First Structural Study of a Stable Arsorane Containing 1,3,2-Dioxarsenane Rings and an N→As Donor−Acceptor Bond: Arsenic *vs* Phosphorus Chemical Behavior

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Introduction

Several unique stereochemical and conformational preferences including hexacoordination *via* intramolecular S→P donor−acceptor bonds have been reported recently for phosphoranes with six-membered and higher membered rings.[1,2] However, as far as arsenic is concerned, the known structural studies for mononuclear penta- or hexacoordinated compounds containing arsenic as a part of the ring have been restricted only to five-membered rings.[3,4] A comparative study with analogous arsoranes may give insight into (a) the effect of "d-block contraction"[5] at arsenic and (b) phosphorus chemistry and biochemistry.[3a] Our initial attempts to obtain structurally characterizable pentaoxyarsoranes with arsenic as a part of six-membered and higher membered rings using oxidative addition of a quinone or a diol to cyclic arsenites have been so far unsuccessful.[6] Since pentaoxyarsoranes can be expected to be good Lewis acids, one way to stabilize pentavalent arsenic is to make it hexacoordinated by internal coordination. In this paper we report the synthesis and structure of the first hexacoordinated arsorane, $(NC_9H_6O)As(OCH_2CMe_2CH_2O)_2$ (**7**), with 1,3,2-dioxarsenane rings and with an internal N→As donor−acceptor bond.

Also reported herein is the structure of the tetracoordinated arsenite $(NC_9H_6O)As(OCH_2CMe_2CH_2O)$ (**5**). The synthetic methodologies and the reaction patterns for phosphorus and arsenic are compared.

Experimental Section

Chemicals were procured from Aldrich or from local manufacturers; they were purified when required. Solvents were purified using standard procedures.[8] All operations, unless stated otherwise, were performed under a dry nitrogen atmosphere. ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR were recorded on a Bruker 200 MHz NMR spectrometer using $CDCl_3$ or C_6D_6 solution with shifts referenced to $SiMe_4$ ($\delta = 0$) or external 85% H_3PO_4 ($\delta = 0$). Elemental analyses were carried out on a Perkin-Elmer 240C CHN analyzer.

Caution! All arsenic compounds reported here should be considered as extremely toxic. Reactions involving these and/or benzene must be done inside an efficient hood with proper care.

Synthesis of the compounds $ClP(OCH_2CMe_2CH_2O)$ (**1**), $ClAs(OCH_2CMe_2CH_2O)$ (**2**), $(ClCH_2CMe_2CH_2O)P(O)(OCH_2CMe_2CH_2O)$ (**4**), and $ClAs(OCH_2CMe_2CH_2O)_2$ (**6**) have been reported before;[6,7] the compound $(NC_9H_6O)P(OCH_2CMe_2CH_2O)$ (**3**) [mp 51 °C; ^{31}P NMR δ 113.5] was prepared by reacting **1** with equimolar quantities of 8-hydroxyquinoline and triethylamine.

(a) Synthesis of the Cyclic Arsenite $(NC_9H_6O)As(OCH_2CMe_2CH_2O)$ (5). To **2** (1.56 g, 7.33 mmol) in dry benzene (30 mL) a mixture of 8-hydroxyquinoline (1.66 g, 7.33 mmol) and triethylamine (1.1 mL) in dry benzene (20 mL) was added dropwise. The reaction mixture was stirred for 4 h and filtered and the solvent removed. The residue was crystallized from a mixture of ether and hexane (1:3). Yield: 1.6 g (66%). Mp: 80 °C. ^{1}H NMR (C_6D_6): 0.41 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 3.48 (d, J = 8.0 Hz, 2H, OCH_2 (A)), 4.48 (d, 2H, OCH_2 (X)), 6.70−8.50 (m, 6H, H(Ar)). ^{13}C NMR (C_6D_6): 21.8, 22.9 (s each, CH_3), 33.2 (s, CMe$_2$), 71.2 (s, OCH_2), 110.6, 117.8, 121.2, 121.6, 127.5, 128.0, 136.0, 147.7, 153.3 (all C(Ar)). Anal. Calcd for $C_{14}H_{16}AsNO_3$: C, 52.55; H, 5.02; N, 4.36. Found: C, 52.84; H, 5.25; N, 4.54.

