

- Chem. Soc.*, **98**, 114 (1976); (d) D. L. Whalen, *ibid.*, **95**, 3432 (1973); (e) D. L. Whalen and A. M. Ross, *ibid.*, **96**, 3678 (1974); (f) P. Y. Bruice, T. C. Bruice, H. G. Selander, H. Yagi, and D. M. Jerina, *ibid.*, **96**, 6814 (1974); (g) P. Y. Bruice, T. C. Bruice, P. M. Dansette, H. G. Selander, H. Yagi, and D. M. Jerina, *ibid.*, **98**, 2965 (1976); (h) J. W. Keller and C. Heidelberger, *ibid.*, **98**, 2328 (1976).
- (5) J. G. Buchanan and K. Z. Sable in "Selective Organic Transformations", Vol. 2, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N.Y., 1972, p 85.
- (6) A. Balsamo, G. Berti, P. Crotti, M. Ferretti, B. Macchia, and F. Macchia, *J. Org. Chem.*, **39**, 2596 (1974).
- (7) The concentration of H^+ was calculated by assuming that it is equal to the hydrogen ion activity measured by the glass electrode. The reactions were monitored spectrophotometrically at 225–235 nm in the thermostated cell compartment of a Cary 16K spectrophotometer.
- (8) Product analyses were carried out with the aid of a Radiometer pH-stat. 2-Indanone (**4**) was unstable at $pH > 10$ in spectrophotometric concentrations. In a control experiment in which a known amount of 2-indanone was allowed to stir at $pH 8.3$ under the conditions for hydrolysis of **1**, only 61% of the ketone was recovered. Product mixtures were analyzed by gas chromatography on a 5% DC-550 column (5 ft, $\frac{1}{8}$ in.) with silylated solid support.
- (9) The detailed mechanism for the hydrolysis of **1** via the k_0 process has not been determined. The mechanism presented in Scheme II is consistent with that found for rearrangement of arene oxides, ref 4a–c.
- (10) H. Bodot, J. Jullien, and E. Leblanc, *Bull. Soc. Chim. Fr.*, 41 (1962).
- (11) Both *cis* and *trans* chlorhydrins **8** have similar solvolysis rates in 80% dioxane–water, ref 10. No attempt was made in this study to determine the relative reactivities of the *cis* and *trans* isomers at $pH > 8$, although the *trans* isomer is presumably more reactive than the *cis* isomer.
- (12) Phenanthrene 9,10-oxide exhibits a pH-rate profile (ref 4f,g) in 1 M KCl that resembles the profile of indene oxide. It was suggested that a change of mechanism from general acid catalysis by water to nucleophilic addition of water to phenanthrene 9,10-oxide was responsible for the inflection point observed, ref 4g. We have determined the pH-rate profiles for phenanthrene 9,10-oxide in both KCl and $NaClO_4$ solutions, and have concluded that the inflection point at $pH 7.2$ reported in 1 M KCl solution is due to a specific effect of chloride ion, D. L. Whalen, A. M. Ross, and D. M. Jerina, unpublished results.
- (13) Some difficulties are encountered in measuring the pH of concentrated perchlorate solutions, D. B. Dennison, G. A. Gettys, D. G. Kubler, and D. Shepard, *J. Org. Chem.*, **41**, 2344 (1976).

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1,1-Dimethyl- λ^5 -phosphabenzene and 1,1-Dimethyl- λ^5 -arsabenzene

Sir:

Despite rather extensive investigation of the chemistry of λ^5 -phosphabenzene **1**,^{1,2} the question whether these structures possess appreciable aromatic stabilization (**1'**) or whether they are better represented as delocalized ylides (**1''**, **1'''**, **1''''**) remains open. The basicity of the ring-unsubstituted 1,1-diphenyl- λ^5 -phosphabenzene **1a**, prepared by a rather laborious route, suggests an ylide type of bonding.³ Unfortunately, data are limited and no NMR spectra have appeared for **1a**. Most of the investigations have focused on the more readily available 1,1-disubstituted-2,4,6-triaryl- λ^5 -phosphabenzene **2**.¹ The chemistry and spectra of **2** have usually been discussed in terms of an aromatic model.^{1,2} Since the heavy substitution of **2** may mask the properties of the parent ring system, a reinvestigation of the ring-unsubstituted- λ^5 -phosphabenzene seems warranted. We now wish to report on a facile synthesis of 1,1-dimethyl- λ^5 -phosphabenzene, **1b**, and on a similar synthesis of the first λ^5 -arsabenzene **3**.³

