J. Am. Chem. Soc. 1982, 104, 2127-2132

Crystal Structures of Two Phenyl Spiroarsoranes. The First Truly Rectangular-Pyramidal Arsenic(V) Compound[1]

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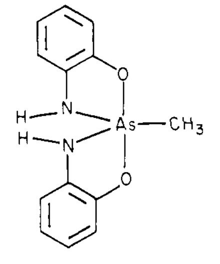
Received September 18, 1981

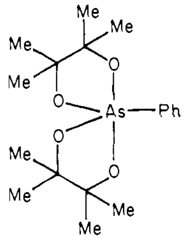
Abstract: Single-crystal X-ray analysis of 2-phenyl-2,2′-spirobi(1,3,2-benzodioxarsole), $(C_6H_4O_2)_2AsPh$ (**5**), and 2-phenyl-2,2′(3*H*,3′*H*)-spirobi(1,3,2-benzoxazarsole), $(C_6H_4ONH)_2AsPh$ (**6**), reveals, respectively, a rectangular-pyramidal structure and a trigonal-bipyramidal structure. **5** crystallizes in the monoclinic space group, $P2_1/c$, with $a = 16.787$ (5) Å, $b = 6.767$ (3) Å, $c = 27.374$ (6) Å, $\beta = 90.37$ (2)°, and $Z = 8$. The structure was refined to $R = 0.041$, $R_w = 0.060$ and showed two independent molecules per asymmetric unit. The displacement along the Berry coordinate for the two molecules, based on unit bond distances, is 99.2% and 94.8% from the trigonal bipyramid toward the rectangular pyramid. For **6**, the orthorhombic space group, *Pbca*, is obtained with $a = 10.933$ (1) Å, $b = 10.726$ (1) Å, $c = 26.710$ (3) Å, and $Z = 8$. The structure refined to $R = 0.032$, $R_w = 0.043$ and is displaced 22.9% from the trigonal bipyramid toward the rectangular pyramid. Comparisons between related group 5A pentacoordinated compounds indicate that structural principles found for phosphoranes apply thus far to arsenic(V) and antimony(V) derivatives. Molecular mechanics calculations on related spirocyclic phosphoranes and arsoranes support this conclusion.

Consideration of dynamic stereochemistry of pentacoordinated arsenic(V) compounds has been hampered by a lack of a well-defined structural basis. In the case of phosphoranes, the extensive structural basis that was developed[2] provided a quantitative model[3] upon which dynamic behavior inferred from NMR investigations[2] could be systematically correlated. It is of interest to ascertain to what extent the underlying structural principles found for phosphoranes apply to arsoranes.

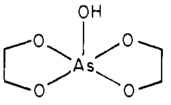
Some effort has been made in the latter context in learning if a range of structures exists for arsoranes like that for phosphoranes, which extends between the two prevalent five-coordinated geometries, the trigonal bipyramid and the rectangular pyramid.[4,5] Thus far, only a few structures are known for five-coordinated arsenic(V) compounds. Ph_5As[6] and AsF_5[7] are trigonal bipyramids. The spiroarsoranes **1**[8] and **2**[9] are close to the ideal trigonal bipyramid, while the structures of **3**[9] and **4**[10] are displaced progressively more toward the rectangular pyramid. The numbers below the structures following the compound identification are a measure of the structural placement along the Berry coordinate from the trigonal bipyramid toward the rectangular pyramid based on a dihedral angle method.[4] Percentage displacement using actual bond distances is followed by the value in parentheses based on unit bond vectors. Owing to hydrogen bonding, **3** is dimeric in the solid[9] and, consequently, may have some lattice distortions that enter into its structural placement.



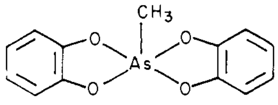
1, 21.6 (23.3)



2, 16.0 (18.0)

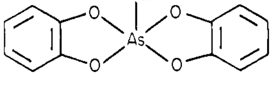


3, 59.8 (58.6)

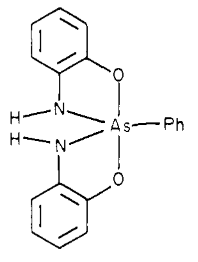


4, 69 (72)

To explore substituent effects to a greater extent, we report the X-ray analysis of the two spiroarsoranes, **5** and **6**, which are the phenyl derivatives of **4** and **1**, respectively. The structures of **5**[11] and **6**[12] in solution are indicated to be pentacoordinated from NMR data.



5



6

Experimental Section

All X-ray crystallographic studies were done with an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation (fine-focus tube, λ $K\alpha_1 = 0.70930$ Å, λ $K\alpha_2 = 0.71359$ Å). Details of the experimental procedures have been previously described.[13]

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† University of Massachusetts.
‡ Vassar College.

(1) (a) Pentacoordinated Molecules. 44. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, Nevada, March 1982; American Chemical Society: Washington, D.C.; INOR 107. (b) Previous paper in this series: Day, R. O.; Holmes, J. M.; Sau, A. C.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 281.

(2) Holmes, R. R. *ACS Monogr.* **1980**, *175*.

(3) Holmes, R. R. *ACS Monogr.* **1980**, *176*.

(4) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(5) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.

(6) Wheatly, P. J. *J. Chem. Soc.* **1964**, 2206.

(7) Clippard, F. B., Jr.; Bartell, L. S. *Inorg. Chem.* **1970**, *4*, 805.

(8) Wunderlich, H. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1492. The % structural displacement from the trigonal bipyramid toward the rectangular pyramid is erroneously given in this reference. The sum of Δ(rp) values in Table IV of this paper should be 170.8° instead of 150.8°. This places **1** exactly on the Berry coordinate with the % displacement as 21.6% (23.3% on the basis of unit vectors).

(9) Goldwhite, H.; Tellor, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 5357.

