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Synthesis and molecular structure of methyl 4,6-benzylidene-3-deoxy-3-diphenylarsino-α-D-altropyranoside

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Abstract

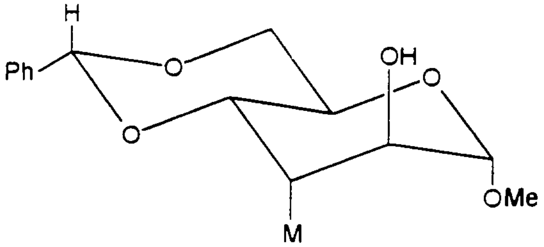
The synthesis, NMR spectra (solution ^1H and ^{13}C, and solid-state ^{13}C) and the crystal structure of methyl 4,6-O-benzylidene-3-deoxy-3-diphenylarsino-α-D-altropyranoside (I) are reported. Air-stable I was obtained by reaction of Ph_2 AsLi with either methyl 2,3-anhydro-4, 6-*O* benzylidene-α-D-mannopyranoside or methyl 4, 6-*O*-benzylidene-2-*O*-*p*-toluenesulphonyl-α-D-glucopyranoside. In both the solid state and in solution, the pyranose ring in compound I adopts a $^4C_1$ conformation. The geometry about the arsenic atom is pyramidal, with the C–As–C valency angles between 97.7(2)° and 100.7(2)°, and the C–As bond lengths in the range 1.965(6)–2.003(6) Å.

Keywords: Arsenic; Carbohydrate; Crystal structure

1. Introduction

Carbohydrates are a vital and well-studied group of organic compounds. However, the use of carbohydrate as C-bonding ligands in organometallic compounds has yet to attract much systematic attention. As a group of functionally substituted organic moieties, carbohydrates can impart useful properties and features to organometallic compounds, including enhanced water solubility and chirality. The ready availability of monosaccharide precursors from natural sources and the extensive literature on their chemical modification and on protecting groups, provide further strong encouragement for the study of metallated carbohydrates.

Our previous reported work on metallated carbohydrates has concentrated on tin compounds [1,2], but we have also been investigating arsenic derivatives. We now report the synthesis and structure of methyl 4,6-*O*-benzylidene-3-deoxy-3-diphenylarsino-α-D-altropyranoside, **I**. Comparison is made with the structures of the triphenyltin (**II**) [1] and diphenylphosphinyl (**III**) [3], analogues of **I**.



(**I**); M = Ph_2As
(**II**); M = Ph_3Sn
(**III**); M = $Ph_2P(O)$
(**VI**); M = Ph_2P

2. Experimental details

4,6-*O* Benzylidene-2-*O*-p-toluenesulphonyl-α-D-glucopyranoside and methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside [4] were obtained by published procedures.

2.1. Preparation of lithium diphenylarsinide

A mixture of lithium and a solution of Ph_3As in anhydrous THF (mole ratio of $Li:Ph_3As = 2:1$) was agitated with ultrasound for several hours under nitrogen. After addition of tert-butyl chloride [$Ph_3As{}^tBuCl = 1:1$] to destroy the PhLi co-product, the resulting solution of Ph_2AsLi was used immediately.

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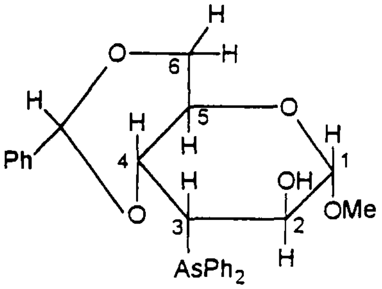
2.2 *Methyl 4,6-O-benzylidene-3-deoxy-3-C-diphenylarsino-α-D-altropyranoside*

To a cooled, stirred solution of lithium diphenylarsinide, obtained from Ph_3As (11 mmol) in anhydrous THF (100 ml) under nitrogen was added dropwise during 30 min, a solution of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (5 g, 19 mmol) in anhydrous THF (100 ml). The mixture was stirred for 2 h after addition was complete, then water was added and tetrahydrofuran removed under reduced pressure. The solid, which formed on removal of the THF was twice recrystallised from ethyl acetate/hexane to yield colourless prisms: yield 8.4 g (89%), m.p. 193–195°C. Anal. Found: C, 63.0; H, 5.5. $C_{26}H_{27}AsO_5$ Calc.: C, 63.2; H, 5.5%. Formula 2, below, shows the numbering system used in the NMR spectra.



