

Figure 1. A comparison of the experimental radial distribution curve for *p*-xylylene with theoretical radial distribution curves for models I, I', and II.

Table I. Structural Parameters for *p*-Xylylene<sup>a</sup>

Parameter <sup>b</sup>	Value <sup>c</sup>	$l_{ij}$ , <sup>d</sup> Å	HMO values, Å
C—C	$1.451 \pm 0.007$ Å	0.059	1.45
C=C (av)	$1.381 \pm 0.008$ Å	0.049	1.39 (C <sub>1</sub> —C <sub>7</sub> ), 1.38 (C <sub>2</sub> —C <sub>3</sub> )
C—H (av)	$1.116 \pm 0.035$ Å	0.078	
∠C <sub>2</sub> —C <sub>1</sub> —C <sub>6</sub>	$122.2 \pm 3.7^\circ$		
∠C <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub>	$118.9 \pm 1.9^\circ$		
∠CCH	120° (assumed)		
∠HCH	120° (assumed)		

<sup>a</sup> The numbering system of the atoms used in defining the parameters is given in the text. <sup>b</sup> Distances are reported as  $r_g$  values, while the angles are derived from the  $r_g$  structure. <sup>c</sup> Uncertainties are  $3\sigma$ . <sup>d</sup> Mean-square amplitudes of vibration.

reasonable fit ( $R = 0.054$ ),<sup>12</sup> but the aromatic C—C and C<sub>1</sub>—C<sub>7</sub> distances were unrealistically lengthened to 1.413 and 1.553 Å, respectively. It is also noteworthy in regard to model I' that spectroscopic studies unanimously agree<sup>4-6</sup> that the ground state of *p*-xylylene is best represented by a singlet structure. Moreover, photoelectron spectroscopic evidence<sup>6</sup> suggests that the singlet biradical is the first excited state of *p*-xylylene and lies 4.0 eV above the ground state. This renders it unlikely that either singlet or triplet biradical species are significantly populated under the conditions of the experiment.

The final pair of models yielded lower  $R$  factors and were in greater harmony with existing experimental and theoretical evidence concerning the structure of *p*-xylylene. In model II a single average double-bond distance was used for C<sub>2</sub>—C<sub>3</sub> and C<sub>1</sub>—C<sub>7</sub>. Two separate distances were employed for C<sub>2</sub>—C<sub>3</sub> and C<sub>1</sub>—C<sub>7</sub> in model III. Early in the analysis it became obvious that the C<sub>2</sub>—C<sub>3</sub> and C<sub>1</sub>—C<sub>7</sub> distances were very closely spaced and highly correlated. In view of the fact that less than perfect data from a single camera distance was being used in the analysis, the final refinements were made on the simpler model II. It is very likely that data of improved quality can be obtained in the future; a meaningful comparison of models II and III may be possible at that time. The least-squares structure

( $R = 0.038$ ) for model II is presented in Table I. The most noteworthy feature of the structural parameters in Table I is that *p*-xylylene is not a simple assemblage of conjugated double and single bonds. The average C—C double-bond length is several hundredths of an Ångström longer than the typical value for a conjugated double bond.<sup>13</sup> Table I also includes several C—C bond lengths estimated<sup>1c,14</sup> from simple HMO theory. The agreement is much better than might reasonably be expected. The extent to which the theoretical and experimental values parallel one another is interesting, however.

**Acknowledgment.** We wish to thank Professor Richard Hilderbrandt for helpful discussions and significant contributions in the early stages of the design of the nozzle assembly.

**Supplementary Material Available:** Raw intensity data (Table II), estimated force fields for models I and II (Tables III and IV), comparison of the experimental leveled intensity curve with the least-squares adjusted curve for model II (Figure 2), the correlation matrix for model II, (Table V), the error matrix for model II (Table VI), and the calculated mean-square amplitudes of vibration for model II (Table VII) (7 pages). Ordering information is given on any current masthead page.