(10) Wunderlich, H. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1000.

(11) Sau, A. C.; Holmes, R. R. *J. Organomet. Chem.* **1981**, *217*, 157.

(12) Like **5**, **6** shows a separation of ortho from meta and para proton signals associated with the phenyl group indicative of pentacoordination.[11] ^1H NMR for **6** (acetone-d_6, 60 MHz) δ 7.9 (m, 2 H, ortho protons of As–Ph), 7.58 (m, 3 H, meta and para protons of As–Ph), 6.85 (m, 8 H, aromatic protons on the spirocyclic rings), 2.92 (single line, 2 H N–H protons).

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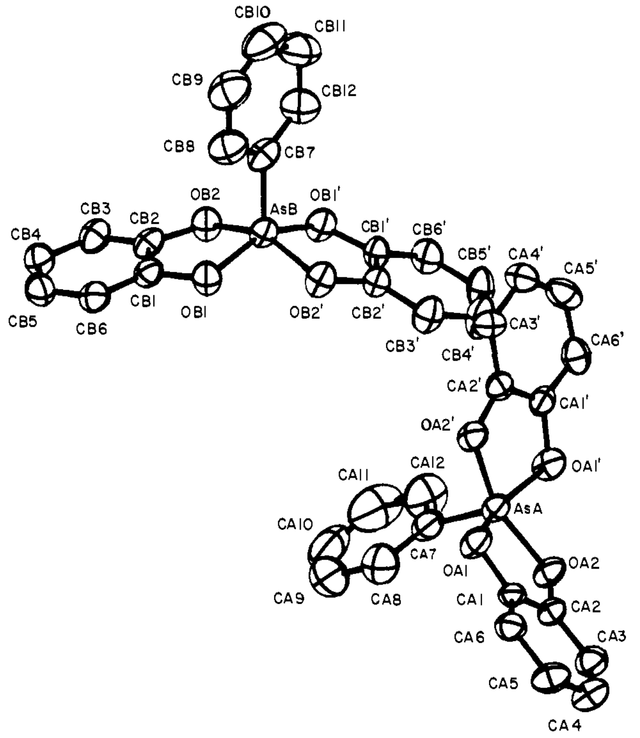

Figure 1. ORTEP plot showing the two independent molecules of $(C_6H_4O_2)_2AsPh$ (**5**). Hydrogen atoms are omitted for purposes of clarity. Thermal ellipsoids are at the 50% probability level.

Crystallography of $(C_6H_4O_2)_2AsPh$ (5). 2-Phenyl-2,2'-spirobi(1,3,2-benzodioxarsole) (**5**) was prepared by the reaction of phenylarsonic acid and catechol in benzene solution according to our previous procedure.[11] A crystal having dimensions of 0.25 × 0.30 × 0.42 mm was cut from a larger light yellow lath and mounted inside a sealed thin-walled glass capillary as a precaution against moisture sensitivity. The diffraction symmetry ($2/m$) and the observed extinctions ($0k0$, $k = 2n + 1$, $h0l$, $l = 2n + 1$) were consistent with the uniquely determined space group $P2_1/c$ [C_{2h}^5 No. 14].[14] The lattice constants based on 25 reflections having $10.31° \leq \theta_{\mathrm{Mo}\ K\bar{\alpha}} \leq 13.88°$ and determined at 23 ± 1 °C are a = 16.787 (5) Å, b = 6.767 (3) Å, c = 27.374 (6) Å, and β = 90.37 (2)°. A unit cell content of eight molecules gives a calculated volume of 16.9 Å^3 per nonhydrogen atom. The assignment of $Z = 8$ (two molecules per asymmetric unit) was confirmed by solution and refinement of the structure.

A total of 4050 independent reflections ($+h,+k,\pm l$) were measured by using the θ–2θ scan mode for $2° \leq 2\theta_{\mathrm{Mo}\ K\bar{\alpha}} \leq 45°$. Scan speeds varied from 0.74 to 4.0°/min, and six intensity control reflections were monitored. No corrections were made for absorption ($\mu_{\mathrm{Mo}\ K\bar{\alpha}}$ = 2.33 mm^{-1}). The structure was solved by using Patterson and difference Fourier techniques and refined by full-matrix least squares.[15a] The 46 independent nonhydrogen atoms were refined anisotropically. The 26 independent hydrogen atoms (calculated coordinates) were included as fixed isotropic scatterers, whose positional parameters were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. During the last cycle of refinement the largest Δ/σ was 0.01, and a final difference Fourier showed a maximum density of 0.402 e/Å^3. The final agreement factors[15b] were R = 0.041, R_w = 0.060, and GOF = 1.890 for the 3107 reflections having $I \geq 2\sigma_I$.

Crystallography of $(C_6H_4ONH)_2AsPh$ (6). 2-Phenyl-2,2'(3H,3'H)-spirobi(1,3,2-benzoxazarsole) (**6**) was prepared by the reaction of phenylarsonic acid and o-aminophenol in benzene according to a procedure of Mallon and Wieber.[16] A colorless to pale yellow crystal which was approximately a cube with an edge length of 0.33 mm was cut from a larger rodlike crystal and mounted as described for **5**. The diffraction symmetry (mmm) and the observed extinctions ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$) were consistent with the uniquely determined space group $Pbca$ [D_{2h}^{15} No. 61].[17] The lattice constants based on 25 reflections having $10.25° \leq \theta_{\mathrm{Mo}\ K\bar{\alpha}} \leq 13.92°$ and determined at 23 ± 1 °C are a = 10.933 (1) Å, b = 10.726 (1) Å, and c = 26.710 (3) Å. A unit cell content of eight molecules gives a calculated volume of 17.0 Å^3 per nonhydrogen atom. The assignment of $Z = 8$ was confirmed by solution and refinement.