(b) Synthesis of the Arsorane $(NC_9H_6O)As(OCH_2CMe_2CH_2O)_2$ (7). To **2** maintained at −60 °C was added a solution of 2,2-dimethyl-1,3-propane diol (1.68 g, 16.17 mmol) and *N*-chlorodiisopropylamine (2.20 g, 16.17 mmol) in ether (40 mL) over a period of 15 min with continuous stirring. The mixture was brought to 30 °C, stirred overnight, and filtered. The precipitate was washed with ether (10 mL) and washings added to the filtrate. To the combined solution, a mixture of 8-hydroxyquinoline (2.38 g, 16.17 mmol) and triethylamine (1.64 g, 16.17 mmol) in ether was added. The obtained solution was stirred for 3 h and filtered. Solvent was completely removed from the filtrate and the residue crystallized from a CH_2Cl_2−hexane mixture (1:4). Yield: 4.5 g (65%). Mp: 187−192 °C. ^{1}H NMR: 0.71 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 3.38−4.76 (m, 8H, OCH_2), 7.22−9.34 (m, 16H, H (Ar)). ^{13}C NMR: 22.0, 22.2, 22.6, 23.5 (s each, CH_3), 71.6, 76.0, 78.7, 78.9 (s each, OCH_2), 111.0, 114.5, 121.5, 127.0, 130.9, 140.7, 151.0 (all C (Ar)). Anal. Calcd for $C_{19}H_{26}AsNO_5$: C, 53.90; H, 6.15; N, 3.31. Found: C, 53.85; H, 6.00; N, 3.20.

The same compound **7** was also prepared by reacting pure **6** with 8-hydroxyquinoline/triethyl amine, but this involved more steps and the final yields were lower.

(c) Reaction of 3 with 2,2-Dimethylpropane-1,3-diol/*N*-Chlorodiisopropylamine. To a mixture of **3** (1.42 g, 4.12 mmol) and 2,2-dimethylpropane-1,3-diol (0.43 g, 4.12 mmol) in ether (40 mL) maintained at −60 °C was added *N*-chlorodiisopropylamine (0.50 g, 4.12 mmol) in ether (30 mL) over a period of 15 min with continuous stirring. The mixture was brought to 30 °C, stirred overnight, and filtered, and the solvent was completely removed from the filtrate to yield an air-sensitive semisolid {δ(^{31}P): −67.3, −67.5}; use of toluene as a solvent also resulted in a semisolid. [^{1}H NMR (major signals, *ca*. 80%): 0.90 (s, *ca*. 6H, 2CH_3), 3.70 (br d, *ca*. 4H, OCH_2), 6.70−8.50 (m, *ca*. 6H, H (Ar)). ^{31}P NMR (major signals, *ca*. 80%): −67.3, −67.5 ppm.[9] MS: 379 {M}$^+$, 235 {P(OCH$_2$CMe$_2$CH$_2$O)$_2$}$^+$, 221, 208, 200 (?), 191, 167 {P(OH)$_2$(OCH$_2$CMe$_2$CH$_2$O)}+, 145.] Over a period of 2 days (from toluene solution), a crystalline solid (*ca*. 0.1 g), mp 110−115 °C, was isolated. ^{1}H NMR spectrum of this compound showed broad peaks at 1.08 (CH_3), 4.23 (d, $J \approx 20$ Hz, OCH_2) and 7.00−9.00 ppm with integrated intensity ratios of oxinate to diol residue ≈ 2:1.

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(1) (a) Prakasha, T. K.; Day, R. O.; Holmes, R. R., *Inorg. Chem.* **1992**, *31*, 1913. (b) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 3391. (c) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1993**, *32*, 4360.

(2) (a) Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6092. (b) Day, R. O.; Kumara Swamy, K. C.; Fairchild, L.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 1627. (c) Burton, S. D.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6104.

(3) (a) Bohra, R.; Roesky, H. W. *Adv. Inorg. Radiochem.* **1984**, *28*, 203. (b) Poutasse, C. A.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *Organometallics* **1985**, *4*, 708.

