Articles

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Tetraphenyl Derivatives of Phosphorus, Arsenic, and Antimony: Exchange Reaction and Reduction. Crystal and Molecular Structure of $[(C_4H_8O_2)NaAsPh_2]_n$, an Extended Array Containing Substantially Linear Na–As–Na Bonds

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The tetraphenyl derivatives of phosphorus(II) and arsenic(II) P_2Ph_4 and As_2Ph_4 were found to undergo a relatively fast exchange reaction to the mixed product Ph_2PAsPh_2, and the corresponding equilibria were studied in benzene, diethyl ether, and chloroform. By measurements of equilibrium constants at different temperatures in benzene as solvent, the reaction was found to be slightly *endothermic* ($\Delta H^\circ = 1.3 \pm 0.3$ kcal/mol of mixed product formed) with a positive entropy contribution ($\Delta S^\circ = +3.5 \pm 1.0$ eu). The corresponding phosphorus and antimony compounds P_2Ph_4 and Sb_2Ph_4 undergo exchange to an even lower extent, presumably due to an even more endothermic character of the reaction. Crystal data: $C_{16}H_{18}AsNaO_2$, $M_r = 340.23$, orthorhombic, $a = 10.280$ (1) Å, $b = 15.053$ (2) Å, $c = 10.735$ (1) Å, $Z = 4$, d(calcd) = 1.360 g·cm^{-3}. The structure consists of an alternating sequence of dioxane-coordinated sodium atoms and Ph_2As groups, giving rise to infinite –Na–As–Na–As– chains parallel to [100]. The chains are almost linear (173.6 (1)°) at arsenic and bent (121.5 (1)°) at sodium. The geometry around arsenic approximates closely that of a trigonal bipyramid. An electron deficient 2e–3c bond involving arsenic and sodium is suggested, which appears to account also for solvation by more polar solvents such as tetrahydrofuran.

Introduction

Mixed tetraorganyl derivatives of phosphorus(II) of the type $R_2PPR'_2$ have been reported in the literature.[1-4] The actual isolation of these diphosphines seems to be dependent on the occurrence of exchange reaction 1. Only in the case of R = CH_3 and R′ = CF_3 is the mixed phosphine stable enough to be isolated and characterized.[1] The other mixed diphosphines obtained by several routes undergo "symmetrization", by the reverse of reaction 1, especially when R and R′ are of similar electronic nature.

$$P_2R_4 + P_2R'_4 \rightleftarrows 2R_2PPR'_2 \qquad (1)$$

The mixed tetraorganyls of phosphorus and arsenic of the type $R_2PAsR'_2$ have been reported[3,5] to be obtained in a pure state by exchange reaction 2 (E = P, E′ = As) when the R groups attached to phosphorus and arsenic are drastically different in their electronic properties.

$$E_2R_4 + E'_2R'_4 \rightleftarrows 2R_2EE'R'_2 \qquad (2)$$

In the course of our current investigation on the ligand properties of organic chalcogenides, E_2Ph_2 (E = S, Se, Te),[6] and organic pnictides, E_2Ph_4 (E = P, As, Sb),[7] toward low-valent metal complexes, we have found that the ligand-exchange reaction between a metal–P_2Ph_4 complex and As_2Ph_4 was accomplished by the fast exchange reaction (2), R = R′ = Ph. In view of this, and of the literature report[8] concerning the isolation of Ph_2PAsPh_2, which appeared to contradict our observations, we decided to obtain better insight into the problem of the exchange reaction (2) (R = R′ = Ph; E = P, E′ = As; E = P, E′ = Sb).

Since the E_2Ph_4 compounds are frequently obtained by oxidation of the $[EPh_2]^-$ anions with organic halides XCH_2CH_2X (eq 3 and 4), it was of interest to investigate the nature of the reduced product in the case of E = As. We report the crystal and molecular structure of the product of reduction of As_2Ph_4 with sodium as the dioxane adduct.

$$2[EPh_2]^- + XCH_2CH_2X \rightarrow E_2Ph_4 + 2X^- + C_2H_4 \qquad (3)$$

E = As, X = Br;[9] E = Sb, X = Cl[10]

$$2[EPh_2]^- + XCH_2CH_2X \rightarrow Ph_2ECH_2CH_2EPh_2 + 2X^- \qquad (4)$$

E = As, X = Cl;[9,10] E = P, X = Br[11]

Experimental Section

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified nitrogen. Solvents were dried prior to use by the conventional methods. The tetraphenyl derivative P_2Ph_4 was prepared from PPh_2Cl and PPh_2H[12] or by reduction of PPh_2Cl