Table I. Atomic Coordinates in Crystalline $(C_6H_4O_2)_2AsPh$, **5**[a]

	coordinates		
atom type[b]	10^4x	10^4y	10^4z
ASA	−102.8 (3)	6894.1 (8)	3848.5 (2)
ASB	4883.1 (3)	3126.8 (8)	3602.9 (2)
OA1	−421 (2)	9438 (6)	3903 (1)
OA2	−1114 (2)	6298 (5)	3662 (1)
OA1'	−80 (2)	4425 (5)	4090 (1)
OA2'	635 (2)	7587 (5)	4305 (1)
OB1	4886 (2)	5540 (5)	3322 (1)
OB2	5630 (2)	2367 (5)	3168 (1)
OB1'	4604 (2)	545 (5)	3602 (1)
OB2'	3864 (2)	3743 (5)	3750 (1)
CA1	−1234 (3)	9612 (7)	3810 (2)
CA2	−1610 (3)	7905 (7)	3671 (2)
CA3	−2417 (3)	7859 (9)	3581 (2)
CA4	−2834 (3)	9591 (9)	3630 (2)
CA5	−2463 (4)	11326 (9)	3775 (2)
CA6	−1641 (3)	11357 (8)	3869 (2)
CA1'	506 (3)	4235 (8)	4449 (2)
CA2'	899 (3)	5967 (8)	4557 (2)
CA3'	1486 (3)	6012 (9)	4915 (2)
CA4'	1679 (3)	4251 (10)	5150 (2)
CA5'	1284 (4)	2567 (9)	5035 (2)
CA6'	677 (4)	2469 (8)	4680 (2)
CA7	503 (3)	6711 (11)	3260 (2)
CA8	543 (4)	8316 (13)	2956 (3)
CA9	1000 (5)	8234 (18)	2525 (3)
CA10	1406 (5)	6525 (20)	2447 (3)
CA11	1380 (5)	4904 (18)	2747 (3)
CA12	924 (4)	5040 (12)	3171 (3)
CB1	5526 (3)	5730 (8)	3011 (2)
CB2	5933 (3)	3963 (8)	2925 (2)
CB3	6569 (3)	3896 (9)	2612 (2)
CB4	6793 (3)	5698 (10)	2392 (2)
CB5	6382 (4)	7419 (9)	2476 (2)
CB6	5738 (3)	7475 (8)	2785 (2)
CB1'	3819 (3)	338 (8)	3736 (2)
CB2'	3419 (3)	2069 (8)	3819 (2)
CB3'	2617 (3)	2063 (8)	3932 (2)
CB4'	2228 (3)	255 (9)	3955 (2)
CB5'	2627 (4)	−1493 (9)	3867 (3)
CB6'	3442 (4)	−1479 (8)	3740 (2)
CB7	5450 (4)	3536 (9)	4201 (2)
CB8	5697 (4)	5386 (10)	4327 (2)
CB9	6102 (4)	5635 (12)	4765 (3)
CB10	6278 (4)	4044 (14)	5063 (3)
CB11	6038 (5)	2215 (12)	4935 (3)
CB12	5616 (4)	1869 (10)	4497 (2)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled to agree with Figure 1.

A total of 2741 independent reflections ($+h,+k,+l$) were measured by using the θ–2θ scan mode for $2° \leq 2\theta_{\mathrm{Mo}\ K\bar{\alpha}} \leq 50°$. Scan speeds varied from 0.80 to 4.0°/min, and six intensity control reflections were monitored. No corrections were made for absorption ($\mu_{\mathrm{Mo}\ K\bar{\alpha}}$ = 2.30 mm^{-1}).

The structure was solved and refined in the same manner as for **5**. The 23 independent nonhydrogen atoms were refined anisotropically. The 13 aromatic hydrogen atoms were treated as described for **5**. Coordinates for the two N–H hydrogen atoms were obtained from a difference Fourier synthesis based on the remaining 36 independent atoms. Thermal parameters for both of these H atoms were fixed, and only the coordinates for one of these (HN) proved refineable. During the last cycle of refinement the largest Δ/σ was 0.07, and a final difference Fourier showed a maximum density of 0.313 e/Å^3. The final agreement

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(13) Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1980**, *19*, 3609.

(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 99.

(15) (a) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from ref 14, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for As and O were taken from the same source, pp 149–150. (b) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; GOF $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, with N_o = 3017 and N_v = 415.

(16) Mallon, T.; Wieber, M. *Z. Anorg. Allg. Chem.* **1979**, *454*, 31.

(17) Reference 14, p 150.

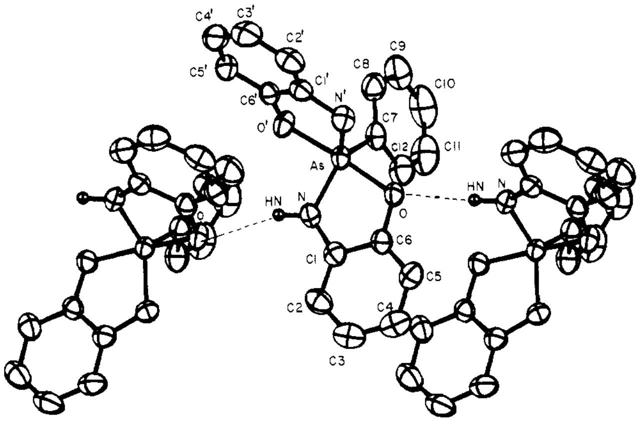

Figure 2. ORTEP plot of $(C_6H_4ONH)_2AsPh$ (**6**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms except for HN have been omitted for purposes of clarity. Two *b*-glide related molecules are also shown to illustrate the hydrogen bonding.

factors[18] were $R = 0.032$, $R_w = 0.043$, and GOF = 1.318 for the 2023 reflections having $I \geq 2\sigma_I$.

