

Asymmetric diarsines: Synthesis of dimeric pentamethylcyclopentadienylchloroarsine, dimeric pentamethylcyclopentadienyl(methyl)arsine and the crystal structure of dimeric pentamethylcyclopentadienyl(methyl)arsine

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Abstract

Reduction of pentamethylcyclopentadienyldichloroarsine (1) with cobaltocene in n-hexane affords dimeric pentamethylcyclopentadienylchloroarsine (2). The reaction of (2) with methyl lithium in ether gives dimeric pentamethylcyclopentadienyl(methyl)arsine (3), whose crystal structure has been determined. The crystal structure of (3) (triclinic, space group $P\bar{1}$, $a = 7.345(1)$, $b = 8.594(1)$, $c = 10.673(1)$ Å, $\alpha = 101.07(1)^\circ$, $\beta = 104.56(1)^\circ$, $\gamma = 113.69(1)^\circ$, $Z = 1$) shows two planes, one determined by two carbon atoms of the pentamethylcyclopentadienyl ligands and the two arsenic atoms, the other from two carbon atoms of the methyl ligands and the two arsenic atoms: these two planes display an angle of 78° alongside the axis formed by the two arsenic atoms. Compounds 2 and 3 are — to the best of our knowledge — the first examples of asymmetric diarsines which combine two asymmetric arsenic centres.

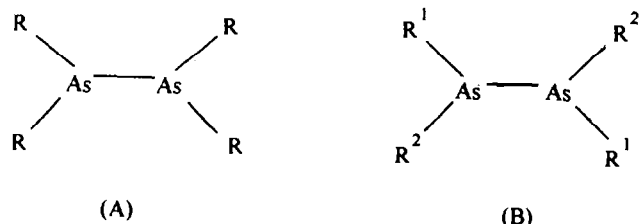
Keywords: Arsenic; Alkyl; Bulky ligands; Cyclopentadienyl; Group 15; X-ray diffraction

1. Introduction

Homonuclear element–element compounds containing As–As bonds have been extensively reported, e.g. cyclopolyarsines (RAs)_n [1–5], cyclopolyarsines R_nAs_m [6,7], and tetraorganodiarsines R₄As₂ [8–9]. Since the 1980's there has been great interest in the investigation of compounds R₄As₂: fitted with suitable organic ligands these molecules may exhibit “secondary contacts” between arsenic atoms of different molecules, exactly the same phenomenon observed in the related distibines and dibismuthines [10–16].

Generally, compounds R₄E₂ (E = As, Sb and Bi) can be synthesized 1) by reduction of R₃E with sodium in liquid ammonia followed by subsequent treatment with 1,2-dichloroethane, 2) by reduction of R₂EX (X = halogen) with sodium in liquid ammonia and 3) by reacting R₂EM (M = Li, Na) with R₂EX. Te-

traphenyldibismuth [17] was synthesized accordingly by reduction of diphenylbismuth chloride with cobaltocene.



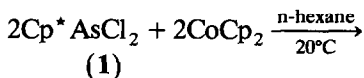
However, to date only compounds with structures like A can be synthesized and only those organo element–element compounds have been reported which contain the same organic ligands bonded to the main group elements. The thermochromic behaviour of compounds R₄E₂ is strongly dependent on the nature of the organic ligands, therefore it is challenging to attempt to synthesize compounds R₄E₂ with different organic ligands: in this paper we report the first examples of asymmetric substituted diarsines (R¹AsR²)₂ (R¹

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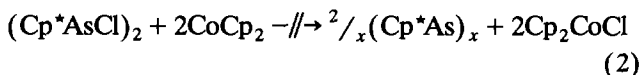
= Cp*, R² = Cl and CH₃) with structures like B incorporating two asymmetric arsenic centres.

2. Results and discussion

Compound **2** was prepared by reduction of **1** with cobaltocene in n-hexane at ambient temperature in high yield (78%) according to Eq. (1):

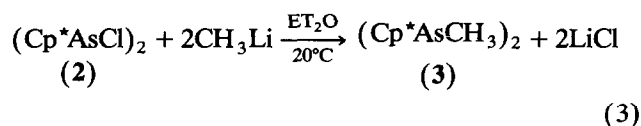


2 is very soluble in n-hexane, whereas Cp₂CoCl is practically insoluble and thus can be easily separated from the reaction mixture. At room temperature **1** cannot be further reduced by cobaltocene to the elusive [Cp*As]_n according to Eq. (2), the reason for this probably is the efficient protection of the As–Cl bonds by the bulky Cp*-ligands:



2 can be recrystallized from n-hexane as a yellow, microcrystalline solid, m.p. 130°C, soluble in inert organic solvents. Rotation around the As–As axis at room temperature is not hindered, but as soon as the temperature decreases, a rotational barrier becomes evident and can be monitored by NMR spectroscopy. In the ¹H-NMR spectrum of **2** at 298 K there is only one signal (δ = 1.74 ppm) for all hydrogen atoms, and in the ¹³C-NMR spectrum two signals (one at δ = 11.92 ppm for the methyl carbon atoms and another at δ = 126.95 ppm for the cyclopentadienyl ring carbon atoms) are observed. Lowering the temperature to 233 K gives rise to five signals in the ¹H-NMR spectrum for the methyl hydrogen atoms and to nine signals in the ¹³C-NMR spectrum for the Cp* and methyl carbon atoms (one signal for the methylene carbon atom of cyclopentadienyl ring maybe obscured by signals for the THF-solvent carbon atoms in the range from δ = 66.96 to 67.84 ppm).

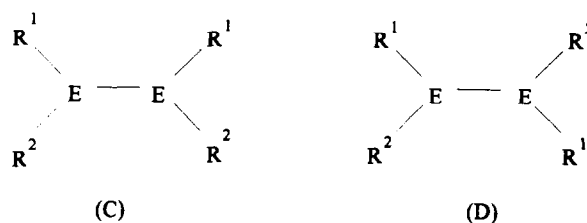
3 was prepared by the reaction of **2** with methyl lithium in ether in 71% yield according to Eq. (3):



3 is readily soluble in all inert organic solvents but can be recrystallized from n-hexane as yellow crystals, m.p. 96°C. The EI mass spectra exhibit the molecular ion at

m/e = 450, and supply all peaks required for a reasonable interpretation of the fragmentation scheme of **3**. In the NMR spectrum six signals for the methyl hydrogen atoms and ten signals for the methyl and Cp* carbon atoms (two signals of two methyl carbon atoms are located together at δ = 11.96 ppm) are displayed even at room temperature, and the ¹³C-NMR spectrum at 203 K gives eleven signals for all carbon atoms, indicating that free rotation around the As–As axis is already blocked at ambient temperature. Clearly, substitution of the two chlorine atoms in **2** by two bulkier methyl ligands in **3** leads to the observed phenomena in the NMR spectra.

These results strongly support our idea that the synthetic method described above can be extended to the preparation of organoelement compounds with structures like (C) and (D) (e.g. E = P, As, Sb and Bi):



Assuming that each lone pair at the arsenic atoms in **3** occupies a spatial segment, we can then assign to each arsenic atom four different ligands: due to the stabilizing bulky Cp* ligands only the centrosymmetric form (D) was obtained. However, if the R¹ and R² ligands are properly designed the alternative molecule (C) seems to be a feasible perspective.

2.1. Crystal structure solution of **3**

The crystal structure of **3** was determined by single crystal X-ray diffraction studies at 223 K. Figs. 1 and 2 represent a plot of the molecular structure and a stereo plot of the unit cell; crystallographic data are listed in Table 1. Some selected bond distances, bond angles plus torsions as well as atomic coordinates and

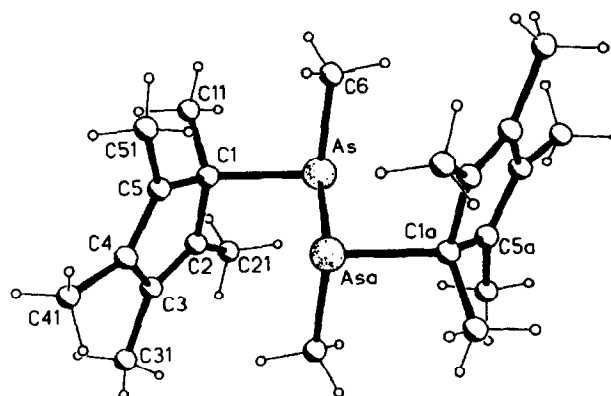


Fig. 1. Molecular structure of **3**.