^1H NMR: (500 MH_z $CDCl_3$ δ: 7.83 (m, 2H) and 7.63 (m, 2H) (*o*-H of Ph_2As), 7.27 (m, 6H, *m*-$^+$*p*-H of Ph_2 As), 7.16 (t, 1H, *p*-H of *Ph* CH), 7.08 (t, 2H, *m*-H of *Ph* CH), 6.69 (d, 2H, *o*-H of *Ph* CH), 5.53 (s, 1H, H-7), 4.50 (s, 1H, H-1), 4.44 [dd, $J(H_3–H_4) = 5.0$ Hz, $J(H_4–H_5) = 9.4$ Hz, H-4] 4.42 [dt, $J(H_4–H_5) = 9.4$ Hz, $J(H_5–H'_6) = 9.5$ Hz, $J(H_5–H_6) = 4.7$ Hz H-5], 4.27 [dd, $J(H_5–H_6) = 4.7$ Hz, $J(H_6–H'_6) = 10.0$ Hz, H-6], 3.82 [*t*, $J(H_5–H'_6) = 9.5$ Hz, $J(H_6–H'_6) = 10.0$ Hz, H-6′], 3.61 [br.t, $J(H_2–H_3) = 1.8$ Hz, $J(H_2–OH) = 1.8H_z$, H-2], 3.44 (s, 3H, OMe), 3.33 [d,d,$J(H_2–H_3) = 1.8$ Hz, $J(H_3–H_4) = 5.0$ H_z, H-3], 2.05 (br.s, OH).

^{13}C NMR(125 MH_z): C_6D_6: δ: 141.44 (*ipso*-C of Ph-CHO), 139.73 and 137.13 (*ipso*-C of Ph_2As), 134.81 and 133.16 (*o*-C of Ph_2As), 128.37 and 128.33 (*p*-C of Ph_2As), 128.25 and 127.98 (*m*-C of Ph_2As), 127.77 (*m* + *p*-C of *Ph* CHO-), 125.86 (*o*-C of *Ph* CHO-), 101.24 (C-7), 100.95 (C-1), 76.89 (C-4), 69.96 (C-2), 69.19 (C-6), 62.02 (C-5), 54.51 (OMe), 42.15 (C-3). ^{13}C NMR (solid state) 138.32–129.58 (aryl-C), 103.70 (C-7), 100.53 (C-1), 77.88 (C-4), 69.58 (C-2 + C-6), 61.42 (C-5), 52.29 (OMe), 43.86 (C-3).

2.3. *Alternate preparation of 4,6-O-benzylidene-3-deoxy 3-C-diphenylarsino-α-D-altropyranoside*

To a stirred solution of Ph_2AsLi [obtained from Ph_3As (12 mmol)] in anhydrous THF (50 ml) was added, dropwise under nitrogen, a solution of methyl 4,6,-*O*-benzylidene-2-*O*-p-toluenesulphonyl-α-D-glucopyranoside (2 g, 4.8 mmol) in anhydrous THF (50 ml). The mixture was stirred at room temperature for 3 h, water (100 ml) was added, and the tetrahydrofurran was removed under reduced pressure. Extraction of the aqueous mixture with ethyl acetate resulted in recovery of methyl 4,6,-*O*-benzylidene-3-deoxy-3-C-diphenylarsino-α-D-altropyranoside (83% yield), identical with the sample obtained above.

2.4. *X-ray diffraction study of I*

2.4.1. *Crystal data*

$C_{26}H_{27}O_5As$. $Mr = 494.40$. monoclinic $P2_1$ $a = 9.204(7)$ Å $b = 8.072(6)$ Å $c = 16.029$ (13) Å. 3 = 96.65(7)°, $Z = 2$, $V = 1183$ (2) $Å^{-3}$, $D_c = 1.388$ g cm^3 $F(000) = 512$, λ(Mo Kα) = 0.71069 Å. μ(Mo Kα) = 1.471 mm^{-1}, $T = 293$ K.