The readily available 1-methyl-2,4-phosphacyclohexadiene, **4**⁴ may be quaternarized with methyl iodide to give 50% of the phosphonium salt **5**, mp 198–199°C dec. ¹H NMR (Me_2SO-d_6) δ 7.1 (ddd, $J = 35, 12, 5.5$ Hz, 1 H), 6.6–6.0 (m, 3 H), 3.3 (dd, $J = 17, 4$ Hz, 2 H), 2.0 (d, $J = 15$ Hz, 6 H). Addition of this salt to Me_2SO containing excess dimsyl anion produced the desired 1,1-dimethyl- λ^5 -phosphabenzene, **1b**. The proton NMR spectrum illustrated in Figure 1 shows signals for H_3 (H_5) centered at δ 6.70 ($J_{PH} = 34$ Hz), for H_4 as

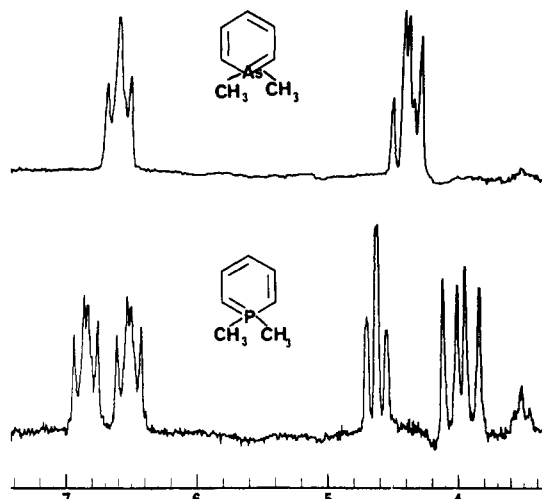
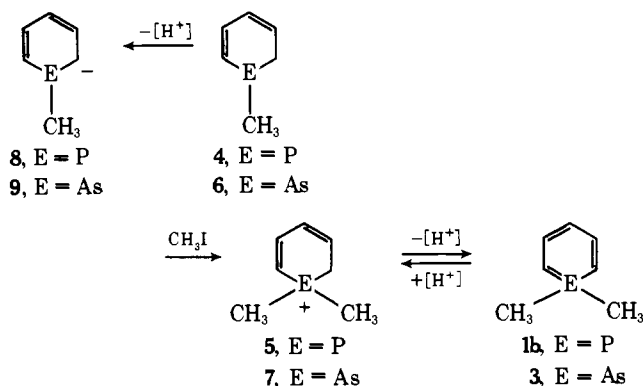
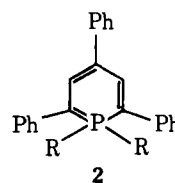
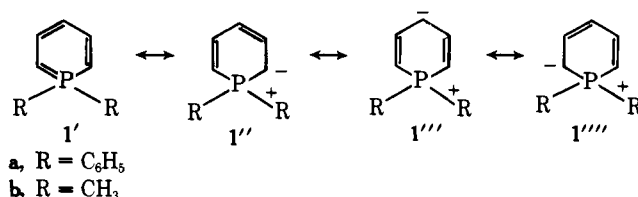


Figure 1. The lower field portion of the 1H NMR spectra of 1,1-dimethyl- λ^5 -arsabenzene, **3** (above), and 1,1-dimethyl- λ^5 -phosphabenzene, **1b** (below). Peak positions are indicated downfield (δ) from internal Me_4Si .



a triplet at δ 4.62 ($J = 7.5$ Hz), for H_2 (H_6) as doublet of doublets at δ 3.98 ($J = 17, 11$ Hz), and for the methyl groups as a doublet at δ 1.5 ($J = 13.5$ Hz). ¹³C NMR (Me_2SO) δ 139.2 (s for C_3, C_5), 94.0 (d, $J = 22$ Hz for C_4), 67.5 (d, $J = 94$ Hz for C_2, C_6), 24.7 (d, $J = 57$ Hz for CH_3). Treating **1b** with acid leads back to the phosphonium salt **5**. Four P-ring protons of **5** readily exchange for deuterium in Me_2SO-d_6 containing D_2O and base. The 1H NMR signals for the protons at H_2, H_4 , and H_6 completely disappear while the peaks for H_3 (a 35 Hz doublet at δ 7.1) and for H_5 (a 22 Hz doublet at δ 6.1) and for the methyl groups remain undiminished. The facile interconversion of **1** and **5** is similar to that reported by Märkl for **1a**.³