Results and Discussion

Molecular Structures of 5 and 6. The atom labeling schemes for **5** and **6**, respectively, are given in the ORTEP plots of Figures 1 and 2. For **5**, atomic coordinates are given in Table I. The corresponding information for **6** is given in Table II. Bond lengths and angles are presented in Tables III and IV for **5** and **6**, respectively. Anisotropic thermal parameters (Tables A and B), parameters for hydrogen atoms (Tables C and D), and least-square planes (Tables E and F) for both **5** and **6** are provided as supplementary materials.

Arsorane **6** lies on the Berry coordinate[19] connecting the trigonal bipyramid (TP) to the rectangular pyramid (RP) and is displaced 21.5% (22.9% by using unit vectors) from the TP toward the RP. The oxygen atoms are axial, the nitrogen atoms are equatorial, and C7 of the phenyl group occupies the equatorial pivotal site. As is often the case for molecules lying on the Berry coordinate, **6** has a pseudo-2-fold axis coincident with the As–C7 bond.[2] For facilitation of the examination of this pseudosymmetry, atoms are named so that the primed ones go into the unprimed ones by the pseudo-2-fold axis.

In the case of tricoordinated N atoms directly bonded to phosphorus, it has been observed[2] that the geometry about the N atom is planar rather than tetrahedral. In the present study, only one of the H atoms bonded to nitrogen (HN) was refined, but the indication is that the geometry about N in **6** is closer to planar than to tetrahedral. For planar geometry the sum of the angles about N would be 360°, whereas for tetrahedral geometry the sum would be 328.4°. In **6**, the sum of the angles about atom N (HN refined) is 352 (8)°.

The fact that HN in **6** was refinable (where HN′ was not) may be due to the fact that it appears to be involved in a hydrogen bond. The distance between HN and O of the adjacent molecule (*b* glide related) is 2.33 (5) Å, which is 0.3 Å less than the van der Waals sum[20] of 2.6 Å. This phenomenon is propagated as a chain of hydrogen bonded molecules in the lattice as illustrated in Figure 2. Similar intermolecular hydrogen bonding was reported for **1**.[8]

For the spiroarsorane **5**, where there are two independent molecules, the geometry about As is seen to be essentially that of the rectangular pyramid. The average displacement along the Berry coordinate for the two molecules is 95.2% (97.0% by using unit vectors) from the TP toward the RP.

Table II. Atomic Coordinates in Crystalline $(C_6H_4ONH)_2AsPh$, **6**[a]

atom type[b]	coordinates 10^4x	 10^4y	 10^4z
As	1280.2 (3)	2062.7 (3)	1142.4 (1)
O	1919 (2)	3426 (2)	1511 (1)
O′	652 (2)	602 (2)	866 (1)
N	2704 (3)	1288 (3)	1286 (1)
N′	−85 (3)	2155 (3)	1523 (1)
C1	3438 (3)	1923 (3)	1632 (1)
C2	4510 (3)	1507 (4)	1842 (1)
C3	5141 (4)	2285 (5)	2167 (2)
C4	4707 (4)	3462 (4)	2279 (1)
C5	3597 (3)	3880 (3)	2073 (1)
C6	2980 (3)	3111 (3)	1749 (1)
C7	1252 (3)	2957 (3)	522 (1)
C8	225 (4)	2890 (3)	218 (2)
C9	240 (5)	3513 (4)	−239 (2)
C10	1276 (5)	4163 (5)	−381 (2)
C11	2278 (5)	4220 (4)	−76 (2)
C12	2277 (4)	3626 (4)	387 (2)
C1′	−802 (3)	1033 (3)	1482 (1)
C2′	−1829 (3)	742 (4)	1757 (1)
C3′	−2440 (4)	−367 (4)	1653 (2)
C4′	−2027 (4)	−1162 (4)	1285 (2)
C5′	−978 (4)	−874 (4)	1005 (2)
C6′	−379 (3)	226 (3)	1110 (1)

[a] See footnote a of Table I. [b] Atoms are labeled to agree with Figure 2.

Molecule **5B** is essentially pure RP, 97.5% (99.2% by using unit vectors) from the TP toward the RP, with an average deviation from the Berry coordinate of ±0.7%. The four oxygen atoms which form the basal plane (plane IIIB, Table E) are coplanar to within ±0.002 Å, with the As atom displaced 0.455 Å out of this plane toward the phenyl group. There is no evidence of residual TP character in the As–O bond lengths which are identical within the limits of the error, and the trans basal angles are similarly identical (differ by 0.3° with an esd of 0.2°).

While molecule **5A** is very similar to molecule **5B**, it appears to have a small amount of residual TP character. Here the displacement along the Berry coordinate is 92.8% (94.8% by using unit vectors), with a very small deviation from the Berry coordinate averaging ±0.2%. The atoms forming the basal plane for **5A** (plane IIIA, Table E) are less coplanar (±0.02 Å) than those for **5B**, with the As atom displaced 0.457 Å out of the basal plane toward the phenyl group. The trans basal angles (152.1 (2)°, axial with respect to the TP; 149.3 (2)°, equatorial with respect to the TP) differ by 2.8°, and while the four As–O bond lengths are nearly within three esd's of each other, the As–O_{ax} bonds average 0.013 Å longer than the equatorial ones.