2.4.2. *Data collection and processing*

A colourless crystal, 0.40 × 0.30 × 0.12 mm was used in the analysis. Data were collected out to $2\theta = 50°$ on a Nicolet P3 automated diffractometer with monochromated Mo Kα radiation. A total of 2380 reflections was obtained from $\theta–2\theta$ scans and a scan width of 2.4–2.7°; 2250 unique reflections were used in the analysis, and 1956 had $I > 2\sigma I$. Two standard reflections monitored every 50 reflections showed no significant variation in intensity. Range of *hkl* collected *h* (0–10), *k*(0–9), *l*(−19–18).The structure was determined by the Patterson method which revealed the approximate position of the arsenic atom. The position was confirmed by a direct-method procedure using SHELX-86 [5]. The remaining non-hydrogen atoms were located from successive Fourier difference maps using SHELXL-93 [6]. All hydrogen atoms were located from geometrical considerations. During refinement the H atoms were allowed to ride on their attached carbon atoms. Full-matrix least-squares calculations with anisotropic temperature factors for the As, O and C and common isotropic temperature factors for the H atoms (methyl and non-methyl) converged at $R1 = 0.0388$ [$I > 2\sigma$ (I)] and $wR2 = 0.0940$ (all data). The absolute configuration is based on the known stereochemistry of the carbohydrate moiety and the lower *R* value obtained by comparison to the inverted configuration. This was confirmed by the Flack *x* parameter = 0.02(2). The scattering factors were taken from SHELXL-93 [6]. All final $\Delta/\sigma = 0.0$, final $\Delta\rho$ min = −0.65e $Å^{-3}$, final $\Delta\rho_{max} = 0.62$e $Å^{-3}$. Molecular diagrams were obtained by the program SNOOPI [7]. The atomic coordinates are listed in Table 1.

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**

Atom	x	y	z	U_{eq} [a]
As	7680(1)	7487(1)	8092(1)	33(1)
O(1)	8621(4)	6476(5)	5704(2)	39(1)
O(2)	10164(4)	7581(9)	6824(2)	50(1)
O(3)	7232(6)	9780(6)	5698(3)	50(1)
O(4)	6226(4)	3101(5)	6154(3)	40(1)
O(5)	5509(4)	5503(5)	6812(2)	34(1)
C(1)	6901(6)	8041(7)	6906(3)	30(1)
C(2)	6448(6)	6525(7)	6391(4)	32(1)
C(3)	7753(7)	5519(8)	6203(5)	34(2)
C(4)	9167(7)	7936(7)	6113(4)	41(2)
C(5)	7984(8)	9045(9)	6427(4)	38(2)
C(6)	11400(9)	6647(13)	6643(6)	79(3)
C(7)	7251(7)	3988(8)	5706(4)	39(2)
C(8)	5025(6)	4142(7)	6303(4)	35(1)
C(9)	3927(6)	3172(8)	6719(4)	38(1)
C(10)	2883(7)	2274(12)	6216(4)	57(2)
C(11)	1823(9)	1428(13)	6562(5)	74(3)
C(12)	1788(9)	1427(11)	7412(5)	64(2)
C(13)	2805(7)	2322(17)	7920(4)	59(2)
C(14)	3883(7)	3187(9)	7567(4)	46(2)
C(15)	5849(6)	7281(9)	8604(4)	36(2)
C(16)	5873(8)	6207(10)	9265(4)	53(2)
C(17)	4644(9)	5940(12)	9679(5)	69(2)
C(18)	3383(9)	6787(13)	9413(5)	74(3)
C(19)	3332(8)	7815(16)	8755(5)	74(3)
C(20)	4544(7)	8132(10)	8333(4)	54(2)
C(21)	8230(6)	9745(7)	8466(3)	31(1)
C(22)	7496(7)	11147(9)	8170(4)	44(2)
C(23)	8000(8)	12725(11)	8404(4)	49(2)
C(24)	9259(8)	12869(8)	8963(4)	50(2)
C(25)	9979(8)	11489(10)	9269(4)	52(2)
C(26)	9488(7)	9925(9)	9019(4)	41(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