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Table I. ^{31}P NMR Data of Some Phosphorus Derivatives

compd	chem shift, ppm[a]	solvent	ref
P_2Ph_4	−14.3	benzene	this work
	−14.1		14
	−15.2		15
	−15.4	toluene	this work
	−15.6	diethyl ether	
	−16.9	thf[b]	
	−14.9	chloroform	
	−15.0		16
Ph_2PAsPh_2	−9.6	benzene	this work
	−10.9	toluene	
	−11.1	diethyl ether	
	−10.3	chloroform	
PPh_2Cl	+81.6	acetonitrile	16
	+81.3	toluene	this work

[a] Positive downfield shifts with respect to 85% H_3PO_4. [b] thf = tetrahydrofuran.

with 1 equiv of sodium.[13] Tetraphenyldiarsine[9] and tetraphenyldistibine[10] were prepared by the published procedures.

The IR spectra were measured with a Perkin-Elmer Model 283 instrument equipped with grating, and each spectrum was calibrated with the appropriate calibrant. The mass spectra were measured with a VG MM-16 F instrument (70 eV, 200 °C). The ^{31}P NMR spectra were measured with a Varian XL 100 instrument equipped with Fourier transform and using the gated decoupling technique in order to minimize the Overhauser effect. For the quantitative measurements, this effect is assumed to operate similarly on reagents and products and therefore not to effect their relative intensities, at least within the limits of the uncertainty reported for our data.

Exchange Reaction between E_2Ph_4 and E'_2Ph_4. Exchange reaction 2 (R = R′ = Ph; E = P, E′ = As or Sb) was studied by ^{31}P NMR and IR spectroscopy. For the NMR experiments, solutions of the tetraphenyl derivatives were sealed under argon or nitrogen in NMR tubes and the spectra were measured until the equilibrium was considered to be attained, the ^{31}P resonances of reagents and products (see Table I) being monitored at successive times. The solutions were protected from light, and care was taken to ensure that the exchange was not acid catalyzed by carrying out a control experiment in NMR tubes that had not been washed with acids. The ratio of intensities between reagents and products was determined. This was related to the equilibrium concentrations as shown below for the P–As exchange. Intensities of the NMR signals and analytical concentrations of the species in solution are related by expressions 5–7. Equilibrium, infinite,

$$\frac{I_{P-P}}{2I_{P-As}} = \alpha = \frac{[P_2Ph_4]_\infty}{[Ph_2PAsPh_2]_\infty} \qquad (5)$$

$$[P_2Ph_4]_\infty = C_0(P\text{–}P) - \tfrac{1}{2}[Ph_2PAsPh_2]_\infty \qquad (6)$$

$$[As_2Ph_4]_\infty = C_0(As\text{–}As) - \tfrac{1}{2}[Ph_2PAsPh_2]_\infty \qquad (7)$$

and known initial C_0 concentrations of the species, related to the intensity ratio, were used to determine the equilibrium constant (eq 8). When C_0's of reagents are the same as in the case of the reaction

$$K = \frac{[Ph_2PAsPh_2]_\infty^2}{[P_2Ph_4]_\infty[As_2Ph_4]_\infty} \qquad (8)$$

between $AsPh_2^-$ and PPh_2Cl, eq 8 reduces to eq 9. From experiments

$$K = 1/\alpha^2 \qquad (9)$$

carried out in different solvents, the values of equilibrium constant of Table II were found.

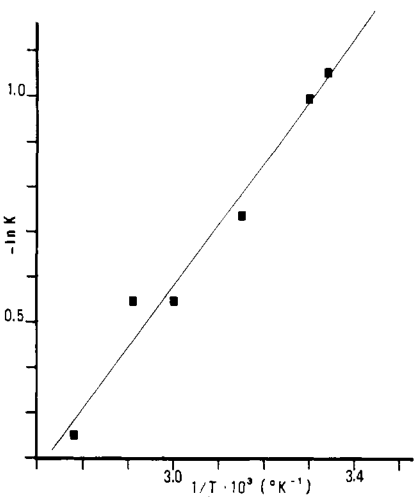

Figure 1. Formation of Ph_2PAsPh_2 from P_2Ph_4 and As_2Ph_4 in benzene as solvent as a function of temperature: plot of $-\ln K$ vs. $1/T$ for the reaction $P_2Ph_4 + As_2Ph_4 \rightleftarrows 2Ph_2PAsPh_2$. From the plot, the following data were obtained: $\Delta H° = +1.3 \pm 0.3$ kcal and $\Delta S° = +3.5 \pm 1.0$ eu (referred to the formation of 1 mol of the mixed product).

