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The first beryllium diorganoarsenide: synthesis and structure of $(\eta^5\text{-}C_5Me_5)BeAs(t\text{-}Bu)_2$

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Abstract

The compound $(\eta^5\text{-}C_5Me_5)BeAs(t\text{-}Bu)_2$ (**1**) was prepared by the reaction of $(\eta^5\text{-}C_5Me_5)BeCl$ with $LiAs(t\text{-}Bu)_2$ in diethyl ether at 0°C. The structure of **1** has been determined by X-ray crystallography and is the first structurally characterized diorganoarsenide derivative of beryllium. It is monomeric in the solid state with the $As\text{-}t\text{-}Bu_2$ ligand acting as a one electron donor. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Beryllium; Diorganoarsenide; X-ray structure; Pentamethylcyclopentadienyl

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1. Introduction

Although alkali metal derivatives of organophosphorus and arsenic species have received considerable study [1–3], there is relatively little information on organogroup 15 derivatives of the alkaline earth metals [4]. In this report we describe the synthesis, spectroscopy and structural characteristics of $(\eta^5\text{-}C_5Me_5)BeAs(t\text{-}Bu)_2$, which to the best of our knowledge is the first beryllium diorganoarsenide.

2. Results and discussion

2.1. Synthesis of $(\eta^5\text{-}C_5Me_5)BeAs(t\text{-}Bu)_2$ (1)

The beryllium arsenide $(\eta^5\text{-}C_5Me_5)BeAs(t\text{-}Bu)_2$ (**1**) was prepared by the reaction of $(\eta^5\text{-}C_5Me_5)BeCl$ with $LiAs\text{-}t\text{-}Bu_2$ in diethyl ether at 0°C (Eq. (1)).

$$(\eta^5\text{-}C_5Me_5)BeCl + LiAs(t\text{-}Bu)_2 \rightarrow (\eta^5\text{-}C_5Me_5)BeAs(t\text{-}Bu)_2\ (\mathbf{1}) + LiCl \qquad (1)$$

The compound is thermally stable at room temperature (r.t.) and may be stored for extended periods under a nitrogen atmosphere. It is moderately air sensitive and decomposes over several hours when exposed to the atmosphere.

2.2. Spectroscopy and X-ray structure study

Spectroscopic data for **1** are in accord with the solid state structure as determined by X-ray crystallography. Thus the ^1H-NMR spectrum in C_6D_6 (25°C) for **1** consists of two singlets at δ 1.76 and 1.41 assigned to the $\eta^5\text{-}C_5Me_5$ and $t\text{-}Bu_2As$ protons, respectively. The $^{13}C\{^1H\}$-NMR spectrum has four lines which is consistent with the molecular structure. The $^9Be\{^1H\}$ spectrum at 42.18 MHz is a simple singlet at δ 14.16 (rel. $Be(NO_3)_2$ (aq.) δ 0.0). The monomeric nature of **1** is confirmed by the observation of the parent ion at $m/e = 333$ amu in the EI mass spectrum.

The molecular structure of **1** was established by a single-crystal X-ray diffraction study. A view of the

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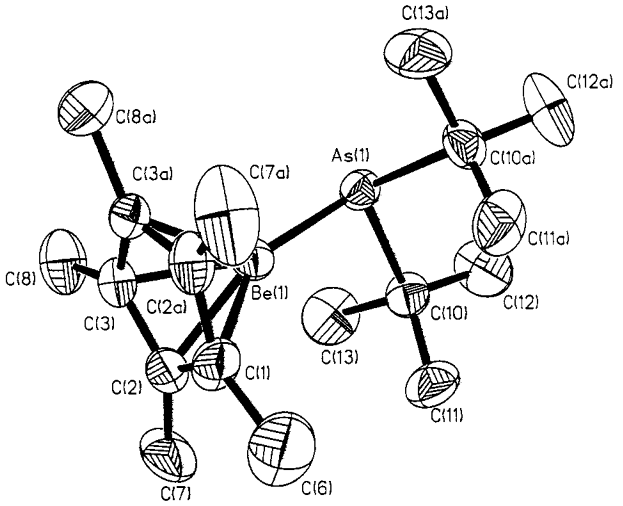

Fig. 1. A view of the molecule (η^5-C_5Me_5)BeAs(t-Bu)$_2$ (**1**). Atoms are shown at the 50% probability level.