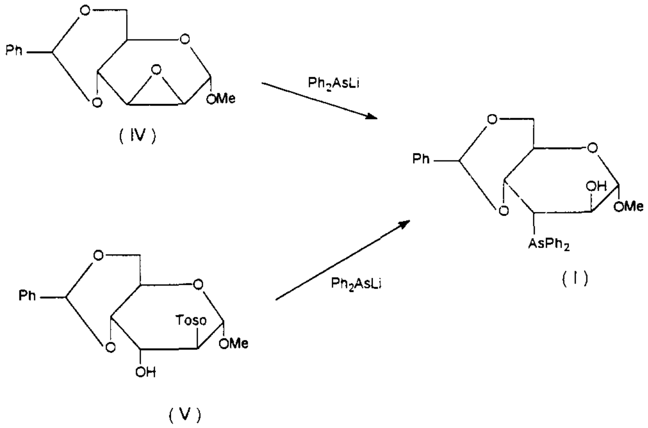
3. Results and discussion

Compound **I** was obtained by the opening of the epoxide ring in methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside, **IV**, on reaction with Ph_2AsLi. Alternatively, methyl 4,6-*O*-benzylidene-2-*O*-*p*-tosyl-α-D-glucopyranoside, **V**, could be used in place of **IV** (Scheme 1).

The epoxide ring opening of **IV** occurred regiospecifically; similar regiospecific ring openings of **IV** occurred on reactions with Ph_3SnLi [1] and with Ph_2PLi [3].

Compound **I** was relatively air-stable and could be handled without precautions to avoid oxygen; in contrast the diphenylphosphino derivative, **VI**, was very air-sensitive and was readily oxidised to **III** [3].

In the IR spectrum of **I** (in a KBr disc), the value of ν (OH) was found to be 3488 em^{-1}; as shown by the X-ray diffraction study, the OH group is not H-bonded in the solid state. The OH group in solid diphenylphosphinyl derivative, **III**, is, however, H-bonded intermolecularly to the O=P unit; the value of ν(OH) in **III** was found to be 3364 cm^{-1} in a KBr disc. The solution ^1H NMR spectra of **I**–**III** also indicated differences between the HO group in **III** [δ^1 H(OH) = 5.49] and those in **I** [δ^1H(OH) = 2.05] and **II** [δ^1H(OH) = 2.04] It thus appears that the H-bonding in **I** persists in chlorocarbon solution. The two phenyl groups in **III** are diastereomeric in solution, as shown by the two sets of NMR signals for the ortho-hydrogens and for the ring carbon atoms.



Scheme 1. Tos≡p-$MeC_5H_4SO_2$

3.1. X-Ray structure of I

The atomic arrangement of **I** and the numbering system used in the crystallography are shown in Fig. 1. Bond lengths and valency angles are listed in Table 2.

The trivalent arsenic atom has a pyramidal geometry with the C–As–C valency angles in the range 97.4(4)–101.2(4)°. The displacement of the arsenic atom from the plane of the three carbon atoms bonded to As is 0.945(4) Å. The As–C (aryl) bond lengths [1.965(6) Å and 1.967(6) Å] and As–C (alkyl) bond length (2.003(6) Å) are in the ranges normally found in organoarsenic

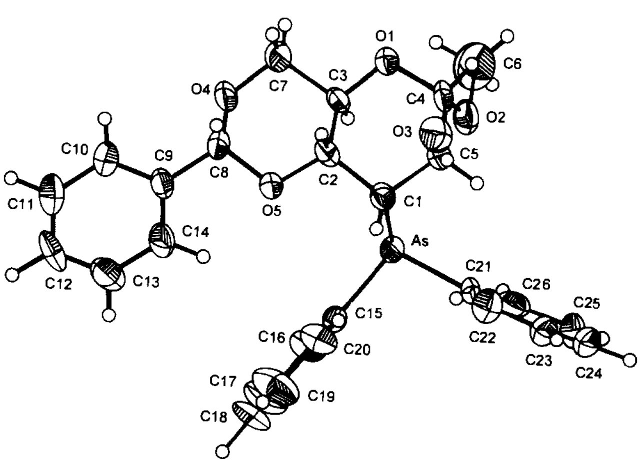


Fig. 1.

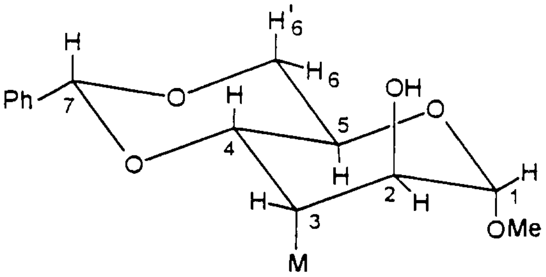
(III) compounds, e.g. As–C bond lengths in Ph_3As [8] and $(Me_3CCH_2)_3As$ [9] are 1.957 Å and 1.997 Å respectively.