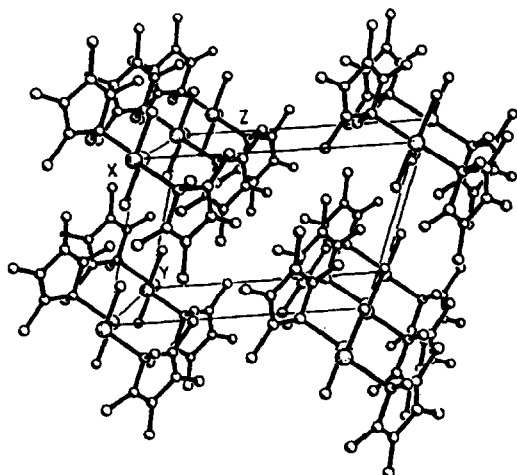


Fig. 2. Unit cell of 3.

equivalent isotropic temperature parameters are given in Tables 2 and 3 respectively.

Each of the arsenic atoms in 3 displays a distorted pyramidal coordination sphere in which each arsenic atom is linked to three different ligands, namely to the carbon atom of a methyl group, to a carbon atom of the Cp* ligand and to another arsenic atom. The bond

Table 2
Selected bond distances (Å), bond angles (°) and torsions (°) of 3 (with standard deviations in parentheses)

As–C(6)	1.982(3)	As–C(1)	2.043(3)
As–As	2.440(1)		
C(6)–As–C(1)	100.57(14)	C(6)–As–As	97.5(2)
C(1)–As–As	98.56(14)		
Torsions (symmetry transformations for equivalent atoms: #1–x, –y+2, –z)			
C(6a)–Asa–As–C(6)	–180.1(2)	Asa–As–C(1)–C(2)	–83.9(3)
C(1)–As–Asa–C(1a)	180.2(1)	C(1)–As–Asa–C(6a)	–78.1(2)

angles C(6)–As–C(1), C(1)–As–As and C(6)–As–As are 100.6°, 98.6° and 97.5°, respectively, each angle is considerably smaller than tetrahedral, indicating that the lone pairs at the arsenic atoms are predominantly of s-character.

Two planes can be defined in a molecule of compound 3: one plane includes two carbon atoms of the pentamethylcyclopentadienyl ligands and two arsenic atoms, the other plane two carbon atoms of the methyl ligands and two arsenic atoms. These two planes embrace an angle of 78° along the axis defined by the two arsenic atoms.

The As–As distance in 3 of 2.440(1) Å is in the same range as those already reported in other diarsines. In 3 we observed two markedly different As–C distances: one with 1.982(3) Å for the As–C (methyl ligand) distance is among the average values of already known arsenic compounds; the other with 2.043(3) Å for the As–C (pentamethylcyclopentadienyl ligand) distance, however, is somewhat longer than the As–C (methyl ligand) bond distance but compares well with the data found for As(C₅H₅)₃ (1.99–2.03 Å) [22] or C₅(CH₃)₅AsCl₂ (2.01 Å) [22]; a comparison of relevant As–As- and As–C distances is given in Table 4.

For the intermolecular As–As distances we observed a mean value of about 4.95 Å, considerably longer than the sum of the van der Waals radii [23] and that of the covalent radii from Pauling [24] of 4.00 Å;

Table 1
Crystallographic data of 3

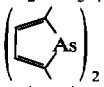
Formula:	C ₂₂ H ₃₆ As ₂
Molecular weight (g/mol):	450.35
Crystal size (mm × mm × mm):	0.50 × 0.40 × 0.15
Crystal system:	triclinic
Space group:	P $\bar{1}$
a (Å):	7.345(1)
b (Å):	8.594(1)
c (Å):	10.673(1)
α (°):	101.07(1)
β (°):	104.56(1)
γ (°):	113.69(1)
V (Å ³):	563.5(1)
Z:	1
D (calculated) g/cm ³ :	1.327
μ (Mo Kα) mm ⁻¹ :	2.966
Measuring temperature (K):	223(2)
2θ (°):	2.09–29.99
Scan type:	ω-scan
Collected data:	1860
Unique data:	1740 (R _{int} = 0.0216)
Absorption correction:	empirical on psi scans [18]
Structure solution:	direct methods [18]
Structure refinement:	on F ² with all data [19]
Hydrogen atoms:	riding model
R1 (on F):	0.0337 [for 1458 F _o > 4σ(F _o)]
wR ₂ (on F ²):	0.0907 (for all 1740 unique data)

Table 3
Atomic coordinates and equivalent isotropic displacement factors of 3 (pm² × 10⁻⁴)