molecule is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. Crystallographic data are given in Table 2 and atomic coordinates and equivalent isotropic displacement coefficients are given in Table 3. Compound **1** crystallizes in the orthorhombic space group *Pnma*. The unit cell contains two independent molecules of **1** (eight in total) which have very similar structural parameters. Each molecule sits on a crystallographically imposed mirror plane which contains the arsenic and beryllium atoms in addition to one carbon atom and its corresponding methyl group of the C_5Me_5 ring. The structure is similar to that of the previously reported phosphorus analog (η^5-C_5Me_5)BeP(t-Bu)$_2$ [4]. The monomeric nature of **1** is no doubt due to the steric demands of the bulky C_5Me_5 and t-Bu_2As groups. Counting the η^5-C_5Me_5 and As(t-Bu)$_2$ groups as five and one electron donors, respectively, gives the beryllium atom an electron count of eight. This is supported by the distorted pyramidal geometry of the As atom. Thus for the first independent molecule of **1** the angles about As(1) are 102.3(3)° (Be(1)–As(1)–C(10) and Be(1)–As(1)–(C 10A)) and 109.3(4)° (C(10)–As–C(10A)). (Values for the second independent molecule are similar).

Table 1
Selected bond lengths (Å) and bond angles (°) for one molecule of **1**

Bond lengths (Å)	
As(1)–Be(1)	2.174(14)
As(1)–C(10A)	2.013(7)
Be(1)–C(2)	1.912(14)
Be(1)–C(1)	1.907(18)
Be(1)–C(3)	1.896(14)
Bond angles (°)	
Be(1)–As(1)–C(10)	102.3(3)
C(10)–As(1)–C(10A)	109.3(4)
A3(1)–Be(1)–C(2)	142.7(4)
A3(1)–Be(1)–C(3)	134.6(7)
A3(1)–Be(1)–C(1)	149.2(8)

Table 2
Crystallographic data for **1**

Empirical formula	$C_{18}H_{33}AsBe$
Color, habit	Colorless, irregular
Crystal size (mm)	0.51 × 0.51 × 0.70
Formula weight	333.4
Crystal system	Orthorhombic
Space group	*Pnma*
Unit cell dimensions	
a (Å)	17.650(2)
b (Å)	15.589(2)
c (Å)	14.416(2)
V (Å^3)	3966(2)
Z	8
$D_{calc.}$ (g cm^{-3})	1.117
Absorption coefficient (cm^{-1})	17.05
Temperature (K)	298
Monochromator	Highly oriented graphite crystal
2θ range (°)	4.0–50.0
Scan speed (° min^{-1})	Max. 5.5 in ω (variable)
Scan range (ω)	1.00° plus K_α separation
Index ranges	$-20 \leq h \leq 10$, $-8 \leq k \leq 18$, $-8 \leq l \leq 17$
Reflections collected	4901
Independent reflections	3618
Reflections observed [$I > 2\sigma(I)$]	1815
Absorption correction	Ψ-scan
Max./Min. transmission	0.228/0.268
Refined parameters	193
R^a (observed data)	$R_1 = 5.73\%$, $wR_2 = 6.34\%$
R (all data)	$R_1 = 11.44\%$, $wR_2 = 17.62\%$
Goodness of fit on F^2	1.35
Data to parameter ratio	9.3:1
Largest difference peak (e Å^{-3})	0.99
Largest difference hole (e Å^{-3})	−0.51

[a] $R_1 = \Sigma||F_o - F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\max.(0, F_o^2)/3 + 2F_c2/3]$.

The C_5Me_5 group is bound in the well-known η^5-geometry with the Be–As vector tilted away from the normal to the ring (angle between Be–As vector and plane to ring = 171.9(5)° for molecule **1**), no doubt due to the steric demands of the t-Bu groups. Thus the As(1)–Be(1)–C(1) angle is 149.2(8)° while As(1)–Be(1)–C(2) and As(1)–Be(1)–C(3) are 142.7(4)° and 134.6(7)° respectively.

The Be–As distance found in the two independent molecules are the same to within experimental error (Be(1)–As(1) = 2.17(2) Å, Be(2)–As(2) = 2.18(2) Å) and to the best of our knowledge they have no precedent. These values may be compared to the sum of the covalent radii for Be and As (2.47 Å) [5]. The Be–C_5Me_5 (centroid) distance of 1.48(1) Å is the same within experimental error, as that found in (η^5-

$C_5Me_5)BeP(t\text{-}Bu)_2$ (1.48 Å) which is similar to that found in $(\eta^5\text{-}C_5H_5)BeMe$ (1.50 Å) [6] and in $(\eta^5\text{-}C_5Me_5)BeMe\cdots Yb(\eta^5\text{-}C_5Me_5)_2$ (1.45 Å) [7].