It is interesting to compare the angle and bond length variations within the five-membered ring in **5** and **6**. The alternation in angle size and bond length for adjacent bonds in the more trigonal-bipyramidal arsorane **6** complements that found in related phosphoranes and is a manifestation of the unequal lengths associated with apical and equatorial bonds of a trigonal bipyramid.[21,22] In the rectangular-pyramidal arsorane **5B**, these alternations largely disappear in line with the equal character of ring basal As–O bonds. One consequence of the presence of the larger arsenic atom (relative to a phosphorus atom) is that the length of the mutual C–C bond of the associated fused six-membered ring averages several hundredths of an angstrom larger than in related phosphorane structures.[2,21]

Structural Principles

Like that for the oxazaspiroarsorane **1**,[8] the apical positions of **6** are occupied by the oxygen atoms, in agreement with the electronegativity rule.[23] The apical O–As–O and equatorial N–As–N bond angles are similar in the two derivatives as reflected in their almost equal structural displacement from the trigonal

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(18) As defined in ref 15b, with $N_o = 2023$ and $N_v = 211$.

(19) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(20) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY **1960**; p 260.

(21) Holmes, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 5379.

(22) Brown, R. K.; Holmes, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 3326.

(23) Muetterties, E. L.; Mahler, W.; Schmutzler, R. *Inorg. Chem.* 1963, *2*, 613.

Table III. Bond Lengths (Å) and Bond Angles (Deg) for $(C_6H_4O_2)_2AsPh$, 5[a]

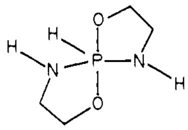
	bond lengths			bond lengths	
type[b]	molecule A	molecule B	type	molecule A	molecule B
As-O1	1.809 (4)	1.806 (4)	C6-C1	1.374 (7)	1.381 (7)
As-O1′	1.797 (4)	1.809 (4)	C1′-C2′	1.377 (7)	1.370 (7)
As-O2	1.816 (3)	1.810 (4)	C2′-C3′	1.386 (7)	1.383 (8)
As-O2′	1.816 (4)	1.809 (3)	C3′-C4′	1.391 (8)	1.389 (8)
As-C7	1.914 (6)	1.908 (6)	C4′-C5′	1.355 (9)	1.381 (8)
O1-C1	1.391 (6)	1.380 (6)	C5′-C6′	1.403 (9)	1.413 (8)
O1′-C1′	1.391 (6)	1.378 (6)	C6′-C1′	1.382 (8)	1.383 (8)
O2-C2	1.370 (6)	1.368 (6)	C7-C8	1.371 (10)	1.363 (8)
O2′-C2′	1.367 (6)	1.371 (6)	C8-C9	1.412 (11)	1.385 (9)
C1-C2	1.369 (7)	1.398 (7)	C9-C10	1.361 (14)	1.381 (10)
C2-C3	1.375 (8)	1.375 (8)	C10-C11	1.371 (14)	1.347 (11)
C3-C4	1.372 (8)	1.411 (8)	C11-C12	1.398 (10)	1.408 (9)
C4-C5	1.387 (9)	1.374 (8)	C12-C7	1.357 (9)	1.417 (9)
C5-C6	1.401 (8)	1.379 (8)			

	bond angles			bond angles	
type	molecule A	molecule B	type	molecule A	molecule B
O1-As-O1′	149.3 (2)	151.0 (2)	O2′-C2′-C3′	124.5 (5)	124.4 (5)
O2-As-O2′	152.1 (2)	150.7 (2)	C6-C1-C2	121.9 (5)	121.9 (5)
O1-As-O2	87.6 (2)	88.4 (2)	C1-C2-C3	121.4 (5)	121.1 (5)
O1′-As-O2′	88.5 (2)	88.7 (2)	C2-C3-C4	117.8 (5)	116.5 (6)
O1-As-O2′	84.1 (2)	83.8 (2)	C3-C4-C5	121.5 (5)	121.8 (5)
O1′-As-O2	85.1 (2)	84.6 (2)	C4-C5-C6	120.3 (5)	121.5 (6)
C7-As-O1	106.9 (3)	103.4 (2)	C5-C6-C1	117.1 (5)	117.2 (5)
C7-As-O1′	103.8 (3)	105.6 (2)	C6′-C1′-C2′	122.7 (5)	122.3 (5)
C7-As-O2	104.4 (2)	105.2 (2)	C1′-C2′-C3′	120.6 (5)	120.9 (5)
C7-As-O2′	103.5 (2)	104.1 (2)	C2′-C3′-C4′	118.0 (5)	118.1 (5)
As-O1-C1	110.8 (3)	110.5 (3)	C3′-C4′-C5′	120.1 (5)	121.2 (5)
As-O1′-C1′	111.1 (3)	110.2 (3)	C4′-C5′-C6′	123.5 (6)	120.5 (5)
As-O2-C2	112.7 (3)	110.9 (3)	C5′-C6′-C1′	115.1 (5)	116.8 (5)
As-O2′-C2′	111.0 (3)	110.9 (3)	As-C7-C8	119.3 (6)	120.0 (5)
O1-C1-C2	115.4 (4)	114.1 (5)	As-C7-C12	119.1 (6)	118.1 (4)
O1′-C1′-C2′	114.1 (5)	115.4 (5)	C12-C7-C8	121.5 (7)	121.9 (6)
O2-C2-C1	113.3 (4)	114.2 (5)	C7-C8-C9	120.4 (8)	118.5 (7)
O2′-C2′-C1′	114.9 (5)	114.5 (5)	C8-C9-C10	116.1 (9)	121.2 (7)
O1-C1-C6	122.6 (5)	124.0 (5)	C9-C10-C11	124.6 (8)	120.0 (7)
O1′-C1′-C6′	123.2 (5)	122.1 (5)	C10-C11-C12	117.7 (9)	121.4 (7)
O2-C2-C3	125.2 (5)	124.7 (5)	C11-C12-C7	119.6 (8)	116.8 (6)

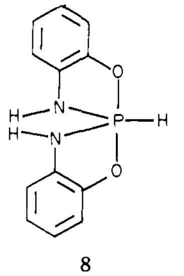
[a,b] See footnotes *a* and *b* of Table I.

bipyramid. For **1**, these angles are 169.6° and 125.9°, respectively, with an esd of 0.2–0.4°, while the corresponding angle values for **6** are 171.8 (1)° and 127.3 (1)°.