In a completely analogous manner 1-methyl-2,4-arsacyclohexadiene, **6**,⁴ can be quaternarized to salt **7**, mp 195–197°C. ¹H NMR (Me_2SO-d_6) δ 7.0 (dm, $J = 12$ Hz, 1 H), 6.6 (d, $J = 12$ Hz, 1 H), 6.2 (m, 2 H), 3.4 (d, $J = 3$ Hz, 2 H), 2.2 (s,

6 H). The arsonium salt **7** reversibly yields 1,1-dimethyl- λ^5 -arsabenzene **3** on treatment with dimsyl anion in Me_2SO . The proton NMR spectrum illustrated in Figure 1 shows signals for H_3 , H_5 as a multiplet centered at δ 6.63, for H_4 as an 8 Hz triplet at 4.43 partially overlapping with 10 Hz doublet at 4.34 for H_2 , H_6 , while the methyl groups are at δ 1.5. ^{13}C NMR (Me_2SO) δ 138.6 (for C_3 , C_5), 91.8 (for C_4), 70.3 (for C_2 , C_6) 22.4 (for CH_3). Again four ring protons of **7** at H_2 , H_4 , and H_6 are washed out with $\text{D}_2\text{O}-\text{Me}_2\text{SO}$ and base.⁶

In the NMR spectra of **1b** and **3** the H_2 , H_4 , and H_6 protons have chemical shift values well outside the aromatic region and are markedly upfield from the range of olefinic protons of their conjugate acids, **5** and **7**. On the other hand the H_3 and H_5 protons of **1** and **3** are relatively highly deshielded. However, the signals for these protons occur approximately half a part per million upfield from the corresponding H_3 protons of conjugate acids **5** and **7**. The absences of any shift to lower fields for H_3 and H_5 as well as the large upfield shift of H_2 , H_4 , and H_6 suggest that there are no appreciable ring current effects in λ^5 -phosphabenzene and λ^5 -arsabenzene.⁷ In fact the NMR spectra, together with proton exchange data, strongly suggest that C_2 , C_4 , and C_6 bear a high electron density. Thus we must view the ring carbon atoms as favoring a pentadienyl anion which is stabilized largely by electrostatic interaction with the positive heteroatom.

The C NMR spectral data on **1** and **3** further support these conclusions.⁷ Signals for C_2 and C_6 occur more than 60 ppm upfield from the signals of C_3 and C_5 .⁸ As in the proton NMR spectra the signal for C_4 is not shifted as far upfield. Very likely this is a consequence of polarization of the carbanionic pentadienyl system by the positive heteroatom.⁹ It is striking that the chemical shift values of ylides **1** and **3** are very nearly identical with those of anions **8** and **9**, available from deprotonation of **1** and **3**.^{4,10} It seems highly likely that the electron density at each carbon is very similar. In contrast to the near identity of chemical shift values of anions and ylides, the $^{31}\text{P}-^{13}\text{C}$ and $^{31}\text{P}-^1\text{H}$ coupling constants are markedly divergent for **1** and **8**,^{4,11} an expected consequence of the different hybridization at P in the two systems.

^1H and ^{13}C NMR spectra of 1,1-dimethyl- λ^5 -phosphabenzene and 1,1-dimethyl- λ^5 -arsabenzene present strong presumptive evidence that these compounds are ylidic in character. In this respect they strongly resemble the thiabenzene.^{9,12,13} Several bonding proposals have been put forward for λ^5 -phosphabenzene¹³ and similar cyclic systems^{15,16,17} conjugated via d-p π -bonding to higher row elements. Our findings do not rule out the use of the ultimate arsenic and phosphorus d orbitals in bonding of the λ^5 -phosphabenzene and the λ^5 -arsabenzene, but they do strongly argue against any bonding proposal in which appreciable electron density is donated from carbon to the heteroatoms.

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References and Notes

- (1) K. Dimroth, *Fortschr. Chem. Forsch.*, **38**, 1 (1973).
- (2) G. Maerkl, *Lect. Heterocycl.*, **1**, 69 (1972).
- (3) G. Maerkl, *Angew. Chem., Int. Ed. Engl.*, **2**, 153, 479 (1963); **4**, 1023 (1965).
- (4) A. J. Ashe, III, and T. W. Smith, *Tetrahedron Lett.*, submitted.
- (5) The NMR spectra were recorded using either a Varian T60 or JEOL JNM-PFT/100 instrument. Me_4Si was used as an internal standard.
- (6) The ^1H NMR spectrum showed only singlets at δ 7.0 (1 H), 6.2 (1 H), and 2.2 (6 H), while there was a strong peak at δ 4 for HOD.
- (7) For comparison see data for λ^5 -phosphabenzene and λ^5 -arsabenzene: A. J. Ashe, III, *J. Am. Chem. Soc.*, **93**, 3293 (1971); A. J. Ashe, III, R. R. Sharp, and J. W. Tolan, *ibid.*, **98**, 5451 (1976).
- (8) Data for **2** are similar: T. Bundgaard, H. L. Jakobsen, K. Dimroth, and H. H. Pohl, *Tetrahedron Lett.*, 3179 (1974).
- (9) See A. G. Hortmann and R. L. Harris, *J. Am. Chem. Soc.*, **93**, 2471 (1971).

