ORGANOMETALLICS

Synthesis, molecular and crystal structure of 2,2',5,5'-tetramethylbiarsolyl

Arthur J. Ashe III, William M. Butler, and Timothy R. Diephouse

Organometallics, **1983**, 2 (8), 1005-1008• DOI: 10.1021/om50002a011 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

of compound IV is not apparent, and we do not wish to speculate upon this at this time.

The formation of the organic product, toluene, and the non-hydride containing cluster compounds could also proceed via radical intermediates. This could involve hydrogen atom abstraction either from I or the $[HOs_3(CO)_9(S)]\cdot$ radicals by the benzyl radicals. Alternatively, the toluene could be formed via an intramolecular reductive elimination involving metal-induced cleavage of the carbon–sulfur bond. Evidence supporting such a mechanism was obtained from the compound $HRu_3(CO)_9(\mu\text{-}PPh_2)$ which eliminates benzene at 80 °C.[20] Studies focusing on the mechanism of toluene elimination from I are currently in progress.

Acknowledgment. This work was supported by the National Science Foundation and the Alfred P. Sloan Foundation through a fellowship to R.D.A. NMR studies were supported by Grant No. CHE-7916210 to the Northeast Regional NSF-NMR Facility from the National Science Foundation. We wish to thank Engelhard Industries for a loan of osmium tetroxide.

Registry No. I, 85442-97-3; III, 85442-98-4; IV, 85442-99-5; V, 85443-00-1; dibenzyl, 103-29-7.

Supplementary Material Available: Tables of structure factor amplitudes for all three structures (37 pages). Ordering information is given on any current masthead page.

---

[20] MacLaughlin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* **1982**, *60*, 87.

Synthesis and Molecular and Crystal Structure of 2,2′,5,5′-Tetramethylbiarsolyl

Arthur J. Ashe, III,* William M. Butler, and Timothy R. Diephouse

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

Received January 10, 1983

2,2′,5,5′-Tetramethylbiarsolyl has been prepared by treating 1-phenyl-2,5-dimethylarsole with lithium followed by iodine. Yellow crystals of the nonthermochromic diarsine form in the $P2/c$ space group with $Z = 4$, $a = 13.247\ (6)$ Å, $b = 7.271\ (3)$ Å, $c = 14.534\ (5)$ Å, and $\beta = 114.79\ (3)$ °. The full structure has been determined and has been compared with that of the thermochromic 2,2′,5,5′-tetramethylbistibolyl.

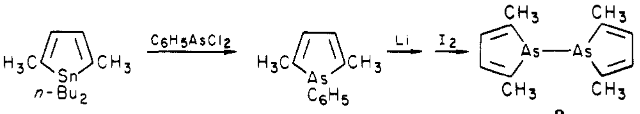
Introduction

We recently reported on the synthesis of 2,2′,5,5′-tetramethylbistibolyl (1), which displays interesting thermochromic behavior.[1] Crystals of 1 appear purple-blue to reflected light but melt reversibly to a pale yellow oil. Similarly, solutions of 1 are pale yellow. The crystal structure of 1 shows that all of the antimony atoms are aligned in a linear chain with very short intermolecular Sb–Sb···Sb–Sb separation as illustrated in Figure 1. Evidently the solid-phase color is associated with intermolecular interaction along this chain.[2]

Thermochromic behavior similar to that of 1 has been found for several other distibines[3-5] and dibismuthines,[3,6-8] although little structural data are yet available.[9,10] On the other hand, the blue-black ladder polymer of arsinomethane 2 has a solid-phase structure strikingly similar to that of 1 (see Figure 1).[11,12] Apparently extended bonding along the two parallel $AsCH_3$ chains of 2 is responsible for its solid-phase color. Other forms of arsinomethane do not show the same color.[13]

In order to clarify the conditions necessary for thermochromic behavior of pictogen compounds, we have investigated the arsenic analogue of 1, 2,2′,5,5′-tetramethylbiarsolyl (3). Compound 3 was easily prepared by a route analgous to that used for 1. Thus, the exchange reaction of phenylarsenic dichloride with 1,1-dibutyl-2,5-dimethylstannole (4) gave a 59% yield of 1-phenyl-2,5-dimethylarsole (5).[14] Reaction of 5 with lithium in THF afforded a brick-red solution of (2,5-dimethylarsolyl)lithium which on reaction with iodide gave 3.

