Acknowledgment. We are grateful to the Natural Science and Engineering Research Council for financial support of this work.

Registry No. $[PtCl(PPh_2)(PPh_2H)]_2 \cdot C_3H_6O$, 80374-73-8; $[Pt(Ph_2PCH_2CH_2PPh_2)(PPh_2)]_2Cl_2 \cdot 2.5C_2H_4Cl_2$, 80340-26-7.

Supplementary Material Available: Tables of observed and calculated structure factors for $[PtCl(PPh_2)(PPh_2H)]_2 \cdot C_3H_6O$ and $[Pt(Ph_2PCH_2CH_2PPh_2)(PPh_2)]_2Cl_2 \cdot 2.5C_2H_4Cl_2$ as well as tables containing thermal parameters, phenyl ring bond lengths and angles, and solvent molecule bond lengths and angles (42 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Alabama, University, Alabama 35486, and The University of Texas at Austin, Austin, Texas 78712

Pyrrolyl Compounds of Main-Group Elements. 1. Synthesis of $(\eta^1\text{-}C_4H_4N)_3As$ and Crystal and Molecular Structures of $(\eta^1\text{-}C_4H_4N)_3P$ and $(\eta^1\text{-}C_4H_4N)_3As$

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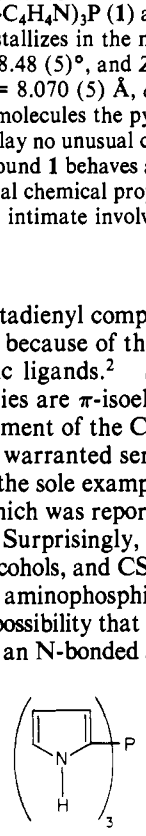
Received August 12, 1981

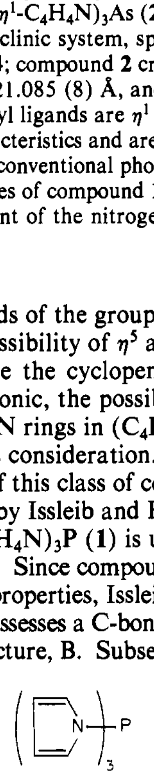
$(\eta^1\text{-}C_4H_4N)_3As$ has been prepared by the action of C_4H_4NLi on $AsCl_3$ in diethyl ether solution. The molecular structures of $(\eta^1\text{-}C_4H_4N)_3P$ (**1**) and $(\eta^1\text{-}C_4H_4N)_3As$ (**2**) have been determined by single-crystal X-ray diffraction methods. Compound **1** crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 12.428$ (6) Å, $b = 5.858$ (3) Å, $c = 17.071$ (8) Å, $\beta = 98.48$ (5)°, and $Z = 4$; compound **2** crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a = 7.251$ (4) Å, $b = 8.070$ (5) Å, $c = 21.085$ (8) Å, and $Z = 4$. The molecular structures of compounds **1** and **2** are very similar; in both molecules the pyrrolyl ligands are η^1 and N bonded. The N-P-N bond angles and N-P bond lengths in compound **1** display no unusual characteristics and are quite normal for a PN_3 system with trigonal-planar nitrogen atoms. Moreover, compound **1** behaves as a conventional phosphine ligand and reacts with $Fe_2(CO)_9$ to afford $(C_4H_4N)_3PFe(CO)_4$ (**3**). The unusual chemical properties of compound **1** such as hydrolytic stability and unreactivity toward alcohols are due therefore to the intimate involvement of the nitrogen lone pair in the pyrrolyl π system.