- (10) The ^{13}C NMR spectrum of **8** consists of doublets at δ 71.8 (3 Hz) for C_2 , 133.0 (8 Hz) for C_3 , and 96.5 (9 Hz) for C_4 , while signals for **9** occur at δ 72.9 for C_2 , 132.1 for C_3 , and 92.6 for C_4 . See ref 4.
- (11) For **8**, $J_{\text{PH}}^2 = 53$ Hz while $J_{\text{PH}}^3 \sim 8$ Hz.
- (12) A. G. Hortmann, R. L. Harris, and J. A. Miles, *J. Am. Chem. Soc.*, **96**, 6119 (1974); A. G. Hortmann and R. L. Harris, *ibid.*, **92**, 1803 (1970).
- (13) B. E. Maryanoff, J. Stackhouse, G. H. Senkler, Jr., and K. Mislav, *J. Am. Chem. Soc.*, **97**, 2718 (1975).
- (14) H. Oehling and A. Schweig, *Tetrahedron Lett.*, 4941 (1970).
- (15) D. P. Craig, M. L. Hoffman, R. Mason, and N. L. Paddock, *J. Chem. Soc.*, 1376 (1961).
- (16) C. A. Coulson, *Nature (London)*, **221**, 1106 (1969).
- (17) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, pp 430-436.
- (18) A. P. Sloan Fellow 1972-1976.

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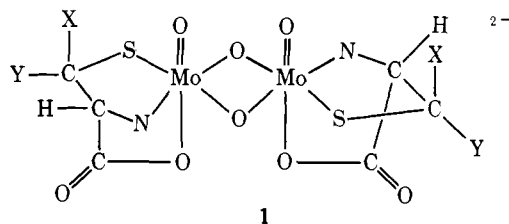
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Ligand Effects and Product Distributions in Molybdothiol Catalyst Systems

Sir:

The reduction of acetylene to ethylene is one of the reactions catalyzed by nitrogenase and is commonly used to assay for the activity of this enzyme.¹ The complex, $\text{Mo}_2\text{O}_4(\text{cys})_2^{2-}$, **1** ($\text{X} = \text{Y} = \text{H}$),² is reported to mimic the enzyme in this re-



spect,³⁻⁶ catalyzing the formation of ethylene (but with small amounts of ethane), the reducing power being supplied either by NaBH_4 ^{3,4} or electrolytically.⁵ Although complexes of molybdenum seem superior as catalysts to those of other transition metals,⁶ structural variations in the ligand have not been systematically pursued. We have therefore initiated a program of preparation and testing of Mo complexes containing cysteine-related ligands as potential catalysts. These studies reveal several rather striking results. Even with the cysteine complex, we find the major reduction product of acetylene in borate buffer to be 1,3-butadiene (C_4H_6), not ethylene. The production of C_4H_6 presumably went unnoticed in all previous investigations. Further, we observe that seemingly minor changes in ligand or buffer have profound effects on the product distribution and/or catalytic activity.

Typical reactions were run in 15-ml "Hypovials" (Pierce Chemical Co.) as follows: Septum-sealed vials containing 25 mg of complex and 3.5 ml of pH 9.6 buffer (0.1 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ or 0.2 M Na_2CO_3) were flushed with acetylene and kept at 30 °C for 4-6 h⁷ before initiating the reaction by injection of 0.10 ml of 2 M NaBH_4 in DMF.⁸ Reaction mixtures were then shaken⁹ (30 °C bath) and the gas phase analyzed¹⁰ by GC on Porapak N (temperature programming). The results are summarized in Table I.

Butadiene (C_4H_6) was found to be a major product for those complexes in Table I which were catalytically active in the reduction of acetylene. A preparative scale reaction using **1** ($\text{X} = \text{Y} = \text{H}$) yielded sufficient C_4H_6 for characterization by methods other than GC. The product was separated by trapping at -50 °C and confirmed to be butadiene by its NMR and mass spectra. Its formation constitutes an overall two-electron reductive dimerization of acetylene.

Our first attempts at ligand variation involved methyl sub-