2,2′,5,5′-Tetramethylbiarsolyl crystallizes at yellow blocks which melt to a yellow liquid at 67 °C. Similarly, solutions of 3 in hexane are indistinguishable in color from the solid. To determine why the biarsolyl is not thermochromic like its antimony analogue, we have obtained an X-ray crystal structure for 3.



4 5 3

X-ray Crystallography

Crystals of 2,2′,5,5′-tetramethyl-1,1′-biarsolyl were obtained by sublimation at 40 °C. A crystal was mounted on a Syntex $P2_1$

---

[1] Ashe, A. J., III; Butler, W.; Diephouse, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 207.

[2] For a molecular orbital model see: Hughbanks, T.; Hoffmann, R.; Whangbo, M.-H.; Stewart, K. R.; Eisenstein, O.; Canadell, E. *J. Am. Chem. Soc.* **1982**, *104*, 3876.

[3] Paneth, F. A. *Trans. Faraday Soc.* **1934**, *30*, 179. Paneth, F. A.; Loleit, H. *J. Chem. Soc.* **1935**, 366.

[4] Breunig, H. J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *B33*, 244, 990.

[5] Meinema, H. A.; Martens, H. F.; Noltes, J. G.; Bertazzi, N.; Barbieri, R. *J. Organomet. Chem.* **1977**, *136*, 173.

[6] Ashe, A. J., III; Ludwig, E. G., Jr. *Organometallics* **1982**, *1*, 1408.

[7] Becker, G.; Rössler, M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *B37*, 91.

[8] Breunig, H. J.; Müller, D. *Angew. Chem.* **1982**, *94*, 448.

[9] Becker, G.; Gutekunst, G.; Witthauer, C. *Z. Anorg. Allg. Chem.* **1982**, *486*, 90.

[10] Becker, G.; Freudenblum, H.; Witthauer, C. *Z. Anorg. Allg. Chem.* **1982**, *492*, 37.

[11] Daly, J. J.; Sanz, F. Helv. *Chim. Acta* **1970**, *53*, 1879.

[12] Rheingold, A. L.; Lewis, J. E.; Bellama, J. M. *Inorg. Chem.* **1973**, *12*, 2845.

[13] Waser, *J.*; *Schomaker*, V. *J. Am. Chem. Soc.* **1945**, *67*, 2014. Burns, J. H.; Waser, J. *Ibid.* **1957**, *79*, 859.

[14] Ashe, A. J., III; Diephouse, T. R. *J. Organomet. Chem.* **1980**, *202*, C95.

Table I. The Positional Parameters and Final Thermal Parameters for 2,2′,5,5′-Tetramethylbiarsolyl[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As(1)	0.17989 (4)	0.35958 (7)	0.27691 (4)	0.0054 (0)	0.0160 (1)	0.0045 (0)	0.0012 (1)	0.0017 (0)	0.0001 (1)
As(2)	0.14421 (4)	0.26489 (7)	0.42146 (4)	0.0057 (0)	0.0162 (1)	0.0057 (1)	−0.0012 (1)	0.0029 (0)	−0.0010 (1)
C(3)	0.3769 (4)	0.6056 (7)	0.3904 (4)	0.0078 (4)	0.017 (1)	0.0068 (4)	−0.0025 (6)	0.0029 (3)	−0.0009 (5)
C(4)	0.3362 (4)	0.4254 (7)	0.3411 (3)	0.0062 (4)	0.016 (1)	0.0044 (3)	−0.0004 (5)	0.0025 (3)	0.0010 (5)
C(5)	0.3960 (4)	0.2887 (7)	0.3265 (3)	0.0057 (4)	0.019 (1)	0.0052 (3)	0.0014 (5)	0.0026 (3)	0.0014 (5)
C(6)	0.3366 (4)	0.1253 (7)	0.2773 (3)	0.0070 (4)	0.019 (1)	0.0052 (3)	0.0026 (6)	0.0026 (3)	−0.0002 (5)
C(7)	0.2270 (4)	0.1219 (7)	0.2491 (3)	0.0072 (4)	0.018 (1)	0.0040 (3)	0.0010 (6)	0.0022 (3)	−0.0001 (5)
C(8)	0.1472 (5)	−0.0316 (8)	0.1976 (4)	0.0087 (5)	0.019 (1)	0.0074 (4)	−0.0010 (7)	0.0022 (4)	−0.0037 (6)
C(9)	0.0720 (5)	0.6566 (8)	0.4362 (4)	0.0094 (5)	0.021 (1)	0.0091 (5)	0.0032 (7)	0.0045 (4)	−0.0009 (7)
C(10)	0.1567 (4)	0.5074 (7)	0.4804 (4)	0.0071 (4)	0.016 (1)	0.0062 (3)	0.0002 (6)	0.0043 (3)	−0.0012 (5)
C(11)	0.2495 (4)	0.5155 (8)	0.5666 (3)	0.0082 (4)	0.021 (1)	0.0051 (3)	−0.0021 (7)	0.0039 (3)	−0.0014 (6)
C(12)	0.3217 (4)	0.3561 (8)	0.5913 (3)	0.0069 (4)	0.025 (1)	0.0037 (3)	−0.0020 (7)	0.0022 (3)	−0.0004 (6)
C(13)	0.2918 (4)	0.2161 (7)	0.5265 (3)	0.0070 (4)	0.017 (1)	0.0049 (3)	0.0015 (6)	0.0032 (3)	0.0033 (5)
C(14)	0.3542 (5)	0.0424 (8)	0.5336 (4)	0.0108 (6)	0.021 (1)	0.0075 (4)	0.0041 (7)	0.0046 (4)	0.0033 (7)