The bond lengths and valency angles within the benzylidene and pyranose rings in **I** have similar values to those determined in **II** [1] and **III** [3]. Both types of ring adopt chair conformations; the conformation of the pyranose rings can be readily assigned as $^4C_1$ in solid **I–III**. The values of the H–C–C–H dihedral angles of the pyranose ring, calculated from the idealized H-atom positions, for **I** [and also for **III**] are indeed close to the values expected for the chair conformation (see Table 3). The best mean plane in the benzylidene ring of **I** involves O(4), C(7), C(2) and O(5) atoms [crystallographic numbering].

Table 2
Bond lengths [Å] and angles [°] of **I**

As–C(15)	1.965(6)	C(9)–C(14)	1.364(9)
As–C(21)	1.967(6)	C(9)–C(10)	1.386(9)
As–C(1)	2.003(6)	C(10)–C(11)	1.361(10)
O(1)–C(4)	1.412(7)	C(11)–C(12)	1.366(11)
O(1)–C(3)	1.422(8)	C(12)–C(13)	1.374(12)
O(2)–C(4)	1.407(8)	C(13)–C(14)	1.387(11)
O(2)–C(6)	1.422(9)	C(15)–C(16)	1.368(9)
O(3)–C(5)	1.417(8)	C(15)–(20)	1.408(9)
O(4)–C(8)	1.430(7)	C(16)–C(17)	1.393(10)
O(4)–C(7)	1.440(7)	C(17)–C(18)	1.371(12)
O(5)–C(8)	1.409(7)	C(18)–C(19)	1.339(13)
O(5)–C(2)	1.420(6)	C(19)–C(20)	1.394(9)
C(1)–C(2)	1.508(8)	C(21)–C(22)	1.375(9)
C(1)–C(5)	1.555(9)	C(21)–C(26)	1.382(8)
C(2)–C(3)	1.510(8)	C(22)–C(23)	1.392(10)
C(3)–C(7)	1.513(9)	C(23)–C(24)	1.385(10)
C(4)–C(5)	1.538(9)	C(24)–C(25)	1.359(10)
C(8)–C(9)	1.495(8)	C(25)–C(26)	1.384(11)
C(4)–C(5)–C(1)	112.2(5)	C(24)–C(23)–C(22)	118.6(8)
O(4)–C(7)–C(3)	108.8(5)	C(25)–C(24)–C(23)	120.0(7)
O(5)–C(8)–O(4)	110.9(4)	C(24)–C(25)–C(26)	121.0(6)
O(5)–C(8)–C(9)	109.5(5)	C(21)–C(26)–C(25)	120.2(7)
O(4)–C(8)–C(9)	110.0(5)	C(15)–As–C(21)	98.9(3)
C(14)–C(9)–C(10)	119.1(6)	C(15)–As–C(1)	100.7(2)
C(14)–C(9)–C(8)	122.6(6)	C(21)–As–C(1)	97.7(2)
C(10)–C(9)–C(8)	118.3(6)	C(4)–O(1)–C(3)	112.7(5)
C(11)–C(10)–C(9)	120.5(6)	C(4)–O(2)–C(6)	113.9(5)
C(10)–C(11)–C(12)	120.5(7)	C(8)–O(4)–C(7)	110.8(4)
C(13)–C(12)–C(11)	119.9(7)	C(8)–O(5)–C(2)	110.2(4)
C(12)–C(13)–C(14)	119.6(6)	C(2)–C(1)–C(5)	107.8(5)
C(9)–C(14)–C(13)	120.5(6)	C(2)–C(1)–As	112.6(4)
C(16)–C(15)–C(20)	119.1(6)	C(5)–C(1)–As	113.9(4)
C(16)–C(15)–As	116.0(5)	O(5)–C(2)–C(1)	110.9(4)
C(20)–C(15)–As	124.9(5)	O(5)–C(2)–C(3)	109.0(5)
C(15)–C(16)–C(17)	121.7(7)	C(1)–C(2)–C(3)	111.7(5)
C(18)–C(17)–C(16)	118.7(7)	O(1)–C(3)–C(7)	107.8(5)
C(19)–C(18)–C(17)	120.4(7)	O(1)–C(3)–C(2)	109.4(5)
C(18)–C(19)–C(20)	122.6(8)	C(7)–C(3)–C(2)	110.1(5)
C(19)–C(20)–C(15)	117.5(7)	O(2)–C(4)–O(1)	111.7(5)
C(22)–C(21)–C(26)	118.5(6)	O(2)–C(4)–C(5)	105.9(5)
C(22)–C(21)–As	124.0(4)	O(1)–C(4)–C(5)	114.2(5)
C(26)–C(21)–As	117.4(5)	O(3)–C(5)–C(4)	105.7(6)
C(21)–C(22)–C(23)	121.7(6)	O(3)–C(5)–C(1)	110.2(6)