(4) Maroni, P.; Holeman, M.; Wolf, J. G.; Ricard, L.; Fischer, J. *Tetrahedron Lett.* **1976**, *15*, 1193.

(5) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, England, 1989; p 655.

(6) Said, M. A.; Kumara Swamy, K. C.; Chandra Mohan, K.; Venkatalakshmi, N. *Tetrahedron* **1994**, *50*, 6989.

(7) Said, M. A.; Kumara Swamy, K. C.; Veith, M.; Huch, V. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2945.

(8) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, England, 1986.

(9) This value is close to the ^{31}P NMR shift value (−66.9) of the product, ascribable to the pentacoordinated phosphorane $(OCH_2CMe_2CH_2O)_2P$(O-2,4,6-$Me_3C_6H_2$), in the reaction of $(OCH_2CMe_2CH_2O)P$(O-2,4,6-$Me_3C_6H_2$) with $HOCH_2CMe_2CH_2OH/ClN(i\text{-}Pr)_2$: Said, M. A.; Kumara Swamy, K. C. Unpublished data. For more ^{31}P NMR correlations see: Holmes, R. R.; Prakasha, T. K. *Phosphorus, Sulfur Silicon* **1993**, *80*, 1.

S0020-1669(95)01621-1 CCC: $12.00

Table 1. Crytallographic Data for **5** and **7**

	5	**7**
formula	$C_{14}H_{16}AsNO_3$	$C_{19}H_{26}AsNO_5$
fw	321.2	423.33
T (K)	293(2)	293(2)
space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.013(7)	9.631(12)
b/Å	10.501(8)	9.969(13)
c/Å	13.553(9)	11.34(2)
α/deg	86.40(6)	114.38(10)
β/deg	83.54(6)	106.25(10)
γ/deg	86.87(6)	93.18(10)
V/Å^3	1412(2)	934(2)
Z	4	2
d_{calcd}/g cm^{-3}	1.511	1.506
λ/Å	0.710 73	0.710 73
μ/cm^{-1}	24.11	18.5
F(000)	656	440
no of reflcns collcd	3859	3286
no. of indep reflcns	3683 ($R_{int} = 0.0201$)	3286 ($Ri_{nt} = 0.0000$)
no. of obsd reflcns	2630 ($I > 2\sigma(I)$)	3036 ($I > 2\sigma(I)$)
final R indices[a]	R1 = 0.0375	R1 = 0.0445
($I > 2\sigma(I)$)	wR2 = .0827	wR2 = 0.1211

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

^{31}P NMR: −127.0 (br). Anal. Calcd for $C_{23}H_{23}N_2O_4P$: C, 65.40; H, 5.45; N: 6.64. Found: C, 65.83; H, 5.10; N, 7.00 (see text). This compound underwent rapid hydrolysis in $CDCl_3$ solution to lead to a phosphate ester ($\delta(^{31}P) = -14$ ppm).

When **5** was treated with 2,2-dimethylpropane-1,3-diol/*N*-chlorodiisopropylamine, no reaction occurred.

X-ray Crystallography. Suitable crystals of **5** and **7** were mounted inside Lindemann capillaries. Data were collected on a Siemens Stoe AED2 diffractometer. The structures were solved and refined by conventional methods.[10] The details pertaining to data collection and refinement are listed in Table 1. The final atomic parameters are listed in Table 2. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed by geometry and refined isotropically.

Results and Discussion

The synthetic routes leading to compound **5** and **7** are shown in Scheme 1 along with those for similar reactions for phosphorus. Two important features are discernible from the Scheme 1.