[a] The form of the anisotropic temperature factor is $\exp[-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$.

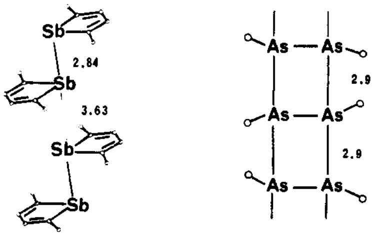


Figure 1. A comparison of the solid-phase structure of 2,2′,5,5′-tetramethylbistibolyl (1; left) with the ladder polymer of arsinomethane (2) (right). Distances (Å) along chains have been indicated. The circles represent carbon atoms.

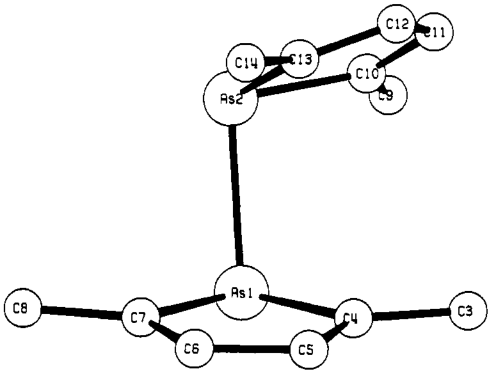


Figure 2. The molecular structure of 2,2′,5,5′-tetramethylbiarsolyl showing the numbering scheme. Hydrogen atoms are omitted.

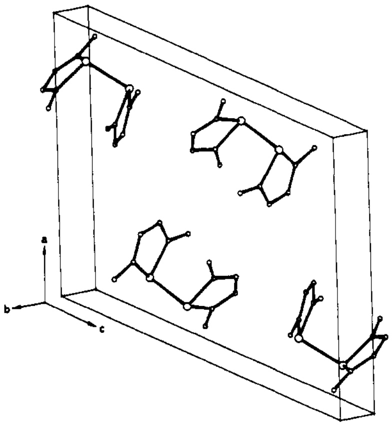


Figure 3. The crystal packing diagram of 2,2′,5,5′-tetramethylbiarsolyl.

Table II. Bond and Selected Nonbonded Distances (Å) for 2,2′,5,5′-Tetramethylbiarsolyl

As(1)As(2)	2.438 (1)	C(6)C(7)	1.334 (7)
As(1)C(7)	1.936 (5)	C(7)C(8)	1.503 (7)
As(1)C(4)	1.941 (5)	C(9)C(10)	1.498 (7)
As(2)C(10)	1.935 (5)	C(10)C(11)	1.340 (7)
As(2)C(13)	1.943 (5)	C(11)C(12)	1.449 (8)
C(3)C(4)	1.482 (7)	C(12)C(13)	1.329 (7)
C(4)C(5)	1.342 (7)	C(13)C(14)	1.489 (7)
C(5)C(6)	1.439 (7)		

Shortest Nonbonded Inter-Ring Distance:
C(4)C(13) = 3.353 (6)

Shortest Intermolecular AsAs Distances:
4.104 (2) and 4.495 (2)