Introduction

Tricyclopentadienyl compounds of the group 5A elements are of interest because of the possibility of η^5 attachment of the carbocyclic ligands.[2] Since the cyclopentadienyl and pyrrolyl moieties are π-isoelectronic, the possibility of *multihapto* attachment of the C_4H_4N rings in $(C_4H_4N)_3E$ (E = P, As, Sb, Bi) warranted serious consideration. Prior to the present work, the sole example of this class of compound was $(C_4H_4N)_3P$ which was reported by Issleib and Brack[3] almost 25 years ago. Surprisingly, $(C_4H_4N)_3P$ (**1**) is unreactive toward water, alcohols, and CS_2.[3,4] Since compound **1** does not exhibit typical aminophosphine properties, Issleib and Brack[3] suggested the possibility that it possesses a C-bonded structure, A, rather than an N-bonded structure, B. Subsequent IR and NMR data,[4] however, indicate that B is the preferred structure. One of the objectives of the present work was to establish the molecular structure of **1** by means of single-crystal X-ray diffraction. Furthermore, realizing that the structures of $(C_4H_4N)_3E$ compounds might be dependent on, e.g., the covalent radius of the central atom, we decided to attempt the synthesis of heavier congeners of **1**. These efforts resulted in the synthesis of $(pyrl)_3As$ (**2**) (pyrl = pyrrolyl), which has also been investigated by X-ray crystallography.



A



B

Experimental Section

Materials and General Procedures. Pyrrole, *n*-BuLi, and ECl_3 (E = P, As, Sb, Bi) were procured commercially and used as supplied, and $Fe_2(CO)_9$ was prepared by UV irradiation of $Fe(CO)_5$ in hexane solution. All solvents were dried carefully prior to use.

Most of the materials described herein are moisture sensitive. Accordingly, it was prudent to perform all operations in vacuo or under an inert atmosphere.

Spectroscopic Measurements. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in the FT mode at spectrometer frequencies of 90, 20, and 32.84 MHz, respectively, on Varian EM 390 (^1H) and Varian FT-80 (^{13}C and ^{31}P) instruments. Dichloromethane (54.19 ppm relative to Me_4Si) was employed as the internal reference for the ^{13}C spectra, and 85% H_3PO_4 was used as the external reference for the ^{31}P spectra. All positive chemical shifts are downfield (deshielded) and vice versa.

The mass spectra were measured on a CEC 21-491 spectrometer operating at an ionizing voltage of 70 eV.

Preparation of $(C_4H_4N)_3P$ (1) and $(C_4H_4N)_3As$ (2). Both compounds were prepared by the same route; however, since $(C_4H_4N)_3P$ is a known compound,[3,4] only the preparation of the arsenical is described. In a typical reaction, 139 mL of a 1.55 M solution of *n*-BuLi in hexane was added slowly to a solution of 14.5 g (216.1 mmol) of pyrrole in 300 mL of diethyl ether at −78 °C. The formation of C_4H_4NLi was signalled by the immediate formation of a white solid. The stirred solution was brought slowly to room temperature in order to eliminate the butane which had formed. After the C_4H_4NLi solution was recooled to −30 °C, a solution of 13.06 g (72.0 mmol) of $AsCl_3$ in 40 mL of diethyl ether was added dropwise. After slow warming to room temperture, the reaction mixture was refluxed for 3 h. Removal of lithium chloride by filtration followed by vacuum evaporation of the solvent left a dark-colored oil which was purified by distillation (bp 125–132 °C at 1 torr). This afforded 7.0 g (35.5% yield) of colorless oily $(C_4H_4N)_3As$, which solidified solwly upon cooling to −15 °C. The compound decomposes slowly at room temperature, thus precluding commercial elemental analysis. Unequivocal characterization of $(C_4H_4N)_3As$ was accomplished by means of single-crystal X-ray diffraction (vide infra). NMR data for **2**: ^1H, α-H's δ 6.84 (m), β-H's δ 6.50 (m); $^{13}C\{^1H\}$ α-C's 122.9 ppm (s), β-C's 112.6 ppm (s). The mass spectrum of **2** exhibits a parent peak at *m/e* 273 (29.7%), and peaks at *m/e* 207 (75.7%) and 141 (70.3%),

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(1) (a) University of Alabama. (b) The University of Texas at Austin.