(a) Whereas the hexacoordinated arsenic compound $(NC_9H_6O)As(OCH_2CMe_2CH_2O)_2$ (**7**) is readily formed from its chloro precursor $ClAs(OCH_2CMe_2CH_2O)_2$ (**6**), such a route is not feasible for phosphorus, because the intermediate $ClP(OCH_2CMe_2CH_2O)_2$ most likely forms the phosphonium salt $[P(OCH_2CMe_2CH_2O)_2]^+[Cl]^-$ which by internal attack of $-Cl^-$ on α-carbon of the ring leads to the tetracoordinated derivative **4**.[6]

(b) Whereas the P(III) precursor $(NC_9H_6O)P(OCH_2CMe_2CH_2O)$ (**3**) reacts readily with the diol/$ClN(i\text{-}Pr)_2$, the reaction with the corresponding arsenic analogue **5** fails completely. The ^{31}P NMR spectrum of the reaction mixture from **3** shows a signal at *ca* −67.0 ppm attributable to the pentacoordinated derivative $(NC_9H_6O)P(OCH_2CMe_2CH_2O)_2$ (without N→P coordination) on the basis of ^{1}H and ^{31}P NMR;[9] however, upon attempted crystallization, it led to an air-sensitive crystalline compound with $\delta(^{31}P) = -127.0$ ppm. The ^{1}H NMR spectrum and elemental analysis of this product show that it is not the expected product and is probably $H[(NC_9H_6O)_2P(OCH_2CMe_2CH_2O)]$ with N→P coordination.

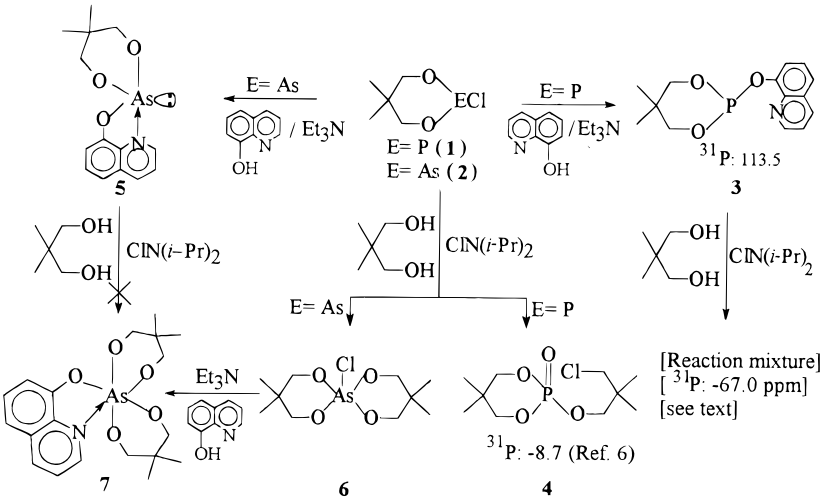
Compound **7** can be obtained as an yellow crystalline solid from dichloromethane−*n*-heptane mixture. Assuming that hexacoordination persists in solution, we can easily recognize that the two six-membered arsenane rings should be chemically and magnetically inequivalent; the ^{1}H NMR spectrum shows four methyl signals (0.72, 1.02, 1.11, and 1.17 ppm) of equal intensity and a large number (15 lines, 3.30−4.80 ppm) for the OCH_2 protons showing the nonequivalence of these protons and

Table 2. Atomic Coordinates ($\times 10^4$) for Non-Hydrogen Atoms in **5** and **7**