Table III. Bond Angles (deg) for 2,2′,5,5′-Tetramethylbiarsolyl

C(7)As(1)As(2)	97.1 (1)	C(6)C(7)C(8)	127.9 (5)
C(4)As(1)As(2)	102.0 (1)	C(6)C(7)As(1)	108.9 (4)
C(10)As(2)As(1)	96.5 (2)	C(8)C(7)As(1)	123.1 (4)
C(13)As(2)As(1)	103.4 (1)	C(11)C(10)C(9)	126.7 (5)
C(7)As(1)C(4)	87.1 (2)	C(11)C(10)As(2)	109.2 (4)
C(10)As(2)C(13)	87.0 (2)	C(9)C(10)As(2)	124.1 (4)
C(5)C(4)C(3)	127.7 (5)	C(10)C(11)C(12)	116.6 (5)
C(5)C(4)As(1)	108.8 (4)	C(13)C(12)C(11)	117.9 (5)
C(3)C(4)As(1)	123.3 (4)	C(12)C(13)C(14)	127.5 (5)
C(4)C(5)C(6)	117.0 (4)	C(12)C(13)As(2)	108.6 (4)
C(7)C(6)C(5)	117.8 (5)	C(14)C(13)As(2)	123.8 (4)

automatic diffractometer and the space group determined to be $P2/c$ with $Z = 4$, $a = 13.247$ (6) Å, $b = 7.271$ (3) Å, $c = 14.534$ (5) Å, $\beta = 114.79$ (3)°, $V = 1271$ (1) Å^3, and d(calcd) = 1.621 g/cm^3. Data were collected by using graphite-monochromated Mo Kα radiation. The data were reduced by methods previously described.[15] The structure contains one molecule of **3** per asymmetric unit. Patterson techniques were used to find the arsenic positions. Other non-hydrogen atoms were located by difference Fourier. Isotropic refinement gave $R_1 = 0.065$ and $R_2 = 0.071$.[16] Further refinement using anisotropic thermal parameters for all non-hydrogen atoms gave $R_1 = 0.048$ and $R_2 = 0.053$. Hydrogen atomic positions were calculated and added as fixed contributions to the structure factors by assuming a bond distance of 1.00 Å and an isotropic temperature parameter of 1.1 times the thermal parameter of the atom to which the hydrogen is attached. Frefinement to convergence gave $R_1 = 0.037$ and $R_2 = 0.039$.

The molecular structure of **3** is illustrated in Figure 2, and a crystal packing diagram is shown in Figure 3. Table I contains the refined positional parameters and final thermal parameters for the non-hydrogen atoms. Tables II and III give the more important distances and the bond angles for non-hydrogen atoms.

---

[15] Computations were carried out on an Amdahl 470-V8 computer. Computer programs used during the structural analysis were SNCOP (data reduction, by W. Schmonsees), FORDAP (Fourier refinement, by A. Zalkin), ORFLS (full-matrix least-squares refinement, by Busing, Martin, and Levy), ORFFE (distances, angles and their esd's, by Busing, Martin, and Levy), ORTEP (thermal ellipsoid drawings, by S. K. Johnson), HATOMS (hydrogen atom positions, by A. Zalkin), and PLANES (least-squares planes, by D. M. Blow).

[16] $R_1 = \sum[|F_o| - |F_c|]/\sum|F_o|$. $R_2 = [\sum w(|F_o| - |F_o|)^2/\sum w|F_o|^2]^{1/2}$.

Table IV. Equations of Planes and Distances (Å) of CH_3 and As from the Planes

Plane 1: C(4)C(5)C(6)C(7)

$$0.247\,66x + 0.388\,05y - 0.887\,74z = -2.206\,04$$

Distance from Plane 1

As(1)	0.149	C(6)	0.003
C(3)	0.011	C(7)	−0.001
C(4)	0.001	C(8)	0.013
C(5)	−0.003		

Plane 2: C(10)C(11)C(12)C(13)

$$0.770\,82x + 0.405\,79y - 0.491\,09z = -2.269\,55$$

Distance from Plane 2

As(2)	0.187	C(12)	0.005
C(9)	−0.066	C(13)	−0.003
C(10)	0.003	C(14)	0.047
C(11)	−0.005		

Table V, a list of observed and calculated structure factors, is available in the supplementary data.