(2) The compounds $(C_5H_5)_3Sb$ and $(C_5H_5)_3Bi$ were first prepared by: Fischer, E. O.; Schreiner, S. *Chem. Ber.* **1960**, *93*, 1417–1422. The bismuth compound exists in orange and black modifications. It was suggested that $(C_5H_5)_3Sb$ and the orange form of $(C_5H_5)_3Bi$ involve σ-bonded C_5H_5 rings but that the black form involves π-bonded C_5H_5 rings. The *monohapto* structure, $(\eta^1\text{-}C_5H_5)_3Sb$, has been confirmed recently by single-crystal X-ray diffraction: Birkhahn, M.; Krommes, P.; Massa, W.; Lorbeth, J. *J. Organomet. Chem.* **1981**, *208*, 161–167.

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Table I. Data Collection Parameters and Crystal Data

	$(\eta^1\text{-}C_4H_4N)_3P$	$(\eta^1\text{-}C_4H_4N)_3As$
space group	$P2_1/n$	$P2_12_12_1$
cryst system	monoclinic	orthorhombic
cell constants		
a, Å	12.428 (6)	7.251 (4)
b, Å	5.858 (3)	8.070 (5)
c, Å	17.071 (8)	21.085 (8)
β, deg	98.48 (5)	90
vol, Å^3	1229.2	1233.8
ρ, g cm^{-3}	1.24	1.47
μ, cm^{-1}	2.04	28.79
molecules/unit cell (Z)	4	4
θ limits, deg	1-20	1-24
measd reflctns	1147	974
obsd reflctns	845	883
R	0.067	0.073
R_w	0.077	0.081
max cryst dimens, mm	0.085 × 0.15 × 0.30	0.70 × 0.25 × 0.35
mol wt	229.2	273.2

which correspond to the loss of one and two pyrrolyl groups, respectively. The phosphorus analogue $(C_4H_4N)_3P$ (**1**) was prepared in 43% yield with the above procedure. The spectroscopic properties of **1** were identical with those reported in the literature.[4]

Preparation of $(C_4H_4N)_3PFe(CO)_4$ (3). A mixture of 2.4 g (10.5 mmol) of $(C_4H_4N)_3P$ and 3.8 g (10.5 mmol) of $Fe_2(CO)_9$ in ~50 mL of pentane was heated under reflux for 4–5 h. The suspended solid went into solution slowly, accompanied by the evolution of gas and a change of color of the reaction mixture from yellow to green. After the solvent was stripped, the product was evacuated for 4 h and then recrystallized from pentane at low temperature. A yellow solid $(C_4H_4N)_3PFe(CO)_4$ (**3**) (mp 88 °C dec) was obtained in virtually quantitative yield. The compound is not stable for long periods of time at room temperature; hence, only poor quality commercial elemental analyses could be obtained. Characterization of compound **3** was therefore effected by means of spectroscopic data. The mass spectrum of compound **3** exhibits a parent peak at m/e 397 (11.2%) and peaks at m/e 369 (7.3%), 341 (38.1%), 313 (69.7%), and 285 (67.1%), which corresponded to the sequential loss of four CO molecules. Following these are peaks at m/e 191 (26.2%) and 122 (40.6%), which correspond to the loss of one and two pyrrolyl moieties from $[(C_4H_4N)_3PFe]^+$. NMR data for **3**: ^1H, α-H's δ 6.75 (m), β-H's δ 6.45 (m); $^{13}C\{^1H\}$ (−80 °C) α-C's 123.2 ppm (d, J_{PNC} = 5.88 Hz), β-C's 114.0 ppm (d, J_{PNCC} = 8.82 Hz), CO 210.2 ppm (d, J_{PFeC} = 22.06 Hz); $^{31}P\{^1H\}$ 152.9 ppm (s).

X-ray Data Collection and Solution and Refinement of the Structures of $(\eta^1\text{-}C_4H_4N)_3P$ (1) and $(\eta^1\text{-}C_4H_4N)_3As$ (2). Clear, colorless crystals of compounds **1** and **2** suitable for single-crystal X-ray diffraction experiments were selected from the masses of crystals which formed upon maintaining the freshly distilled oils at −15 °C. Both data crystals were sealed in 0.5-mm o.d. Lindemann glass capillaries prior to X-ray examination. Both data sets were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The diffracted intensities were collected in the ω–2θ scan technique in a manner similar to that described previously.[5] The intensities were corrected for Lorentz and polarization effects. Absorption corrections were made for $(\eta^1\text{-}C_4H_4N)_3As$ but not for $(\eta^1\text{-}C_4H_4N)_3P$. A summary of data collection parameters and crystal data is presented in Table I. As pointed out above, the arsenic compound is not very stable at room temperature, consequently the crystal mounting and data collection were accomplished as expeditiously as possible.