	x	y	z
	Compound **5**		
As(1)	1547(1)	1873(1)	4398(1)
O(1)	1163(3)	3486(3)	4678(2)
O(2)	3062(3)	2118(3)	3588(3)
O93)	607(3)	1824(4)	3319(2)
N(1)	−939(4)	1544(4)	5109(3)
C(1)	1387(5)	4474(5)	3899(4)
C(2)	2829(5)	4474(5)	3402(4)
C(3)	3166(5)	3225(5)	2916(4)
C(4)	2923(6)	5543(6)	2578(4)
C(5)	3794(6)	4674(6)	4162(4)
C(6)	−743(5)	1703(5)	3341(4)
C(7)	−1314(5)	1710(5)	2480(4)
C(8)	−2698(5)	1569(5)	2487(4)
C(9)	−3516(5)	1419(6)	3355(4)
C(10)	−2955(5)	1431(5)	4269(4)
C(11)	−3725(5)	1299(5)	5215(4)
C(12)	−3087(6)	1275(5)	6047(4)
C(13)	−1711(6)	1402(5)	5962(4)
C(14)	−1569(5)	1547(5)	4264(3)
As(2)	799(1)	1080(1)	8914(1)
O(4)	2294(3)	1901(4)	9014(2)
O(5)	513(3)	1690(3)	7708(2)
O(6)	−203(3)	2285(4)	9643(3)
N(2)	−1705(4)	524(4)	8908(3)
C(15)	2408(5)	3189(6)	8608(4)
C(16)	2203(5)	3344(5)	7520(4)
C(17)	779(5)	2976(5)	7394(4)
C(18)	3233(6)	2537(6)	6900(4)
C(19)	2296(6)	4768(6)	7186(4)
C(20)	−1563(5)	2445(5)	9717(4)
C(21)	−2185(6)	3477(6)	10171(4)
C(22)	−3588(7)	3633(6)	10280(4)
C(23)	−4378(6)	2804(6)	9928(4)
C(24)	−3780(5)	1750(5)	9429(4)
C(25)	−4500(5)	825(6)	9009(4)
C(26)	−3827(6)	−178(6)	8565(4)
C(27)	−2434(6)	−298(6)	8542(4)
C(28)	−2371(5)	1546(5)	9337(3)
	Compound **7**		
As	3686(1)	2137(1)	2222(1)
O(1)	2473(3)	2079(3)	3253(3)
N	4124(3)	220(3)	2376(3)
O(2)	4893(3)	1939(3)	1239(3)
O(3)	5138(3)	3066(3)	3831(3)
O(4)	2232(3)	847(3)	720(3)
O(5)	3154(3)	3817(3)	2243(3)
C(1)	2556(4)	1004(4)	3644(4)
C(2)	1826(5)	804(5)	4448(5)
C(3)	2004(5)	−381(6)	4798(5)
C(4)	2867(5)	−1380(6)	4358(5)
C(5)	3606(4)	−1237(5)	3501(4)
C(6)	3453(4)	−29(4)	3176(4)
C(7)	4484(5)	−2207(5)	2908(5)
C(8)	5107(5)	−1948(5)	2077(5)
C(9)	4923(5)	−712(4)	1808(4)
C(10)	6022(5)	3186(5)	1630(4)
C(11)	7076(5)	3783(5)	3070(4)
C(12)	6210(5)	4269(4)	4055(4)
C(13)	7948(5)	2613(6)	3249(5)
C(14)	8128(6)	5178(6)	3364(6)
C(15)	1627(6)	1181(6)	−376(5)
C(16)	1129(5)	2669(5)	22(5)
C(17)	2415(6)	3880(6)	985(6)
C(18)	−146(8)	2673(7)	500(10)
C(19)	603(9)	2854(8)	−1293(7)

(10) (a) Sheldrick, G. M. SHELX-86. *Acta Crystallogr*. **1990**, *A46*, 467. (b) Sheldrick, G. M. SHELXL-93. Göttingen University.

Scheme 1



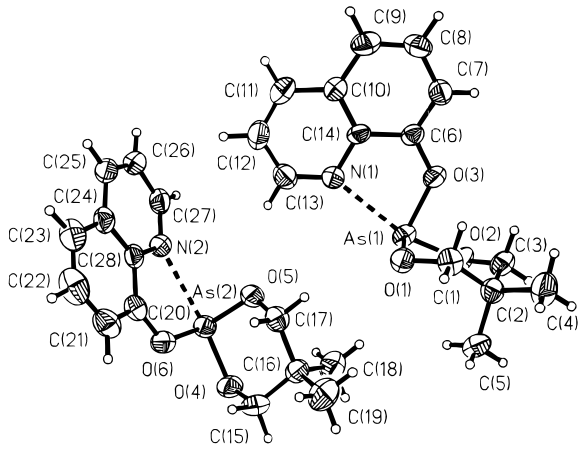


Figure 1. Molecular structure of **5**.