Discussion of the Structure

The molecular structure illustrated in Figure 2 shows that the biarsolyl **3** has a considerably different structure than does bistibolyl **1**. The bond angles about the arsenic atoms (97.1°, 102.0°, and 87.1° for C(7)As(1)As(2), C(4)-As(1)As(2), and C(7)As(1)C(4) and 96.5°, 103.5°, and 87.0° for C(10)As(2)As(1), C(13)As(2)As(1), and C(10)As(2)C(13), respectively) are consistently larger than the corresponding bond angles for the distibine (91.4°, 92.2°, and 81.5°).[1] This trend of decreasing bond angles with increasing atomic number is shown by other group 5 element compounds and is consistent with increasing p character of the bonding.[17,18] The larger bond angles effectively cant the dimethylarsolyl rings away from the As–As axis, so that the rings cannot be parellel to each other.

Unlike the dimethylstibolyl rings of **1**, the dimethylarsolyl rings are not strictly planar. The arsenic atoms extended out of the plane of the remaining four ring atoms toward the other arsolyl ring by 0.15 and 0.19 Å (see Table IV). Interestingly, the same type of deviation from planarity is found for the π-bonded 2,5-dimethylarsolyl moiety of 2,2′,5,5′-tetramethyl-1,1′-diarsaferrocene (**6**).[19] Similarly, the phosphorus atoms of the related 1-benzylphosphole (**7**)[20]and and (**8**) show out of plane deviation.[21]

The combined effect of these two structural features is that the backside of the As–As axis is partially blocked. It would be somewhat difficult to have intermolecular stacking along this axis. Alternatively, it might be argued that the electronic interactions responsible for the solid-phase color of **1** are sensitive to the torsional angle about the Sb–Sb bond.

While distibine **1** crystallizes in a transoid conformation about the Sb–Sb bond (point symmetry C_{2h}), diarsine **3** adopts and almost eclipsed gauche conformation about the As–As bond (point symmetry C_2). Figure 4 illustrates a Newman projection about the As–As bond. The torsional angle C(4)As(1)As(2)C(13) is −18.7°.

In recent years there has been considerable interest in the conformational properties of hydrazine analogues. Many of of these compounds preferentially populate gauche conformations. Whether this "gauche effect" is due to steric or electronic interactions has been somewhat controversial.[22-24] Structural information is available for several diarsines. Tetrakis(trimethylsilyl)diarsine (**9a**) crystallizes in a gauche conformation with a torsional angle of +18.0°.[9] On the other hand, 2,2′,3,3′,4,4′-hexa-*tert*-butyl-1,1′-diarsa-2,2′,3,3′,4,4′-hexaphosphabicyclobutane (**10**) crystallizes in a transoid arrangement.[25] Both tetramethyldiarsine[26] (**11a**) and tetrakis(trifluoromethyl)diarsine[27] crystallize in transoid conformations, but in the liquid phase **11a** exists as a mixture of transoid and gauche conformations.[26,28] In general, diarsines appears to have a delicate energy balance between various conformations.

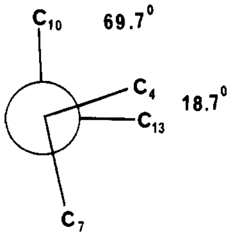
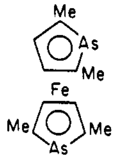
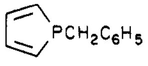


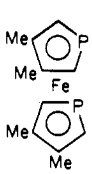
Figure 4. Newman projection of 2,2′,5,5′-tetramethylbiarsolyl along the As_1As_2 axis.



6



7

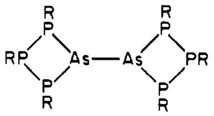


8

$(Me_3Si)_4E_2$ **9a–c**

Me_4E_2 **11a–c**

Et_4E_2 **12a–c**



10, R = *t*-C_4H_9

a, E = As; b, E = Sb; c, E = Bi

It is not obvious why 2,2′,5,5′-tetramethylbiarsolyl prefers the gauche over the anti-trans conformation. The observed conformation appears to minimize nonbonded $CH_3 \cdots CH_3$ interaction between the dimethylarsolyl rings. Formal rotation about the As–As bond, keeping all other structural parameters the same, brings two sets of CH_3 groups within 3.6 Å of each other. However, the observed gauche conformation has an even shorter nonbonded C-(4)···C(13) distance of 3.35 Å.