Table 3
Selected torsional angles for **I** and **III**



	M = $Ph_2P(0)$ **III**	M = Ph_2As **I**	Ideal torsion angles for chair conformation
H(1)–C(1)–C(2)–H(2)	−67	−70	−60
H(2)–C(2)–C(3)–H(3)	76	76	60
H(3)–C(3)–C(4)–H(4)	47	51	60
H(4)–C(4)–C(5)–H(5)	180	177	180
H(5)–C(5)–C(6)–H(6)	−61	−53	−60
H(5)–C(5)–C(6)–H(6^1)	−179	−172	180

The shortest intramolecular arsenic–oxygen contacts within **I** involve O(5) [As…0(5)=3.129(5) Å] and O(2) [As….O(2) = 3.232(5) Å]. These are just within the sum of the Van der Waal radii for As and O (= 3.4 Å) but are appreciably longer than a normal As–O single bond length, e.g. the As–O bond length in $(C_6F_5)_2$As–O–As$(C_6F_5)_2$ [10] is 1.792 (3) Å. From the angles at As in **I**, it appears that there are no distortions away from a pyramidal geometry, and so there is no evidence for As–O interactions.

The exocyclic angles arsenic makes with the pyranose ring in **I** are similar: As–C(1)–C(2) = 112.6 (4)° and As–C(1)–C(5) = 113.9(4)°. However the exocyclic angles with each of the phenyl rings are different [As–C(15)–C(16) 116.0(5)° and As–C(15)–C(20) 124.9(5)°; As–C(21)–C(22) 117.4(5)° and As–C(21)–C(26) 124.0(4)°].

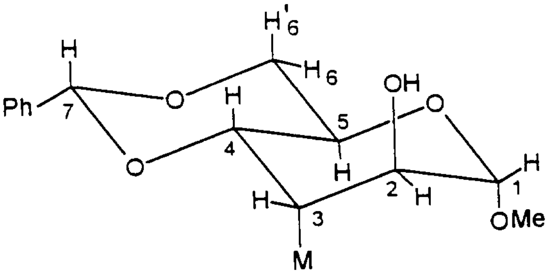
3.2. Comparison of the molecular structure of I in the solid state and in solution

The solid-state ^{13}C NMR spectrum of **I** was also obtained. As shown in Table 4, the $\delta^{13}C$ values for each individual carbon atom are similar in both the solid state and in solution. No significant differences in the conformation are indicated on changing the phase. Using a version [11] of the Karplus equation, eqn. 1, similar dihedral angles (θ) were calculated for the solution conformation of **I** using J(H, H) values as were deduced from the torsional angles revealed by the X-ray structure determination.

$$J(\text{H–H}) = 10.5\ \text{COS}^2\ \theta - 1.2\ \text{COS}\ \theta \qquad (1)$$

Table 4 also lists selected $\delta^{13}C$ values for **II** and **III**; as can be seen, the values for each carbon are similar

Table 4
Selected $\delta^{13}C$ values for **I**-**III**



	I		**III**	**II**	
	M = Ph_2As		M = $Ph_2P(O)$-	M = Ph_3Sn	
	Solution	Solid	Solution	Solution	Solid
C_1	101.0	100.5	101.1	100.2	99.5
C_2	70.0	69.6	69.2	70.8[12.7] [b]	69.8
C_3	42.2	43.9	43.5[67.0] [a]	34.8[379] [b]	34.4
C_4	76.9	77.9	76.7	76.8[ca. 30] [b]	76.7
C_5	62.0	61.5	61.6	63.7[15.2] [b]	63.7
C_6	69.2	69.6	70.2	69.1	69.8
C_7	101.2	103.7	101.9	100.9	100.9
OMe	54.6	52.3	53.3	54.1	52.8

[a] J(P–C) values. [b] J(Sn–C) values.

except for C-3- the bonding site of the different metal/metalloid.

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