Table II. Equilibrium Constants for the Exchange Reaction[a]

$P_2Ph_4 + E_2Ph_4 \rightleftarrows 2Ph_2PEPh_2$ (E = As or Sb)

$10^2[E]$, M[b,h]	$10^2[E']$, M[b]	solvent	α[c]	K[d]
3.35	3.32 (As)	benzene	1.6	0.37 0.37[e]
4.86	4.90 (As)	diethyl ether	1.8	0.31 0.31[e]
4.2	3.58 (As)	chloroform	2.3	0.23
14.2	5.24 (As)	chloroform	3.6	0.27
6.3	5.80 (Sb)	chloroform	f	
1.1	0.81 (Sb)	thf[g]	f	

[a] Temperature = 30 ± 0.1 °C. The values of the equilibrium constant are estimated to be accurate to 10%. The exchange reaction was usually found to be complete within 7 h. The solutions were, however, maintained in the thermostated bath and monitored by NMR for several days. An experiment was carried out with $KAsPh_2 \cdot 2C_4H_8O_2$[9] (9.82×10^{-2} M) and PPh_2Cl (12.91×10^{-2} M) in toluene: from the ratio of the intensities (α = 2.11), the equilibrium constant of 0.22 was calculated from eq 9. [b] This is the C_0 specified in the text. [c] See text. [d] See eq 8. [e] Calculated from eq 9. In experiments carried out in benzene at different temperatures, the following values of the equilibrium constant K were calculated (temperatures in K in parentheses): 0.35 (299); 0.37 (303); 0.48 (317); 0.58 (333); 0.58 (343); 0.78 (359). From these values, the van't Hoff plot of Figure 1 was obtained. [f] No significant amount of the mixed complex was detected after 10 days. [g] thf = tetrahydrofuran. [h] E = P.

For the IR spectroscopic investigation of the exchange reaction, a benzene solution 3.96×10^{-2} M in P_2Ph_4 and 3.64×10^{-2} M in As_2Ph_4 was monitored in the 600–300-cm^{-1} region at about 25 °C. A new band at 535 cm^{-1} appeared, whose absorbance did not change any further after 6 h (see Table III).

Reduction of E_2Ph_4. The potassium derivative $KAsPh_2 \cdot 2C_4H_8O_2$ was prepared according to the literature.[9]

The sodium derivative $NaAsPh_2 \cdot C_4H_8O_2$ ($C_4H_8O_2$ = dioxane) was prepared from As_2Ph_4 (1.141 g, 2.49 mmol) and sodium sand (0.125 g, 5.43 mmol) in tetrahydrofuran (100 cm^3) at 0 °C by stirring for 1 h. The red tetrahydrofuran solution was filtered and evaporated under reduced pressure. To the resulting viscous liquid was added dioxane (50 cm^3) together with some sodium sand (0.037 g, 1.6 mmol) for protection against adventitious oxidation. The resulting suspension was heated to the reflux temperature and then filtered while still hot. By slow cooling to room temperature, well-formed crystals of the orange-yellow compound were obtained, which were filtered and dried briefly in vacuo (0.85 g, 54% yield). The sodium derivative is extremely sensitive to oxygen and moisture and had to be handled under the most rigorous exclusion of these agents. The crystals obtained as

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Table III. IR Spectra of Tetraphenyl Derivatives of Group 5A Elements in the 600–300-cm^{-1} Region

compd	medium	$\tilde{\nu}$, cm^{-1}								
P_2Ph_4	Nujol		557 w[a]		502 s	462 m				
	benzene		555 m[a]		500 s	470 w		418 w		
As_2Ph_4	Nujol	612 w				472 s	457 s			315 w
	benzene					470 s	455 s			
Sb_2Ph_4	Nujol						460 m	440 w		
P_2Ph_4 + As_2Ph_4	benzene		555 w[a]	535 m[b]	500 s	470 s	455 s	418 w		
	Nujol[c]	612 w	557 w[a]	537 m	502 s	472 s	457 s	427 w	397 w	315 w

[a] This band increases in intensity on exposure to air: it was therefore attributed to an oxidation product. [b] This band, initially absent, increases with time (see text). [c] Spectrum obtained on the residue left after evaporation of the solvent from a diethyl ether solution containing the P_2Ph_4–As_2Ph_4 mixture. Reference 8 reports bands at 618 w, 560 w, 539 w, 499 s, 470 s, 458 s, 398 s, 353 w, 321 s, and 306 w cm^{-1} for the mixed product Ph_2PAsPh_2.