Circumstantial evidence can be cited that the same gauche conformation is exclusively populated in the liquid. The Raman spectrum of solid **3** shows a strong polarized band at 241 cm^{-1}, which we assign to the gauche As–As stretch. The Raman spectrum of the liquid shows the same band at 239 cm^{-1}, while no new bands appear above 125 cm^{-1}. This should be contrasted with the Raman

---

[17] Gibbs, J. H. *J. Phys. Chem.* **1955**, *59*, 644.

[18] Ashe, A. J., III *Top. Curr. Chem.* **1982**, *105*, 125.

[19] Chiche, L.; Galy, J.; Thiollet, G.; Mathey, F. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1344.

[20] Coggon, P.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1973**, 1888.

[21] de Lauzon, G.; Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 994.

[22] Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102.

[23] Baxter, S. G.; Dougherty, D. A.; Hummel, J. P.; Blount, *J. F.*; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 7795. Baxter, S. G.; Fritz, H.; Hellmann, G.; Kitschke, B.; Lindner, H. J.; Mislow, K.; Rüchardt, C.; Weiner, S. *Ibid.* **1979**, *101*, 4493.

[24] Durig, J. R.; Gimarc, B. M.; Odom, J. D. In "Vibrational Spectra and Structure": Durig, J. R., Ed.; Marcel Dekker: New York, 1975; Vol. 2, p 1.

[25] Baudler, M.; Aktalay, Y.; Heinlein, T.; Tebbe, K.-F. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *B37*, 299.

[26] Durig, J. R.; Casper, J. M. *J. Chem. Phys.* **1971**, *55*, 198.

[27] Thompson, J. W.; Witt, J. D; Durig, J. R. *Inorg. Chem.* **1973**, *12*, 2124.

[28] For a gas-phase study see: Cowley, A. H.; Dewar, M. J. S.; Goodman, D. W.; Padolina, M. C. *J. Am. Chem. Soc.* **1974**, *96*, 2648.

spectrum of liquid tetramethyldiarsine, which showed bands at 272 and 254 cm^{-1} for the trans and gauche conformers, respectively.[26]

While the Raman spectra of **3** show no evidence for the presence of the trans conformer, it can be argued that there is unlikely to be any large energy difference between the gauche and trans forms. The molecular structure of **3** shows two nonequivalent methyl groups (C(3),C(14) and C(8),C(9)). Rotation about the As–As bond through the transoid (or less likely the cisoid) conformation will interconvert different methyl (C(3) $\rightarrow$ C(8), C(9) $\rightarrow$ C(14). The ^{1}H NMR spectrum of **3** in tetrahydrofuran-d_8 shows only a single methyl and methine signal even at −100 °C. The implied fast rotation about the As–As bond on the NMR time scale suggests only a small energy of difference between the gauche and trans forms.

Since biarsolyl **3** is not isostructural with bistibolyl **1**, it is difficult to compare solid-phase effects for the two compounds. However, it is interesting to note the four series of dipictogen compounds **1** and **3**, **9a–c**, **11a–c** and **12a–c**. In each case the diarsines are not thermochromic while the distibines and for **9c**, **11c**, and **12c** the dibismuthines are thermochromic. Structural data have now been reported for **1**,[1] **3**, **9a**,[9] and **9b**.[10] Clearly, comparable data for other members of these series are needed.

Experimental Section

General Data. All operations were performed under an atmosphere of nitrogen or argon. NMR spectra were taken on a Brüker WM 360 MHz spectrometer. The IR spectrum was obtained on a Beckmann IR 4240 spectrometer calibrated with polystyrene 1601.4-cm^{-1} absorption band. The mass spectrum was determined by using a Finnigan 4023 GC/MS using methane chemical ionization. The Raman spectra were taken with a Spex 1401 double spectrometer using the 6328-Å excitation line of a Spectra Physical Model 125 He–Ne laser. The combustion analysis was determined by the Spang Microanalytical Laboratory, Eagle Harbor, MI.