Both structures were solved with the direct-methods program[6] and refined with the SHELX system.[7]

Results and Discussion

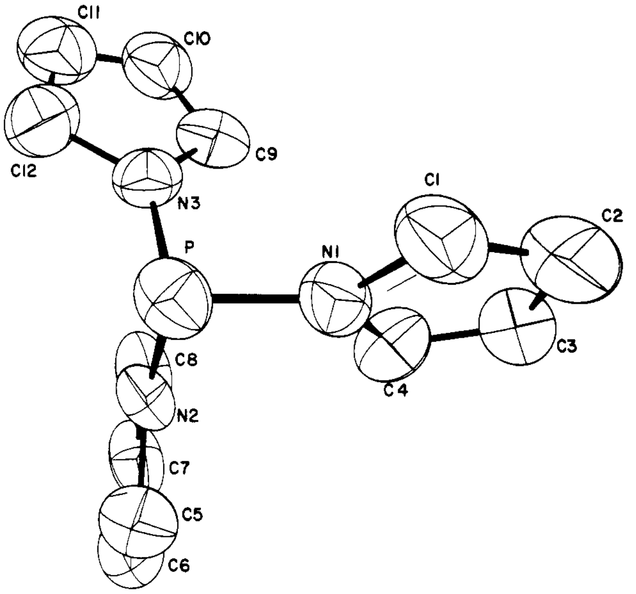

Figure 1. Structure of $(\eta^1\text{-}C_4H_4N)_3P$ (1), illustrating the atom numbering scheme. The hydrogen atoms are omitted.

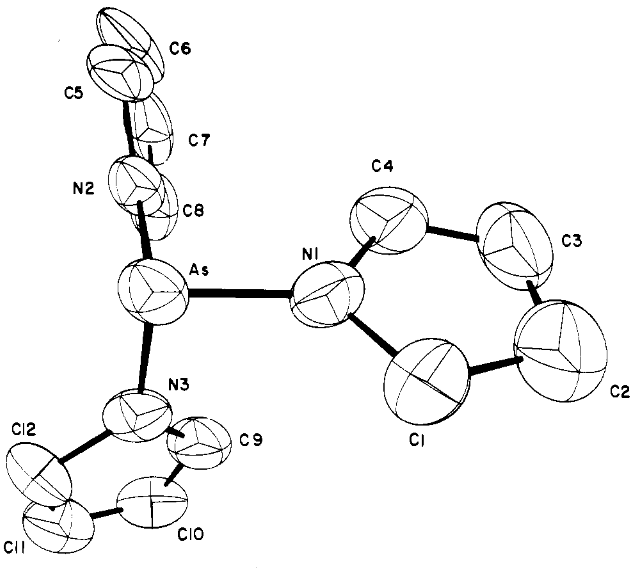

Figure 2. Structure of $(\eta^1\text{-}C_4H_4N)_3As$ (2), illustrating the atom numbering scheme. The hydrogen atoms are omitted.

Preparation of $(C_4H_4N)_3E$ Compounds. Tripyrrolylphosphine (**1**) and -arsine (**2**) are readily prepared by the action of C_4H_4NLi on PCl_3 or $AsCl_3$ in diethyl ether solution. The arsenic compound is considerably less thermally stable than the phosphorus compound and undergoes decomposition at room temperature. Evidently this stability trend continues down group 5A because we were unable to prepare $(C_4H_4N)_3Sb$ and $(C_4H_4N)_3Bi$ using the above synthetic approach.