In the analogously structured phosphoranes **7**[24,25] and **8**,[24] these apical and equatorial angles are 177.1 (1)° and 130.8 (1)° for **7** and 177.8 (1)° and 121.8 (1)° for **8**. The structure of **7** is



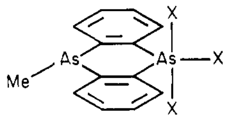
7, 25 (22)



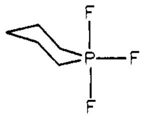
8

displaced 25% (22%) from the trigonal bipyramid, similar to that of **1** and **6**. For lack of refinement of the equatorial proton position for **8**, the structural displacement based on the dihedral angle is not calculated but appears similar to that for **7**.

When a six-membered ring is included as part of the framework as in arsorane **9**, X-ray analysis[26] shows that the ring assumes diequatorial positions, presumably because of reduced ring strain relative to occupancy of an apical–equatorial pair. X-ray analysis of an analogous phosphorane seems lacking, but ^{19}F NMR data[23] indicate this geometry in $(CH_2)_5PF_3$ (**10**) with no evidence of ligand exchange.



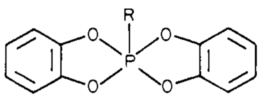
9, X = Br, I



10

In agreement with the factors found to stabilize the rectangular-pyramidal geometry for phosphoranes,[2,5] the presence of unsaturated five-membered rings and like ligands bound to phosphorus in any one ring, and the presence of an acyclic ligand which is bulky and of low electronegativity, the structure of the spiroarsorane **5** is rectangular pyramidal. The related methyl derivative **4**[10] is less so, 69% on the basis of bond distances.

The structures of the corresponding spirophosphoranes **11**[22] and **12**[27] are available for comparison. Here the opposite situation prevails. The structure of the phenyl derivative **11** is less displaced toward the rectangular pyramid, 72%, than that for the methyl spirophosphorane **12**, 82%, both on the basis of bond distances.



11, R = Ph, 72
12, R = CH_3, 82

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(24) Meunier, P. F.; Day, R. O.; Devillers, J. R.; Holmes, R. R. *Inorg. Chem.* **1978**, *17*, 3270.

(25) Meunier, P. F.; Deiters, J. A.; Holmes, R. R. *Inorg. Chem.* **1976**, *15*, 2572.

(26) Mann, F. G. *J. Chem. Soc.* **1963**, 4266.

(27) Wunderlich, H. *Acta Crystallogr., Sect. B* **1974**, *B30*, 939.

Table IV. Bond Lengths (Å) and Bond Angles (Deg) for $(C_6H_4ONH)_2AsPh$, **6**[a]

type[b]	bond length	type	bond length
As-O	1.896 (2)	C1'-C2'	1.378 (5)
As-O'	1.863 (2)	C2'-C3'	1.392 (6)
As-N	1.806 (3)	C3'-C4'	1.379 (6)
As-N'	1.807 (3)	C4'-C5'	1.403 (6)
As-C7	1.914 (4)	C5'-C6'	1.378 (5)
N-C1	1.401 (5)	C6'-C1'	1.397 (5)
O-C6	1.366 (4)	C7-C8	1.388 (5)
C1-C2	1.373 (5)	C8-C9	1.393 (6)
C2-C3	1.388 (6)	C9-C10	1.383 (7)
C3-C4	1.381 (6)	C10-C11	1.366 (7)
C4-C5	1.405 (5)	C11-C12	1.390 (6)
C5-C6	1.372 (5)	C12-C7	1.379 (5)
C6-C1	1.404 (4)	N-HN	0.87 (6)
N'-C1'	1.404 (4)	N'-HN'	1.041 (3)[c]
O'-C6'	1.362 (4)	HN- - -O	2.33 (5)

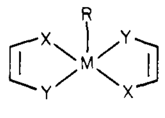
type	bond angle	type	bond angle
N-As-N'	127.3 (1)	C4-C5-C6	118.6 (4)
N-As-O'	90.9 (1)	C1-C6-C5	120.7 (3)
N-As-O	85.8 (1)	O-C6-C5	124.2 (3)
N-As-C7	115.4 (1)	O-C6-C1	115.1 (3)
N'-As-O'	86.8 (1)	As-C7-C8	119.5 (3)
N'-As-O	89.3 (1)	As-C7-C12	118.4 (3)
N'-As-C7	117.3 (1)	C8-C7-C12	122.0 (4)
O'-As-O	171.8 (1)	C7-C8-C9	118.6 (4)
O'-As-C7	94.2 (1)	C8-C9-C10	119.5 (4)
O-As-C7	94.0 (1)	C9-C10-C11	121.1 (4)
As-O-C6	111.4 (2)	C10-C11-C12	120.6 (5)
As-O'-C6'	111.4 (2)	C11-C12-C7	118.2 (4)
HN-N-C1	120 (4)	N'-C1'-C2'	126.9 (3)
HN-N-As	118 (4)	N'-C1'-C6'	112.6 (3)
As-N-C1	114.2 (2)	C2'-C1'-C6'	120.6 (4)
HN'-N'-C1'	116.4 (3)[c]	C1'-C2'-C3'	118.6 (4)
As-N'-C1'	113.0 (2)	C2'-C3'-C4'	120.9 (4)
HN'-N'-As	117.5 (2)[c]	C3'-C4'-C5'	120.8 (4)
N-C1-C2	126.9 (3)	C4'-C5'-C6'	117.9 (4)
C2-C1-C6	120.5 (4)	C5'-C6'-C1'	121.2 (3)
N-C1-C6	112.6 (3)	C5'-C6'-O'	123.3 (3)
C1-C2-C3	119.0 (4)	O'-C6'-C1'	115.5 (3)
C2-C3-C4	120.9 (4)	N-HN- - -O	159 (5)
C3-C4-C5	120.3 (4)		

[a,b] See footnotes *a* and *b* of Table II. [c] Esd based on nonhydrogen atoms only.