Table IV. Mass Spectral Data of E_2Ph_4 Molecules[a]

ion	m/e[b]		
	P	As	Sb
E_2Ph_4	370 (75)	458 (35)	550 (63)
E_2Ph_3	293 (2)	381 (<0.5)	473 (43)
EPh_3	262 (4)	306 (1.5)	352 (26)
E_2Ph_2	216 (1.5)	304 (<0.5)	396 (4)
E_2Ph		227 (84)	319 (3)
EPh_2	185 (100)	229 (100)	275 (100)
EPh	108 (18)	152 (24)	198 (47)

[a] Similar mass spectra were obtained from (a) a diethyl ether solution containing equimolar quantities of P_2Ph_4 and As_2Ph_4 evaporated to dryness and (b) an approximately equimolar mechanical mixture of P_2Ph_4 and As_2Ph_4. The spectrum of (a) is reported in detail (*m/e*, % relative intensity, ion): 458, 22, $As_2Ph_4^+$; 414, 52, $AsPPh_4^+$; 370, 70, $P_2Ph_4^+$; 262, 9, PPh_3^+; 229, 65, $AsPh_2^+$; 227, 42, As_2Ph^+; 185, 100, PPh_2^+; 152, 35, $AsPh^+$; 108, 27, PPh^+. An approximately equimolar mechanical mixture of P_2Ph_4 and Sb_2Ph_4 gave the following results: 550, 0.5, $Sb_2Ph_4^+$; 473, <0.1, $Sb_2Ph_3^+$; 460, 0.7, $SbPPh_4^+$; 370, 17.5, $P_2Ph_4^+$; 352, 0.9, $SbPh_3^+$; 293, 0.5, $P_2Ph_3^+$; 275, 5, $SbPh_2^+$; 262, 22, PPh_3^+; 198, 16, $SbPh^+$; 185, 100, PPh_2^+, 108, 15, PPh^+. [b] Relative intensities in parentheses.

Table V. Summary of Crystal Data and Intensity Collection Details

formula	$C_{16}H_{18}AsNaO_2$
mol wt	340.23
cryst syst	orthorhombic
space group	$P2_12_12_1$ (from systematic absences)
a, Å	10.280 (1)
b, Å	15.053 (2)
c, Å	10.735 (1)
V, Å^3	1661.2 (3)
Z	4
d(calcd), g·cm^{-3}	1.360
F(000)	696
μ(Cu Kα), cm^{-1}	30.1
cryst dimens, mm^3	0.36 × 0.37 × 0.46
T, °C	22
reflcns used for unit cell	21
radiation	Ni-filtered Cu Kα (λ = 1.541 78 Å)
takeoff angle, deg	6
2θ range, deg	6.0–130.0
data collection range	$+h,+k,+l$
scan type[a]	θ(crystal)–2θ(counter)
scan rate, deg·min^{-1}	2.5–10.0
no. of unique data	1640
no. of data with $I > 2\sigma(I)$	946
standard reflcns	one (613) every 75 reflcns, no decay obsd
reduction to F_o	correcn for bkgd and Lorentz and polarizn effects

[a] The individual reflections profiles were analyzed as described by Lehmann and Larsen.[17]

Table VI. Fractional Atomic Coordinates (×10^4) of $[(C_4H_8O_2)NaAsPh_2]_n$ with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c
As	6 (1)	−2401 (1)	−19 (1)
Na	2439 (3)	−3420 (3)	363 (4)
O(1)	2179 (10)	−4235 (7)	2180 (9)
O(2)	2273 (10)	−5302 (6)	4210 (9)
C(1)	−582 (7)	−2482 (5)	1737 (6)
C(2)	−1821 (7)	−2763 (5)	2091 (6)
C(3)	−2187 (7)	−2737 (5)	3342 (6)
C(4)	−1313 (7)	−2430 (5)	4239 (6)
C(5)	−74 (7)	−2149 (5)	3884 (6)
C(6)	291 (7)	−2175 (5)	2633 (6)
C(7)	−894 (6)	−3391 (4)	−866 (6)
C(8)	−1442 (6)	−4130 (4)	−282 (6)
C(9)	−1985 (6)	−4810 (4)	−995 (6)
C(10)	−1979 (6)	−4752 (4)	−2292 (6)
C(11)	−1431 (6)	−4013 (4)	−2876 (6)
C(12)	−888 (6)	−3333 (4)	−2163 (6)
C(13)	1023 (19)	−4734 (14)	2588 (17)
C(14)	1104 (13)	−4878 (11)	3849 (16)
C(15)	3443 (17)	−4824 (14)	3853 (19)
C(16)	3372 (18)	−4722 (15)	2572 (20)