Atom	x	y	z	U _{eq}
As	0.15863(5)	0.98132(4)	0.01005(3)	0.0356(2)
C(1)	0.3355(6)	1.1353(4)	0.2112(3)	0.0334(13)
C(11)	0.4916(8)	1.0670(6)	0.2651(4)	0.059(2)
C(2)	0.4427(6)	1.3258(5)	0.2102(3)	0.0431(15)
C(21)	0.6026(7)	1.3822(7)	0.1415(4)	0.075(2)
C(3)	0.3819(7)	1.4247(5)	0.2794(4)	0.050(2)
C(31)	0.4441(10)	1.6221(5)	0.3041(5)	0.086(3)
C(4)	0.2270(6)	1.3146(6)	0.3334(3)	0.051(2)
C(41)	0.1245(9)	1.3835(9)	0.4177(5)	0.093(3)
C(5)	0.2032(6)	1.1463(5)	0.2955(3)	0.043(2)
C(51)	0.0727(7)	0.9891(6)	0.3338(4)	0.080(2)
C(6)	0.0433(8)	0.7373(5)	0.0259(4)	0.048(2)

Supplementary material to the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76433 Eggenstein-Leopoldshafen 2, Germany, under specification of deposit no. CSD380064, names of the authors and the journal reference.

Table 4
Comparison of some structural data for selected organoarsines and diarsines

Compound	As–As distance (Å)	As–C distance (Å)	Ref.
As ₂ (SiMe ₃) ₄	2.46		8
As ₂ (CMe ₃) ₄	2.44–2.45	2.02–2.03	5
(AsCF ₃) ₄	2.45	2.02	4
As ₂ (CH ₃) ₄	2.43	1.97	20
	2.44	1.94	23
As(tolyl) ₃		1.96	21
AsCp ₃		1.99–2.03	22
Cp*AsCl ₂		2.01	22
(Cp*AsCH ₃) ₂	2.440	1.982 2.043	this work

in conclusion, to our belief there is no “secondary bonding” in compound 3

Fig. 3 shows a Newman projection of 3: the two bulky pentamethylcyclopentadienyl ligands are *trans*-positioned with reference to the As–As axis (assuming hindered rotation) in order to minimize steric repulsion.

3. Experimental section

All manipulations were carried out under an argon atmosphere. Solvents were dried by standard methods and were freshly distilled prior to use. Cp*AsCl₂ was prepared according to the literature [25]. Methyl lithium was purchased from Aldrich. CH-analyses were performed on a CHN-Rapid automat (Heraeus); NMR spectra were recorded on a Bruker AMX-500 (500 MHz) spectrometer. EI mass spectra were obtained with a Varian MAT CH 7A spectrometer, IR spectra were recorded on a Perkin-Elmer spectrometer.

3.1. Synthesis of 2

A solution of cobaltocene (4.53 g; 24 mmol) in *n*-hexane (100 ml) was added to a stirred solution of 1 (3.37 g; 12 mmol) at –78°C for 1 h. After 1 h stirring at

this temperature, the mixture was allowed to warm to 0°C and stirred for another 20 h. The originally red coloured solution turned to yellow and a precipitate was formed; the mixture was then stirred at room temperature for an additional 10 h. The solid was filtered and the yellow solution concentrated to about 50 ml and cooled to –30°C. After 50 h a first crop of yellow crystals was formed, separated by filtration and dried in vacuo; m.p. 130°C, yield 2.30 g (4.6 mmol, 78%). Found (%): C, 48.74; H, 6.14; As, 31.57; Cl, 14.48. C₂₀H₃₀As₂Cl₂ calc.: C, 48.90; H, 6.17; As, 30.15; Cl, 14.44%. ¹H-NMR (THF-*d*₈, 298 K): δ (ppm): 1.74, s, 15H, –CH₃. ¹³C-NMR (THF-*d*₈, 298 K): 11.92, –CH₃; 126.95, –C₅H₅. ¹H-NMR (THF-*d*₈, 233 K): 1.42, s, 3H, As–CH₃; 1.73, s, 3H, –CH₃; 1.76, s, 3H, –CH₃; 1.79, s, 3H, –CH₃; 1.84, (s, 3H), –CH₃. ¹³C-NMR: (THF-*d*₈, 233 K): 9.70, –CH₃; 10.48 –CH₃; 11.91 –CH₃; 12.55, –CH₃; 15.30, –C=C–; 130.80, –C=C–; 133.46, –C=C–; 142.39, –C=C–; 147.93, –C=C–. EI-MS (70 eV): *m/e*, ion, intensity (%): 490, M⁺, 0.2; 455, C₂₀H₃₀As₂Cl, 0.8; 355, C₁₀H₁₅As₂Cl, 0.6; 319, C₁₀H₁₅As₂Cl, 0.6; 245, C₁₀H₁₅AsCl, 100.0; 210, AsC₁₀H₁₅, 13.8; 150, As₂, 4.5; 135, C₁₀H₁₅, 31.0; 119, C₉H₁₁, 18.3; 105, C₈H₉, 11.3; 91, C₇H₇, 6.6; 77, C₆H₅, 2.4; 75, As, 0.5. IR (Nujol, ν cm^{–1}): 192m br, 280m, 294m br, 356m, 399m br, 416m br, 460vst, 487vst br, 571vw, 590vw, 639vw, 696vw, 721vw, 800vw, 919vw br, 1056w, 1138w, 1249w, 1304w, 1459m, 1561w, 1623w, 1655w br, 2365w br.