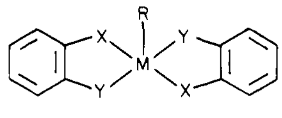
It is difficult to account for this reversal at present. Evidence thus far accumulated shows that arsoranes are more nonrigid than phosphoranes both in their dynamic NMR behavior and in data derived from vibrational motions associated with intramolecular ligand exchange.[5] Both lines of evidence indicate that the order of nonrigidity for group 5A pentacoordinated elements is Sb > As > P. The lower energy difference between the trigonal bipyramid and rectangular pyramid implied by these lines of evidence makes it easier to stabilize pentacoordinated arsenic in this structural form relative to phosphorus. This would rationalize the structure obtained for the phenylspiroarsorane **5** relative to the phenylphosphorane **11**. The subtle differences in bonding, possibly including some measure of lattice effect, is elusive at present in rationalizing the structural displacement between the phosphoranes **11** and **12** or the arsoranes **4** and **5**.

Following our previous method,[28,29] we have carried out molecular mechanics calculations on the series of model phosphoranes and arsoranes shown in Table V. The results are expressed as % displacement along the Berry coordinate and show two features that are in agreement with pentacoordinate structural principles.[2,3,5,23] Increasing the steric requirements of the acyclic substituent from the proton to the methyl group drastically increases the % displacement toward the RP, in line with X-ray structural determinations.[10,27,30,31]

Table V. Comparison of Structural Distortions[a]



model structure



exptl structure

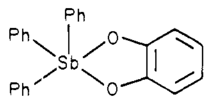
			M = P		M = As	
R	X	Y	calcd	exptl[b]	calcd	exptl[b]
CH_3	O	O	92	82[27]	93	(72)[10]
H	O	O	13	(1.7)[30,c]		
CH_3	S	S	93	79[31]		
H	S	S	−11			
CH_3	O	S	23			

[a] Displacement (%) along the Berry coordinate from the trigonal bipyramid toward the rectangular pyramid. The unparenthesized values are based on the use of actual bond distances; parenthesized values, on unit bond distances. [b] References are given as superscripts. [c] There are two independent molecules per unit cell with slightly different parameters.[30]

When the ring atoms attached to phosphorus are made different, as in the methyl phosphorane containing ring oxygen and sulfur atoms in Table V, the calculation shows the structure is strongly displaced back toward the trigonal bipyramid with the more electronegative ligands occupying the apical sites. Although direct experimental verification is not available with this specific model derivative, the related arsoranes, **1**[8] and **6**, and phosphoranes, **7**[24,25] and **8**,[24] all have structures near this calculated displacement.

Even though the agreement between calculated and experimental structures in Table V is satisfactory, the calculation appears insensitive, in its present form, to differentiate between the substitution of ring oxygen for ring sulfur atoms or between substitution of arsenic for phosphorus.

In line with the order of nonrigidity expressed above, Sb > As > P, pentacoordinated antimony in **13**[32] apparently is stabilized in a near rectangular-pyramidal geometry with the presence of only one unsaturated five-membered ring containing like atoms bonded to it. This derivative, which is a hemihydrate $(Ph_3SbO_2C_6H_4)_2\cdot H_2O$, has both pentacoordinated antimony, **13**, and hexacoordinated antimony in the unit cell.[32] The latter has the water molecule occupying the sixth coordination site. The trans basal angles for **13** are 154.9 (1)° and 147.4 (2)°.



13, 84.0 (85.3)

As with spirocyclic phosphoranes,[2,5] the presence of saturated five-membered rings in related pentacoordinated arsenic and antimony derivatives allows the structure to go more toward the trigonal bipyramid. Presumably, ring puckering reduces ring strain and offsets any ring strain advantage that is encountered for unsaturated five-membered rings in dibasal positions of the rectangular pyramid relative to the apical–equatorial orientation in the trigonal bipyramid.[21] The structures of the pentacoordinated arsenic derivative **2** and antimony derivative **14**,[33] like the phosphorane **15**,[34] are not too far from the ideal trigonal bipyramid.

In the case of **2** and **14**, dynamic ^{1}H NMR data give ligand exchange barriers ($\Delta G^{\ddagger}$) of 22.2[35] and 19.1[33,36] kcal/mol, re-

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[28] Deiters, J. A.; Gallucci, J. C.; Clark, T. E.; Holmes, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 5461.

[29] Reference 2, p 293.

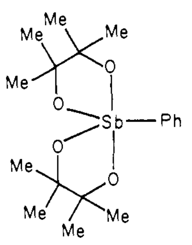
[30] Wunderlich, H.; Wussow, H.-G. *Acta Crystallogr., Sect. B* **1978**, *B34*, 2663.

[31] (a) Eisenhut, M.; Schmutzler, R.; Sheldrick, W. S. *J. Chem. Soc., Chem. Commun.* **1973**, 144. (b) Sheldrick, W. S., personal communication.

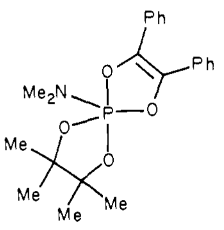
[32] Hall, M.; Sowerby, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 628.

[33] Wieber, M.; Baumann, N.; Wunderlich, H.; Rippstein, H. *J. Organomet. Chem.* **1977**, *133*, 183.

[34] Szobota, J. S., Holmes, R. R. *Inorg. Chem.* **1977**, *16*, 2299.