described were used for the X-ray diffractometric study (vide infra). A red tetrahydrofuran solution of $NaSbPh_2$ was obtained similarly by treating Sb_2Ph_4 (0.269 g, 0.487 mmol) at room temperature with sodium sand (0.026 g, 1.130 mmol) in tetrahydrofuran (50 cm^3) and used as such. Attempts to recrystallize the sodium derivative by a procedure similar to that used for the corresponding arsenic compound (by heating up to 75 °C) failed due to decomposition.

Reactions of $[EPh_2]^-$ with EPh_2Cl. Diphenylchlorophosphine, PPh_2Cl (0.513 g, 2.32 mmol), was treated with $KAsPh_2{\cdot}2C_4H_8O_2$ (0.786 g, 1.77 mmol) in toluene (18 cm^3). The resulting colorless solution was filtered, and its ^{31}P NMR spectrum was measured, which showed resonances at +81.3 ppm (PPh_2Cl), −10.9 ppm (Ph_2PAsPh_2), and −15.4 ppm (P_2Ph_4). The reaction between $[SbPh_2]^-$ and PPh_2Cl carried out in tetrahydrofuran did not show any ^{31}P NMR resonance except that at −16.9 ppm due to P_2Ph_4.

Collection and Reduction of X-ray Data of $[(C_4H_8O_2)NaAsPh_2]_n$. Two complete data sets were collected with a computer-controlled Siemens AED single-crystal diffractometer using a small crystal sealed in a Lindemann-glass capillary. The first set was obtained by using Mo Kα radiation (λ = 0.710 69 Å; θ range 3.0–24.5°; reflections measured, 1505; reflections observed, 531), but only the Na and As positions could be determined accurately. Therefore, a further data set was collected with Cu Kα radiation, which successfully solved and refined the structure. Crystal data and intensity collection details are given in Table V.

Solution and Refinement of the Structure. A Patterson map computed with all measured data was utilized to determine the positions of the arsenic atom. This was followed by a series of structure factor calculations and difference Fourier syntheses, which revealed the positions of all remaining non-hydrogen atoms. Full-matrix least-squares refinement of positional and anisotropic thermal parameters led to convergence at R = 0.0435, R_w = 0.0470, and R_g = 0.0594. At this point, the space group being polar, it was possible to determine the absolute configuration of the crystal from the effects of anomalous dispersion. To do so, the signs of all the coordinates were inverted ($x, y, z \rightarrow \bar{x}, \bar{y}, \bar{z}$) and the structure was refined to convergence again. The resulting residuals (R = 0.0427, R_w = 0.0456, and R_g = 0.0580) provide evidence that the correct crystal chirality is defined by the "inverted" coordinates, which are listed in Table VI. Because of the

Table VII. Relevant Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for $[(C_4H_8O_2)NaAsPh_2]_n$[a]

As-Na	2.962 (4)	O(1)-C(13)	1.47 (2)
As-Na^{i}	2.937 (4)	C(13)-C(14)	1.37 (2)
As-C(1)	1.983 (7)	C(14)-O(2)	1.41 (2)
As-C(7)	1.976 (6)	O(2)-C(15)	1.45 (2)
Na-O(1)	2.320 (11)	C(15)-C(16)	1.39 (3)
Na-O(2^{ii})	2.307 (10)	C(16)-O(1)	1.49 (2)