3.2. Synthesis of 3

A solution of methyl lithium in diethyl ether (4.4 mmol methyl lithium) was added to a stirred solution of 2 (1.10 g, 2.2 mmol) in diethyl ether (50 ml) at –70°C for 5 min and then stirred for 2 h. After warming to room temperature the mixture was stirred for 40 h. A precipitate was formed; the solvents were evaporated in vacuo and the residue extracted with petrol ether (80 ml). After filtration, the yellow filtrate was concentrated in vacuo until the first crystals appeared. Cooling this concentrated solution to –30°C for 48 h affords yellow crystals which were separated and dried in vacuo; m.p. 96°C, yield 0.70 g (1.6 mmol, 71%).

Found (%): C, 57.45; H, 7.88. C₂₀H₃₀As₂(CH₃)₂ calc. C, 58.67; H, 8.06%. ¹H-NMR (THF-*d*₈, 298 K): δ (ppm): 0.72, s, 6H, CH₃; 1.13, s, 6H, CH₃; 1.75, s, 6H, CH₃; 1.77, s, 6H, CH₃; 1.80, s, 6H, CH₃; 1.83, s, 6H, CH₃. ¹³C-NMR (THF-*d*₈, 298 K): δ (ppm): 3.15, As–CH₃; 10.58, CH₃; 11.02, CH₃; 11.96, CH₃; 18.05, CH₃; 58.06, –C–; 133.28, –C=C–; 133.86, –C=C–, 140.03, –C=C–; 140.74, –C=C–. ¹³C-NMR (THF-*d*₈, 203 K): δ (ppm): 2.99, As–CH₃; 10.97, CH₃; 11.42, CH₃; 12.10, CH₃; 12.21, CH₃; 18.22, CH₃; 57.30, –C–; 133.16, –C=C–; 133.78, –C=C–; 139.88, –C=C–;

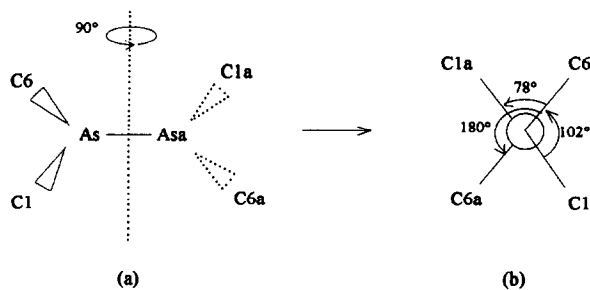


Fig. 3. Newman projection of 3.

140.76, $-\text{C}=\text{C}-$. EI-MS (70 eV): m/e , ion, intensity (%): 450, M^+ , 1.9; 315, $\text{M}-\text{Cp}^*$, 33.1; 225, $\text{M}-\text{Cp}^*-\text{CH}_3$, 33.8; 210, AsCp^* , 2.7; 150, As_2 , 1.3; 135, Cp^* , 100.0; 75, As, 0.5. IR (Nujol, cm^{-1}): 175w, 230m, 280vst, 398vst br, 404st, 480m br, 496m br, 430vw, 520w, 562m, 594m, 619vw, 706m, 723st/br, 792m, 813m, 833m, 872m, 930m br, 1006m, 1057st br, 1132m, 1115m br, 1238st, 1299m, 1638m, 1690w, 1714w, 2387m br, 3603w.

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