1-Phenyl-2,5-dimethylarsole. A solution of 4.0 g (18 mmol) of phenylarsenic dichloride in 10 mL of tetrahdyrofuran was added dropwise with stirring to 3.0 g (10 mmol) of 1,1-dibutyl-2,5-dimethylstannole[14] in 15 mL of tetrahydrofuran. After being stirred at 25 °C for 2 h, the reaction mixture was added to 100 mL of dilute NaOH. A large precipitate formed which was extracted with 3 × 50 mL of pentane. The extracts were washed with excess water and then dried over anhydrous magnesium sulfate. Distillation gave 1.3 g (59%) of 1-phenyl-2,5-dimethylarsole, bp 60–65 °C (0.15 torr). The ^{1}H NMR spectrum was identical with that reported in the literature.[29]

2,2′,5,5′-Tetramethyl-1,1′-biarsolyl. Lithium wire (0.25 g, 36 mmol) was cut into pieces approximately 2 mm in diameter and then placed in 20 mL of tetrahydrofuran. 1-Phenyl-2,5-dimethylarsole (1.5 g, 6.5 mmol) in 10 mL of tetrahydrofuran was added in one batch. The initially light yellow solution became brick-red and the solution spontaneously warmed to 50 °C over 15 min. After 3 h, the solution was decanted from the excess lithium, and a solution of iodine in tetrahydrofuran was added dropwise until the brown iodine color persisted. Removal of solvent left an oil which sublimed at 40 °C (0.05 torr) over a period of 2 days. Blocklike yellow crystals of product, mp 74–75 °C, were obtained. This product is oxygen sensitive: ^{1}H NMR (C_4D_4O) δ 1.99 (12 H, s), 6.49 (4 H, s), MS (CI-CH_4), *m/e* (relative intensity) 311 (36) ($M^+ + 1$ for $C_{12}H_{16}As_2$), 251 (17), 233 (12), 193 (19), 191 (13), 190 (16), 171 (26), 161 (30), 157 (25), 155 (13), 151 (20), 115 (57), 113 (100); IR (CCl_4) 3010, 2960, 2920, 2860, 1450, 1250, 1130, 900, 825 cm^{-1}; Raman (He–Ne laser, 6328-Å exciting line) solid (cm^{-1}) 50 (14), 105 (10), 124 (51) 218 (24), 241 (100), 285 (1), 315 (vw), 334 (w), 391 (2), 432 (1), 502 (3), 529 (3), 695 (w), *liquid* (cm^{-1}) 94 (74), 125 (10), 215 (51), 239 (100), 280 (4), 322 (w), 391 (1), 428 (3), 502 (vw), 530 (23), 696 (w). Anal. Calcd for $C_{12}H_{16}As_2$: C, 46.48; H, 5.20. Found: C, 46.29; H, 5.10.

Acknowledgment. Support of our work by A.F.O.S.R. (Grant No. 81-099) is gratefully acknowledged.

Registry No. **3**, 85650-31-3; **4**, 77214-60-9; **5**, 20527-10-0; $C_6H_5AsCl_2$, 696-28-6.

Supplementary Material Available: A table of observed and calculated structure factors for **3** (8 pages). Ordering information is given on any current masthead page.

---

(29) Märkl, G.; Hauptmann, H. *Tetrahedron Lett.* 1968, 3257.

Bonding in Phosphaferrocenes and Reactivity of the Phospholyl Ligand Studied by Molecular Orbital Calculations

Nenad M. Kostić† and Richard F. Fenske*

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received July 26, 1982

We carried out nonparametrized molecular orbital calculations on PpFeCp and on three conformations of Pp_2Fe; Pp represents η^5-$C_4H_4P^-$ and Cp represents η^5-$C_5H_5^-$. The Pp and Cp ligands have similar bonding abilities and form π bonds with the metal d orbitals. The P lone pair is not affected appreciably by the coordination of Ph to the Fe atom. The calculated and observed distributions of electron density in PpFeCp fully agree with each other. Compound Pp_2Fe adopts the conformation in which those molecular orbitals that are important for bonding are stabilized most. Electrophilic substitutions into these "sandwich" molecules are highly regioselective, apparently because these reactions are charge controlled. Although the phosphorus lone pair in Pp remains localized on this atom, the P atoms in the "sandwich" molecules are not nucleophilic because the lone pair is not in a frontier molecular orbital. The P atoms are even weakly electrophilic; the nucleophilic substitutions into the "sandwich" molecules apparently are controlled by orbital and charge effects in concert.

Introduction

Since the discovery of ferrocene, transition-metal "sandwich" complexes have attracted attention of many chemists. Several cyclic molecules or ions containing heteroatoms are isoelectronic with η^5-$C_5H_5^-$ anion (designated Cp) and also from π complexes with transition metals. One such ligand is the phospholyl anion, $C_4R_4P^-$ drawn schematically in 1. Regardless of the groups R, which in our study are H atoms, we will designate it Pp.

---

† Present address: Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.

0276-7333/83/2302-1008$01.50/0 © 1983 American Chemical Society