Na-As-Na^{i}	173.6 (1)	As-Na-As^{iii}	121.5 (1)
Na-As-C(1)	95.4 (2)	As-Na-O(1)	107.0 (3)
Na-As-C(7)	93.9 (2)	As-Na-O(2^{ii})	117.8 (3)
Na^{i}-As-C(1)	82.6 (2)	As^{iii}-Na-O(1)	115.6 (3)
Na^{i}-As-C(7)	80.7 (2)	As^{iii}-Na-O(2^{ii})	99.7 (3)
C(1)-As-C(7)	104.4 (3)	O(1)-Na-O(2^{ii})	91.4 (4)
As-C(1)-C(6)	116.0 (5)	Na-O(1)-C(13)	127.8 (9)
As-C(1)-C(2)	123.8 (5)	Na-O(1)-C(16)	113.8 (9)
As-C(7)-C(12)	114.2 (4)	Na-O(2^{ii})-C(14^{ii})	129.2 (9)
As-C(7)-C(8)	125.7 (5)	Na-O(2^{ii})-C(15^{ii})	116.6 (9)
C(13)-O(1)-C(16)	109 (1)	C(14)-O(2)-C(15)	114 (1)
O(1)-C(13)-C(14)	109 (1)	O(2)-C(15)-C(16)	106 (1)
C(13)-C(14)-O(2)	113 (1)	C(15)-C(16)-O(1)	112 (1)

[a] The nonbonding As···As^{iii} distance is 5.149 (4) Å. Symmetry transformations are given by the following superscripts: (i) $^1/_2 + x, ^1/_2 - y, \bar{z}$; (ii) $-^1/_2 - x, 1 - y, ^1/_2 + z$; (iii) $x - ^1/_2, ^1/_2 - y, \bar{z}$.

relatively few observed data, the hydrogen atoms were not introduced, and the phenyl rings were treated as rigid bodies restricted to idealized geometry (C–C = 1.395 Å, C–C–C = 120.0°).

A final difference Fourier map showed no feature greater than 0.24 e·Å^{-3}. Complex neutral-atom scattering factors were taken from ref 18. All calculations were carried out on a Cyber 76 computer using the SHELX-76 crystallographic programs.[19]

The bond distances and angles are given in Table VII. The thermal parameters and a table of observed and calculated structure amplitudes are available as supplementary material.

Results and Discussion

This paper reports the behavior of tetraphenyl derivatives of phosphorus and arsenic as far as the quantitative assessment of exchange reaction 2 is concerned (E = P, E′ = As). The data confirm that the exchange reaction (the average value of the equilibrium constant in different solvents at 30 °C is 0.3) proceeds by about 30% toward the formation of the mixed compound. The reaction is therefore characterized by a small and positive $\Delta G°$ of about 0.4 kcal/mol of mixed product. A high kinetic barrier is not associated with such an exchange (the reaction was found to be rather fast and the equilibrium was substantially reached in a few hours in most cases); it is perhaps surprising that the reaction does not proceed to a larger extent. By measurements at different temperatures, it was established that the formation of the mixed product is slightly endothermic ($\Delta H° = +1.3 \pm 0.3$ kcal/mol of Ph_2PAsPh_2 formed), while the entropy change is slightly positive ($\Delta S° = +3.5 \pm 1.0$ eu). The positive entropy contribution corresponding to the formation of the mixed molecule is probably partly compensated by the reorganization of the solvent around the product, as evidenced by the fact that the equilibrium constant tends to be smaller in more polar solvents (diethyl ether and chloroform). The experimental observation of the occurrence of reaction 2 for phosphorus and arsenic to such a small extent is somewhat apparently in contradiction with the established notion that chemical bonds within different elements of the same group are stronger than the average of the homonuclear molecules, which is the basis of the electronegativity principle.[20] On the other hand, the electronegativity difference in the P–As–Sb–Bi sequence is very small indeed.

It is interesting to note that, since the literature[1] reports the isolation of the stable $(CH_3)_2P-P(CF_3)_2$, it appears that the effect of two alkyl substituents of largely different electronic properties modifies the group 5 element quite effectively.

That the lack of observation of larger values of the equilibrium constant for reaction 2 is not due to any kinetic control is demonstrated not only by the constancy of the α value (see Experimental Section) with time but also by the fact that similar values of the equilibrium constant were obtained from reaction 10 between PPh_2Cl and the anionic $[AsPh_2]^-$ (in

$$PPh_2Cl + [AsPh_2]^- \rightarrow Ph_2PAsPh_2 + Cl^- \qquad (10)$$

toluene). Reaction 10 was followed by the reequilibration to the homonuclear species, by the reverse of reaction 2. Reaction 10 was also carried out in diethyl ether, and the presence of the homonuclear species in addition to the mixed product was established qualitatively. The $[EPh_2]^-$ anions obtained by sodium reduction of E_2Ph_4 in tetrahydrofuran (see eq 11) had

$$E_2Ph_4 \xrightarrow{\text{Na, thf}} 2[EPh_2]^- \qquad (11)$$

$$E = P, As, Sb$$

to be used in order to prevent secondary reactions when the anions were prepared by sodium reduction of EPh_3 in liquid ammonia as solvent. The use of ammonia as solvent or even the presence of some ammonia in the dry $NaEPh_2(NH_3)_x$ led to side reactions with PPh_2Cl, thus altering the results.