3. Experimental

3.1. General procedures

All reactions were carried out under a dry, oxygen free nitrogen atmosphere using standard Schlenk techniques or a Vacuum Atmospheres drybox. Diethyl ether and hexane were distilled under nitrogen from sodium–benzophenone ketyl immediately prior to use. $(\eta^5\text{-}C_5Me_5)BeCl$ was prepared as previously described [8] and $LiAs\textit{t}\text{-}Bu_2$ was prepared in situ from $t\text{-}Bu_2AsH$ and n-BuLi in diethyl ether [9]. NMR spectra were recorded on a GE-QE 300 spectrometer (^1H, 300.16 MHz; ^{13}C, 75.48 MHz; ^9Be, 42.18 MHz). ^1H and ^{13}C chemical shifts are referenced to $SiMe_4$ (δ 0.0) and ^9Be chemical shifts to $Be(NO_3)_2$ in D_2O (external standard). Infrared data was obtained on a Digilab FTS-40 spectrometer and mass spectral data on a Bell and Howell CE C 24-491 (EI) instrument. Melting point data was obtained in sealed capillaries under nitrogen (1 atm) and is uncorrected. Satisfactory microanalytical data (C, H) was obtained from Atlantic Microlab, Norcross, GA.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}
As(1)	1901(1)	2500	7789(1)	59(1)
Be(1)	2774(8)	2500	8851(9)	58(5)
C(1)	3823(6)	2500	9172(8)	87(6)
C(2)	3445(5)	1762(6)	9521(5)	76(3)
C(3)	2849(4)	2053(5)	10071(4)	63(3)
C(6)	4499(7)	2500	8573(10)	174(11)
C(7)	3667(6)	849(6)	9364(6)	137(5)
C(8)	2288(5)	1485(6)	10577(6)	107(4)
C(10)	2160(5)	1447(5)	7046(5)	72(3)
C(11)	3007(5)	1353(6)	6816(6)	103(4)
C(12)	1713(6)	1382(6)	6173(6)	131(5)
C(13)	1952(5)	697(6)	7680(7)	118(5)
As(2)	442(1)	2500	2158(1)	57(1)
Be(2)	−444(7)	2500	1105(9)	53(5)
C(21)	−1492(6)	2500	801(8)	86(6)
C(22)	−1111(5)	1774(5)	448(5)	77(3)
C(23)	−517(4)	2062(4)	−116(4)	62(3)
C(26)	−2165(7)	2500	1415(8)	181(11)
C(27)	−1331(6)	855(6)	594(7)	153(6)
C(28)	45(5)	1482(6)	−619(6)	117(5)
C(31)	185(5)	1446(5)	2910(5)	75(3)
C(32)	649(6)	1413(6)	3782(7)	141(5)
C(33)	−657(5)	1369(5)	3151(6)	109(4)
C(34)	396(5)	715(6)	2278(7)	117(5)

3.2. Synthesis of $(\eta^5\text{-}C_5Me_5)BeAs(t\text{-}Bu)_2$, **1**

A solution of $LiAs\text{-}t\text{-}Bu_2$ in diethyl ether (4.0 ml of a 0.70 M solution, 2.8 mmol) was added slowly to a stirred solution of $(\eta^5\text{-}C_5Me_5)BeCl$ (0.5 g, 2.78 mmol) in diethyl ether (100 ml) at 0°C. The mixture was allowed to warm to r.t. and was stirred for an additional 12 h. Volatile materials were removed under vacuum, the residue extracted into hexane (50 ml) and the solution filtered and concentrated to ca. 10 ml under vacuum. Cooling (−30°C) produced colorless crystals of **1** which were decanted from the supernatant liquid and dried under vacuum. Yield: 0.65 g, (70%) m.p. 75–76°C. NMR: $^1H(C_6D_6)$; δ 1.76 s, $(C_5\textit{Me}_5)$, 1.41 s, $(As\text{-}t\text{-}\textit{Bu}_2)$. $^{13}C\{^1H\}$ (C_6D_6); δ 109.34 s $(\textit{C}_5Me_5)$, 35.37 s $(C_5\textit{Me}_5)$, 29.85 s $(As\text{–}\textit{C}(CH_3)_3)$, 9.69 s $(As\text{–}C\text{–}(\textit{C}H_3)_3)$. $^9Be\{^1H\}(C_6D_6)$; δ 14.16 s. FT-IR (cm^{-1}): 2965 s, 2934 s, 2891 s, 2861 s, 1469 m, 1367 s, 1357 s, 1261 m, 1157 m, 1100 wbr, 1031 sh, 1016 m, 981 w, 821 sbr, 666 w. MS: M^+ 333 (EI).

3.3. X-ray crystallography

X-ray quality crystals of **1** were obtained by slow cooling of hexane solutions to −30°C. A suitable crystal was mounted in a thin-walled glass capillary and sealed under a nitrogen atmosphere. Data were collected on an Enraf–Nonius CAD-4 diffractometer at 25 ± 1°C. Data were collected in the 2θ–θ scan mode using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz, polarization, decay and absorption and the structure was solved by Patterson methods using the SHELXTL-PLUS software package [10]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in idealized positions with a common isotropic displacement parameter.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 103322 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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