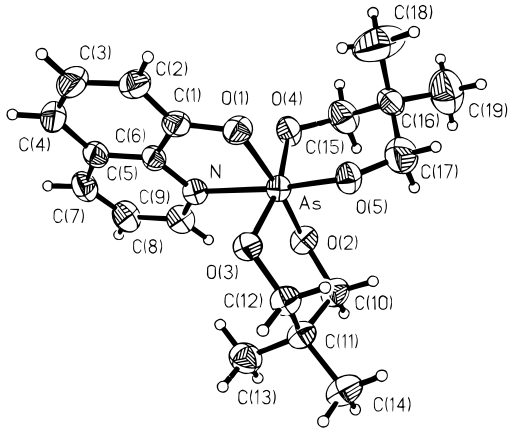


Figure 2. Molecular structure of **7**.

thus the rigidity of the hexacoordinated structure. It should be noted here that both $ClAs(OCH_2CMe_2CH_2O)_2$[6] and $PhP(OCH_2CMe_2CH_2O)_2$,[11] which contain two six-membered rings, each show only one signal for either OCH_2 or CH_3 protons because of Berry pseudorotation. The ^{13}C NMR spectrum of **7** also exhibits four distinct signals for the methyl and the OCH_2 carbons.

The X-ray structures of both **5** (Figure 1) and **7** (Figure 2) have been determined; bond distances and bond angles for these are shown in Table 3. Compound **5** is the first four-coordinated arsenic compound with a 1,3,2-dioxarsenane ring, while **7** represents the first six-coordinated arsorane with 1,3,2-dioxarsenane rings. Other significant features include the following.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **5** and **7** with Eds's in Parentheses

Compound **5**			
As(1)−O(1)	1.771(4)	As(2)−O(4)	1.790(4)
As(1)−O(2)	1.790(3)	As(2)−O(5)	1.767(3)
As(1)−O(3)	1.830(4)	As(2)−O(6)	1.838(4)
O(1)−C(1)	1.442(6)	O(4)−C(15)	1.433(6)
O(2)−C(3)	1.433(6)	O(5)−C(17)	1.420(6)
C(1)−C(2)	1.523(7)	C(15)−C(16)	1.510(7)
C(2)−C(3)	1.510(8)	C(16)−C(17)	1.528(7)
As(1)−N(1)	2.599(4)	As(2)−N(2)	2.606(5)
O(1)−As(1)−O(2)	97.7(2)	O(5)−As(2)−O(4)	97.6(4)
O(1)−As(1)−O(3)	98.9(2)	O(5)−As(2)−O(6)	99.0(2)
O(2)−As(1)−O(3)	90.1(2)	O(4)−As(2)−O(6)	90.1(2)
C(1)−O(1)−As(1)	119.0(3)	C(15)−O(4)−As(2)	119.7(3)
C(3)−O(2)−As(1)	120.2(3)	C(17)−O(5)−As(2)	120.7(3)
O(1)−C(1)−C(2)	113.7(4)	O(4)−C(15)−C(16)	113.3(5)
C(3)−C(2)−C(1)	109.1(4)	C(15)−C(16)−C(17)	108.9(4)
O(2)−C(3)−C(2)	114.3(4)	O(5)−C(17)−C(16)	114.0(4)
O(3)−C(6)−C(14)	120.6(4)	O(6)−C(20)−C(28)	121.4(5)
N(1)−C(14)−C(6)	116.8(4)	N(2)−C(28)−C(20)	116.5(5)
N(1)−As(1)−O(1)	84.3(2)	N(2)−As(2)−O(6)	74.08(15)
N(1)−As(1)−O(2)	164.1(2)	N(2)−As(2)−O(5)	80.0(2)
N(1)−As(1)−O(3)	74.02(14)	N(2)−As(2)−O(4)	163.3(2)
C(14)−N(1)−As(1)	102.2(3)	C(28)−N(2)−As(2)	101.9(3)
Compound **7**			
As−O(5)	1.771(3)	As−O(4)	1.781(5)
As−O(3)	1.782(4)	As−O(2)	1.789(3)
As−O(1)	1.883(3)	As−N	2.045(4)
O(1)−C(1)	1.317(5)	N−C(6)	1.341(5)
O(2)−C(10)	1.432(5)	O(3)−C(12)	1.426(5)
O(4)−C(15)	1.398(6)	O(5)−C(17)	1.434(7)
C(1)−C(6)	1.412(6)	C(10)−C(11)	1.501(6)
C(11)−C(12)	1.516(6)	C(15)−C(16)	1.510(7)
C(16)−C(17)	1.474(8)		
O(5)−As−O(4)	97.8(2)	O(5)−As−O(3)	94.5(2)
O(4)−As−O(3)	166.30(13)	O(5)−As−O(2)	98.4(2)
O(4)−As−O(2)	90.3(2)	O(3)−As−O(2)	93.9(2)
O(5)−As−O(1)	89.9(2)	O(4)−As−O(1)	88.1(2)
O(3)−As−O(1)	85.8(2)	O(2)−As−O(1)	171.69(12)
O(5)−As−N	171.79(13)	O(4)−As−N	82.6(2)
O(3)−As−N	84.4(2)	O(2)−As−N	89.8(2)
O(1)−As−N	81.9(2)	C(10)−O(2)−As	119.4(3)
C(12)−O(3)−As	119.4(3)	C(15)−O(4)−As	121.4(3)
C(17)−O(5)−As	120.5(3)	O(2)−C(10)−C(11)	114.5(3)
C(10)−C(11)−C(12)	108.7(4)	O(3)−C(12)−C(11)	112.8(3)
O(4)−C(15)−C(16)	114.5(4)	C(17)−C(16)−C(15)	108.8(4)
O(5)−C(17)−C(16)	116.0(5)		