The isolation of pure Ph_2PAsPh_2 was reported in diethyl ether as solvent.[8] Although it cannot be excluded that the mixed product had a specific kinetic inertness to form the homonuclear species when prepared from the special reagents of eq 12, in view of our results we tend to believe that

$$Me_3SnEPh_2 + E'Ph_2Cl \rightarrow Me_3SnCl + Ph_2EE'Ph_2 \qquad (12)$$

$$E = P, E' = As; E = As, E' = P$$

Ph_2PAsPh_2 was contaminated by the homonuclear species. Fragment recombination (or gas-phase exchange) was also observed in the course of mass spectral measurements of mixtures of P_2Ph_4 and As_2Ph_4 (and to a much smaller extent for mixtures of P_2Ph_4 and Sb_2Ph_4; see Table IV).

It is interesting to note that the P_2Ph_4–Sb_2Ph_4 reaction did not proceed to any important extent either in chloroform or in tetrahydrofuran as solvent. This result was confirmed by the reaction of $[SbPh_2]^-$ with PPh_2Cl in tetrahydrofuran, which led to the predominant formation of Sb_2Ph_4 and P_2Ph_4, as shown by IR and ^{31}P NMR measurements. By considering the thermodynamic parameters obtained for the P_2Ph_4–As_2Ph_4 system, it is quite reasonable to assume that in the case of the phosphorus–antimony system the reaction is even more endothermic and the compensation by the positive entropy term is not sufficient.

When the E_2Ph_4 species are available, we find that reaction 11 is the best method for preparing solutions of $[EPh_2]^-$ anions. Sodium reduction of P_2Ph_4 in refluxing diethyl ether was reported earlier.[13] We find that in tetrahydrofuran as solvent the reaction is clean and fast even at 0 °C. The sodium derivatives are quite soluble in tetrahydrofuran, and recyrstallization from less solvating oxygen-containing molecules, such as 1,4-dioxane, can be easily carried out after evaporation of tetrahydrofuran under reduced pressure.

The arsenic–sodium derivative, obtained according to reaction 11 and recrystallized from 1,4-dioxane as $[(C_4H_8O_2)NaAsPh_2]_n$, was studied by X-ray diffractometric methods.

As shown in Figure 2, which also gives the atom labeling, the crystal structure consists of an alternating sequence of dioxane-coordinated Na atoms and $AsPh_2$ groups, which gives

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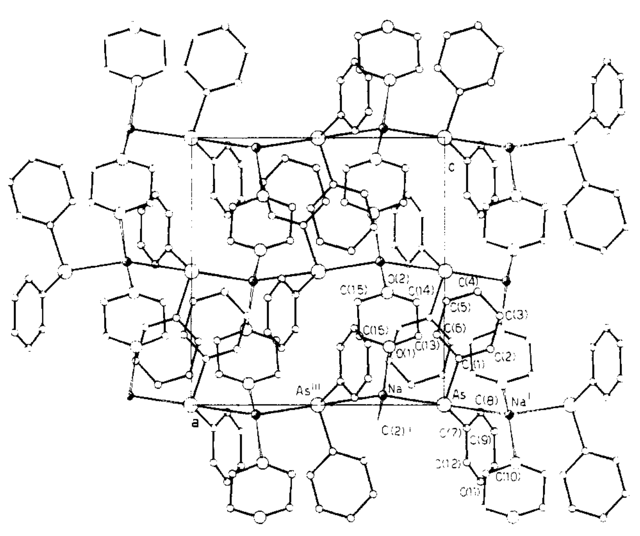


Figure 2. Molecular packing of $[(C_4H_8O_2)NaAsPh_2]_n$, viewed along [010].

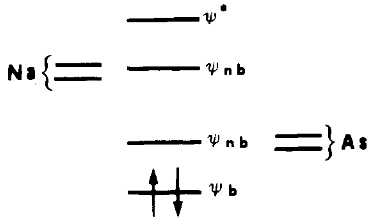
rise to infinite –Na–As–Na–As– zigzag chains parallel to [100]. These chains are nearly linear at the As atoms (173.6 (1)°) and bent at the Na atoms (121.5 (1)°). The dioxane molecule bridges pairs of Na atoms to form zigzag chains running along [001].

Owing to interactions between the two different kinds of chains, which have Na in common, the title compound exists in the crystalline form as polymeric entities.

