.48 (LiAsH), 1.39 (THF), 1.47 (Si*t*Bu$_3$), 3.66 (THF) ppm. ^{7}Li{^{1}H} NMR: δ = 4.9 ppm. ^{13}C{^{1}H} NMR: δ = 23.9 (SiC), 25.2 (THF), 32.0 (SiCMe$_3$), 68.4 (THF) ppm. ^{29}Si{^{1}H} NMR: δ = 38.2 (Si*t*Bu$_3$) ppm. IR: $\tilde{\nu}$ = 2042 cm^{-1} s, 1495 w, 1477 s, 1444 m, 1388 m, 1381 s, 1359 m, 1354 m, 1316 w, 1293 vw, 1261 vw, 1246 vw, 1193 m, 1184 m, 1049 s, 1013 s, 973 m, 932 m, 917 m, 892 m, 817 vs, 729 s, 695 m, 673 w, 636 w, 621 m, 593 s, 563 s, 497 vs, 463 s, 454 s, 410 s, 393 s, 386 s, 348 m, 320 m, 308 m, 299 w. $C_{16}H_{36}AsLiOSi$ (354.40): calcd. C 54.22, H 10.24; found C 53.71, H 9.93.

Crystal Structure Determinations of 2 and 3: The data sets were collected on a STOE-IPDS diffractometer (operating at –73 °C) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) using oil-coated, rapidly cooled single crystals.[34] Crystallographic parameters, details of data collection and refinement procedures are summarised in Table 3. The structures were solved by direct methods with the program SIR97[35] and refined with the software packages SHELXL-93 and SHELXL-97.[36] Neutral scattering factors were taken from Cromer and Mann[37] and for the hydrogen atoms from Stewart et al.[38] The hydrogen atoms were considered with a riding model under the restriction of ideal tetrahedral symmetry at the corresponding carbon atoms. The arsenic-bound H atoms were taken from the residual electron density maps and refined isotropically.

CCDC-269668 (for **2**) and -269669 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystallographic data and details of the refinement procedures for the lithium tri(*tert*-butyl)silylarsanides of the type [(L)-LiAs(H)SiR$_3$] [L = DME (**2**), THF (**3**)].

	2	**3**·½C_6H_6
Empirical formula	$C_{16}H_{38}AsLiO_2Si$	$C_{19}H_{38}AsLiOSi$
Mol. mass	372.420	392.453
Temp. [K]	200(3)	200(3)
Crystal system	monoclinic	monoclinic
Space group[33]	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a [pm]	856.00(5)	1187.79(7)
b [pm]	2234.95(15)	873.01(4)
c [pm]	1167.09(7)	2245.39(16)
β [°]	105.427(7)	104.685(8)
V [Å^3]	2152.3(2)	2252.3(2)
Z	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.1493	1.1574
μ [mm^{-1}]	1.636	1.564
F(000)	800	840
No. of measured data	11393	15521
No. of independent data N_o (R_{int})	4055 (0.0396)	4127 (0.0421)
Abs. correction	numerical	numerical
T_{min}/T_{max}	0.567/0.774	0.666/0.811
Restraints	0	0
No. of parameters N_p	194	217
N_o/N_p	20.9/1	19.0/1
wR_2 (all data, on F^2)[a]	0.0604	0.0704
No. of data with $I > 2\sigma(I)$	3239	3163
wR_2 [$I > 2\sigma(I)$ on F^2]	0.0585	0.0675
R_1 [$I > 2\sigma(I)$]	0.0251	0.0284
Goodness of fit, s,[b] on F^2	0.926	0.942
Residual density [e Å^{-3}]	0.260/–0.277	0.541/–0.368

[a] $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

Acknowledgments

This work was generously supported financially by the German Research Foundation (Deutsche Forschungsgemeinschaft DFG, Bonn/Germany). We also thank Dr. H. Görls for his valuable support.

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Received: April 22, 2005