(11) Kumara Swamy, K. C.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6095.

(i) Compound **5** has a stereoactive lone pair approximately in the equatorial plane of a trigonal bipyramid, with the axial positions being occupied by an oxygen of the six-membered ring and (the less electronegative) nitrogen of the oxinate. The dihedral angle between the planes O(2)−O(1)−O(3) and O(1)−O(3)−N(1) is 47.2° while that between O(4)−O(5)−O(6) and O(5)−O(6)−N(2) is 43.8° for the two molecules in the asymmetric unit of **5**; these represent a distortion of nearly 11% and 17% respectively from trigonal bipyramidal geometry for the two molecules.

(ii) To our knowledge compound **7** has the shortest N→As donor−acceptor bond (2.04 Å). [The N→As distances in **5**, $MeN(CH_2CH_2O)_2As(Me)(O_2C_6Cl_4)$[4] and $Me_3N-AsCl_3$[12] are 2.60, 2.18 and 2.28 Å respectively.]

(iii) Even after hexacoordination, the As−O bond lengths to the oxygens of the six-membered rings in **7** are surprisingly very close to that for the tetracoordinated compound **5**.

(iv) For **7** and for both the molecules (enantiomers) in the asymmetric unit of **5**, the 1,3,2-dioxarsenane rings are in a chair conformation; this contrasts with the twist−boat conformation observed for $ClAs[OCMe_2CH_2CMe_2O]$[13] and the boat conformations observed for $PhP(OCH_2CMe_2CH_2O)_2$.[7]

Finally it should be mentioned that our route employed here for arsoranes is new and allows flexibility for the synthesis of penta- or hexacoordinated derivatives with rings of different sizes on the arsenic atom.

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Supporting Information Available: Tables of atomic coordinates with equivalent isotropic displacement parameters, anisotropic thermal parameters, and complete of bond lengths and bond angles (6 pages). Ordering information is given on any current masthead page.

IC951621+

(12) Webster, N.; Keats, S. *J. Chem. Soc. A* **1971**, 836.

(13) Nufted, P. V.; Lenstra, A. T. H.; Geise, H. J.; Yuldasheva, L. K.; Chadeva, N. *Acta Crystallogr.* **1982**, *B38*, 3089.

Additions and Corrections

1995, Volume 34

B. Scott Jaynes, Linda H. Doerrer, Shuncheng Liu, and Stephen J. Lippard*: Synthesis, Tuning of the Stereochemistry, and Physical Properties of Cobalt(II) Tropocoronand Complexes.

Pages 5735 and 5737. The *a* and *c* crystallographic axes for [Co(TC-4,5)] should be interchanged, and the space group should be *P*2/*a*. The positional parameters, bond distances and angles, and all discussion are unaffected by this correction.

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