14, 13 (12.1)



15, 31

spectively, for pseudorotation which has the phenyl group apical and one of the rings diequatorial in an intermediate trigonal bipyramid.[37]

We conclude that the basic structural principles developed for phosphorane stereochemistry[2,3,38] apply to the stereochemistry of pentacoordinated arsenic compounds and apparently also to pentacoordinated antimony.[39,40] The ease of attainment of the rectangular-pyramidal geometry appears to be reflected in the relative fluxional character assigned to these elements in their pentacoordinated state.[5]

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE 79-10036) is gratefully acknowledged. We also thank the University of Massachusetts Computing Center for generous allocation of computer time.

Registry No. 5, 79677-99-9; **6**, 72409-78-0.

Supplementary Material Available: Compilations of observed and calculated structure factor amplitudes and thermal parameters (Tables A and B), parameters for hydrogen atoms (Tables C and D), and least-squares planes (Tables E and F) for **5** and **6**, respectively (26 pages). Ordering information is given on any current masthead page.

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(35) Casey, J. P.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1970**, 1410.

(36) Wieber, M.; Baumann, N. *Z. Anorg. Allg. Chem.* **1975**, *418*, 279.

(37) Reference 3, p 163.

(38) Recently, we discovered the first discrete rectangular pyramids for the group 4A elements Si, Ge, and Sn (Harland, J. J.; Day, R. O.; Vollano, J. F.; Sau, A. C.; Holmes, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 5269. Sau, A. C.; Day, R. O.; Holmes, R. R. *Ibid.* **1980**, *102*, 7972; **1981**, *103*, 1264, respectively). Pentacoordinate principles regarding the stereochemistry of group 4A elements also are very similar to those for phosphoranes (Day, R. O.; Holmes, J. M.; Sau, A. C.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 281. Sau, A. C.; Day, R. O.; Holmes, R. R. *Ibid.* **1981**, *20*, 3076).

(39) In view of the trigonal-bipyramidal structures for **14**,[33] (p-tolyl)$_5$Sb (Brabant, C.; Hubert, J.; Beauchamp, A. L. *Can. J. Chem.* **1973**, *51*, 2952), and the cyclohexane solvate, Ph$_5$Sb·0.5C$_6$H$_{12}$ (Beauchamp, A. L. *J. Organomet. Chem.* **1974**, *82*, 231), it is felt that the square-pyramidal structure of Ph$_5$Sb (Wheatley, P. J. *J. Chem. Soc.* **1964**, 3718; Beauchamp, A. L.; Bennett, M. J.; Cotton, F. A. *J. Am. Chem. Soc.* **1968**, *90*, 6675) is a result of lattice effects. Strong support for this assertion results from calculations showing that the most fluxional pentacoordinated member of the group 5A elements, antimony(V), can be stabilized by lattice effects in a square-pyramidal geometry (Brock, C. P. *Acta Crystallogr., Sect. A* **1977**, *A33*, 898).

(40) Reference 2, p 10.

Vibrational Fine Structure in the Valence Ionizations of Transition-Metal Hexacarbonyls: New Experimental Indication of Metal-to-Carbonyl π Bonding

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Received June 29, 1981

Abstract: The first observations of metal–carbon vibrational structure in photoionization bands are reported. Attention is focused on the predominantly metal d ionizations of M(CO)$_6$ (M = Cr, Mo, and W), and the methods for obtaining high resolution and very high signal-to-noise He I ionization data are detailed. The $^2T_{2g}$ ionization band of Cr(CO)$_6$ and the spin–orbit split $^2E''$ and $^2U'$ bands of W(CO)$_6$ show distinct vibrational progressions which correspond to the totally symmetric (a$_{1g}$) metal–carbon stretching mode in the positive ion states. The metal–carbon stretching frequencies are found to be significantly less in the positive ion states than in the ground states, indicating a reduction of metal–carbon bond order upon the loss of a t$_{2g}$ electron. Evaluation of the vibrational progressions shows that the metal–carbon bond length increases on the order of 0.10 Å upon t$_{2g}$ ionization in the case of W(CO)$_6$ and about 0.14 Å in the case of Cr(CO)$_6$. In addition, the beginning of a short progression in the a$_{1g}$ carbon–oxygen stretching mode is observed in the Mo(CO)$_6$ spectrum and is clearly seen in the W(CO)$_6$ spectrum. All of these observations show that removal of an electron from the predominantly metal t$_{2g}$ orbitals, which are strictly π symmetry with respect to the carbonyls, substantially weakens the metal-to-carbonyl bond.

The synergic bonding model is one of the most fundamental and pervasive concepts in the description of transition-metal–ligand interactions.[1] A commonly invoked example is the bonding of a carbonyl ligand with a transition metal, in which the σ donation by the carbonyl is described as being accompanied by π back-donation from the metal. The significance of this interaction continues to prompt many theoretical studies at varying levels of sophistication.[2-5] In general, the calculations have been consistent with the π back-bonding scheme, although a lack of clarity in evaluation of the π interaction has led to some confusion concerning its relative magnitude.[4] Considerable indirect experimental support for this scheme has been provided by the interpretation of vibrational,[6,7] mass spectrometric,[8] and core level XPS[9] data,

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(1) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1979.

(2) Hillier, I. H.; Saunders, V. R. *Mol. Phys.* **1971**, *22*, 1025–1034.

(3) Bursten, B. E.; Freir, D. G.; Fenske, R. F. *Inorg. Chem.* **1980**, *19*, 1810–1811.

(4) Hall, M. B.; Sherwood, D. E. *Inorg. Chem.* **1980**, *19*, 1805.

(5) Larsson, S.; Braga, M. *Int. J. Quantum Chem.* **1979**, *15*, 1–5.

(6) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432–4438.

(7) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349–2363.

(8) Svec, H. J.; Michels, G. D.; Flesch, G. D. *Inorg. Chem.* **1980**, *19*, 479–485.

0002-7863/82/1504-2132$01.25/0