Molecular Structures of $(\eta^1\text{-}C_4H_4N)_3P$ (1) and $(\eta^1\text{-}C_4H_4N)_3As$ (2). Both molecules exhibit *monohapto* attachment of all pyrrolyl groups via N–P or N–As bonds (Figures 1 and 2). Neither molecule has crystallographically imposed symmetry, and both molecules adopt a C_1 arrangement of pyrrolyl groups around the central atom because of unequal rotations of the rings about the nitrogen-element bonds.

Within experimental error, the pyrrolyl rings are planar and all the sums of angles at nitrogen are 360° in both **1** and **2**. However, the pyrrolyl groups in **1** and **2** exhibit significant differences in the C–C bond lengths. This suggests that the degree of localization of π-electron density in **1** and **2** is similar to that in pyrrole[8] and in pyrrolyl complexes of the early

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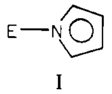
Table II. Bond Lengths (Å) and Bond Angles (Deg) in $(\eta^1\text{-}C_4H_4N)_3E$, E = P (1) and As (2)

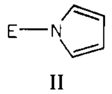
	E = P	E = As
Bond Lengths		
E-N(1)	1.710 (8)	1.86 (2)
E-N(2)	1.700 (9)	1.87 (2)
E-N(3)	1.677 (8)	1.84 (2)
N(1)-C(1)	1.38 (1)	1.37 (3)
N(1)-C(4)	1.40 (1)	1.40 (2)
N(2)-C(5)	1.39 (1)	1.37 (2)
N(2)-C(8)	1.41 (1)	1.40 (3)
N(3)-C(9)	1.38 (1)	1.39 (2)
N(3)-C(12)	1.37 (1)	1.42 (2)
C(1)-C(2)	1.35 (1)	1.36 (3)
C(2)-C(3)	1.40 (1)	1.41 (3)
C(3)-C(4)	1.34 (1)	1.35 (3)
C(5)-C(6)	1.34 (2)	1.38 (3)
C(6)-C(7)	1.40 (2)	1.35 (4)
C(7)-C(8)	1.35 (1)	1.34 (3)
C(9)-C(10)	1.37 (1)	1.35 (3)
C(10)-C(11)	1.40 (2)	1.41 (3)
C(11)-C(12)	1.33 (1)	1.33 (3)
Bond Angles		
N(1)-E-N(2)	100.4 (4)	96.3 (7)
N(1)-E-N(3)	100.1 (4)	94.7 (7)
N(2)-E-N(3)	100.7 (4)	98.9 (7)
E-N(1)-C(1)	122.2 (8)	123 (2)
E-N(1)-C(4)	130.7 (7)	130 (2)
C(1)-N(1)-C(4)	107.1 (8)	107 (2)
E-N(2)-C(5)	122.4 (9)	122 (2)
E-N(2)-C(8)	130.0 (8)	129 (2)
C(5)-N(2)-C(8)	107 (1)	108 (2)
E-N(3)-C(9)	130.7 (8)	132 (1)
E-N(3)-C(12)	124.1 (9)	123 (1)
C(9)-N(3)-C(12)	105.2 (9)	105 (2)
N(1)-C(1)-C(2)	109 (1)	111 (2)
C(1)-C(2)-C(3)	107.4 (9)	105 (2)
C(2)-C(3)-C(4)	109 (1)	109 (2)
N(1)-C(4)-C(3)	108.0 (9)	108 (2)
N(2)-C(5)-C(6)	110 (1)	108 (2)
C(5)-C(6)-C(7)	107 (1)	107 (2)
C(6)-C(7)-C(8)	110 (1)	111 (3)
N(2)-C(8)-C(7)	106 (1)	106 (2)
N(3)-C(9)-C(10)	109 (1)	111 (2)
C(9)-C(10)-C(11)	107 (1)	107 (2)
C(10)-C(11)-C(12)	107 (1)	108 (2)
N(3)-C(12)-C(11)	111 (1)	110 (2)
E-N(1)-Cent $(\eta^1\text{-}C_4H_4N)^b$	175.9	173.3
E-N(2)-Cent $(\eta^1\text{-}C_4H_4N)^b$	172.8	171.5
E-N(3)-Cent $(\eta^1\text{-}C_4H_4N)^b$	175.7	171.8