The As atom is four-coordinated by two phenyl carbon atoms at 1.983 (7) and 1.976 (6) Å and two symmetry-related Na atoms at 2.962 (4) and 2.937 (4) Å. The resulting geometry closely approximates a trigonal bipyramid, the bond angles at As being fully consistent with the apportionment of the lone pair in the equatorial plane and the sodium atoms occupying the apical positions. That this view represents an appropriate description of the electronic situation around the arsenic atom is substantiated also by the observation that the angle around arsenic (173.6 (1)°) is slightly bent in the direction opposite to the region of space allocated to the lone pair, as predicted by the electron repulsion by the latter. The average As–Na distance of 2.949 Å is appreciably shorter than those observed in compounds containing sodium–arsenic bonds (average: 3.287 Å in NaAs,[21] 3.11 Å in Na_2CuAs,[22] 3.14 Å in Na_2AgAs,[23] and 3.172 Å in Na_2AuAs[24]).

The dihedral angle between the two phenyl rings is 137.2°, and the deviations of the arsenic atoms are 0.14 and 0.11 Å. The sodium atoms are coordinated to two arsenic and to two oxygen atoms from two symmetry-related dioxane groups, forming a distorted tetrahedron with coordination angles ranging from 91.4 (4) to 121.5 (1)°. The two Na–O bond distances are 2.320 (1) and 2.307 (10) Å and compare well with the corresponding bonds found in $Na_2Fe(CO)_4 \cdot 1.5C_4H_8O_2$[25] (2.253 (5) and 2.339 (6) Å), while they are significantly shorter than that of 2.432 (3) Å found in $NaClO_4 \cdot 3C_4H_8O_2$.[26]

Chart I. Approximate MO Diagram Showing the Overlapping of Sodium and Arsenic Hybrid Orbitals for the Formation of the 2c–3c Bond



We believe that our sodium derivative can best be described in terms of an electron-deficient bond involving arsenic and sodium, in approximate trigonal-bipyramidal and tetrahedral geometries, dsp^3 and sp^3, respectively. Chart I represents the sodium and arsenic orbitals involved in the formation of the As–Na–As bridge. The bond formation substantially would arise from the overlapping of hybrid orbitals, giving rise to a two-electron–three-center bond comprising two arsenic atoms and one sodium atom.

While electron-deficient bonds with lithium are well established, for example in the case of $Li_4(CH_3)_4$,[27] sodium acting as a bridge in electron-deficient structures is less common, an example that was proposed being that of $[NiPh_2 \cdot C_2H_4]_2Na_4(thf)_4$.[28] Alkali-metal derivatives of group 5 anions with sterically hindered organic residues of the type $Li[E(Si(CH_3)_3)_2] \cdot CH_2CH_2(OMe)_2$, E = As,[29] Sb,[30] are known. The former compound has dimeric $Li_2As_2(Si(CH_3)_3)_2$ units with bridging lithium atoms and approximately tetrahedrally arranged As atoms. No electron deficiency can be envisaged, and the dimeric units are prevented from further interaction by the steric bulk of the alkyl groups. In the antimony derivative, a polymeric structure has been found,[30] with alternating –Li–Sb–Li–Sb– bonds, the angle at Sb being 144.6 (4)°.

Our sodium derivative appears to be associated in dioxane solution, as indicated by cryoscopic determinations, in agreement with a rather limited solubility in this solvent. On the other hand, the compound shows a high solubility in more basic solvents such as tetrahydrofuran. The qualitative MO diagram of Chart I can be used to explain solvation: interaction with a basic solvent corresponds to filling the higher energy orbitals with electron pairs from the solvent, thus making the 2e–3c bond less stable and favoring ion separation by solvent.

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Registry No. $NaAsPh_2 \cdot C_4H_8O_2$, 89557-19-7; $KAsPh_2$, 21498-51-1; P_2Ph_4, 1101-41-3; As_2Ph_4, 2215-36-3; Sb_2Ph_4, 2654-44-6; Ph_2PAsPh_2, 27652-57-9; Ph_2PSbPh_2, 89193-71-5; PPh_2Cl, 1079-66-9.

Supplementary Material Available: Tables of observed and calculated structure amplitudes and thermal parameters and figures showing a perspective view of the –Na–As–Na–As– chains along [100] and a portion of $[(C_4H_8O_2)NaAsPh_2]_n$ with the bridging dioxane groups (10 pages). Ordering information is given on any current masthead page.

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