[a] See Figures 1 and 2 for the atom numbering schemes. [b] Cent $(\eta^1\text{-}C_4H_4N)$ is the centroid of the pyrrolyl group.

transition metals[9] where the differences in ring C–C bond lengths are ~0.04 Å. The average E–N–ring centroid angle in $(\eta^1\text{-}C_4H_4N)_3P$ (174.8°) is slightly larger than that in $(\eta^1\text{-}C_4H_4N)_3As$ (172.2°). In pyrrolyl-metal complexes, metal–N–ring centroid angles have been observed[9] in the range 164–179°. Taken collectively, the foregoing metric parameters for the pyrrolyl groups in **1** and **2** suggest that the dominant bonding mode can be better represented by I than II.



I



II

The sum of N–P–N bond angles in compound **1** is 301.2°. This compares favorably with other uncoordinated PN_3 systems for which X-ray crystallographic data are available, namely $(pip)_3P$ (pip = piperidino) (304.7° and 305.1°),[10,11] $(morph)_3P$ (morph = morpholino) (306.6°),[10,12] and $(PhNH)_3P$ (298.5°).[13] The sum of N–As–N bond angles in compound **2** is 289.9°. This reduction of central atom bond angles on descending group 5A is a well-known stereochemical phenomenon[14] and is usually discussed in terms of the apportionment of valence s and p character between the lone pair and the various σ bonds.

In previous discussions of N–P bond lengths[10,12,15] it has been noted that their values depend on the state of hybridization of the nitrogen atoms. For tricoordinate phosphorus atoms, typical values are $P\text{–}N_{sp^2} \approx 1.68\text{–}1.69$ Å $P\text{–}N_{sp^3} \approx 1.74\text{–}1.75$ Å. The P–N bond lengths in **1**, which fall in the range 1.677 (8)–1.710 (8) Å are thus entirely normal for phosphorus bonded to trigonal-planar nitrogen. Considerably less information is available concerning arsenic–nitrogen bond lengths. On the basis of one X-ray crystallographic study, Rømming and Songstad[12] have suggested the values $As\text{–}N_{sp^2} \approx 1.84$ Å and $As\text{–}N_{sp^3} \approx 1.87\text{–}1.88$ Å. Our values for **2** range from 1.84 (2) to 1.87 (2) Å and, once again, indicate that the E–pyrrolyl bond has no unusual characteristics.

Comments on the Chemical Properties of $(\eta^1\text{-}C_4H_4N)_3P$ (1). It is clear from the foregoing structural results that the P–N bond lengths and N–P–N bond angles of $(\eta^1\text{-}C_4H_4N)_3P$ display no unusual characteristics and that these metric parameters are quite normal for trigonal-planar nitrogens bonded to a tricoordinate phosphorus atom. Moreover, we find that compound **1** behaves as a normal phosphine ligand and reacts with $Fe_2(CO)_9$ to afford $(pyrl)_3PFe(CO)_4$ (**3**). The unusual properties of compound **1**—namely, the unreactivity toward water, alcohols, and CS_2—must therefore be a consequence of the involvement of the nitrogen lone pairs in the pyrrolyl ring systems. This aspect was clear from the pattern of pyrrolyl C–C bond lengths and P–N–ring centroid angles in **1** which was discussed above.

Finally, we note that compound **3** is not thermally stable at room temperature; hence it was characterized spectroscopically. The NMR data presented in the Experimental Section establish that the pyrrolyl moieties in this compound are N-bonded.

Acknowledgment. We are grateful to the National Science Foundation (Grants CHE79-10155 and CHE78-09729) and the Robert A. Welch Foundation for generous support.

Registry No. **1**, 60259-30-5; **2**, 80327-96-4; **3**, 80340-25-6; pyrrole, 109-97-7; $AsCl_3$, 7784-34-1; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Tables of observed and calculated structure factors for **1** and **2** and fractional coordinates and anisotropic thermal parameters for nonhydrogen atoms in **1** and **2** (13 pages). Ordering information is given on any current masthead page.

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