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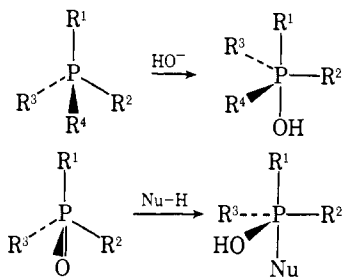
Received November 5, 1976

## Direct Observation of a Hydroxyphosphorane in Equilibrium with a Phosphate Ester

Sir:

In the hypothesis that transient intermediates with penta-coordinate phosphorus are formed in nucleophilic displacements at tetracoordinate phosphorus, hydroxyphosphoranes are involved when the nucleophile is hydroxide ion in the case of phosphonium salts, and with any protic nucleophile in the case of phosphine oxides, phosphinates, phosphonates, and

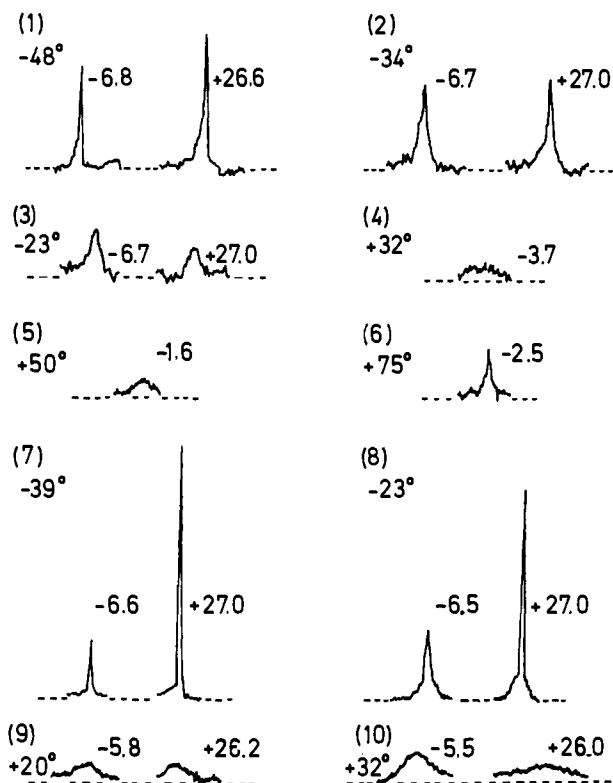
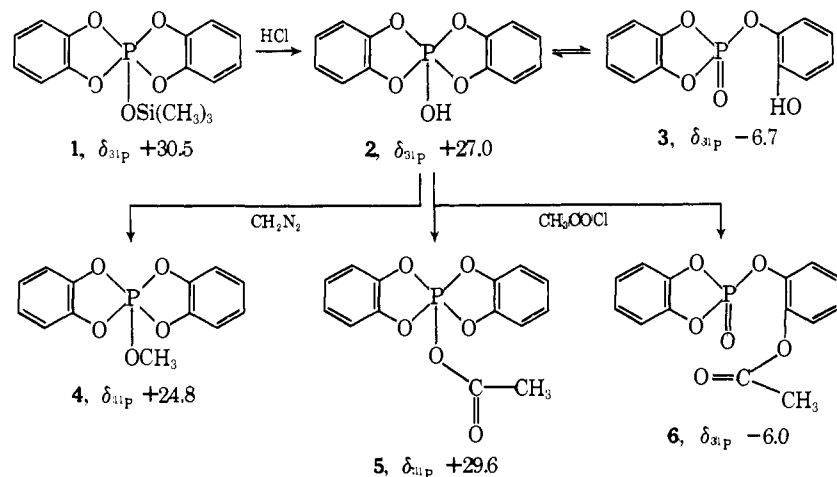
phosphate esters.<sup>1</sup> To our knowledge, the direct observation of a hydroxyphosphorane has not been reported, although oxyphosphorane intermediates have been trapped in reactions of five-membered cyclic phosphate esters of phenol and of *O*-trimethylsilylcatechol,<sup>2</sup> and subsequently in isomerizations of four-membered cyclic phosphinate esters of 3-methylcatechol.<sup>3</sup>



We wish to report the isolation of a crystalline compound<sup>4,5</sup> which may have the hydroxyphosphorane structure **2** or the hydroxyphenylphosphate structure **3**, but which exists in solution as a mixture of the two forms, **2** ⇌ **3**, in dynamic equilibrium. The <sup>31</sup>P NMR signals of both structures can be observed at low temperatures in aprotic solvents; cf. Figure 1. In the more polar (ε 38 at 20 °C) and basic solvent acetonitrile-*d*<sub>3</sub>, the ratio of the P(5)/P(4) compounds is 1.5/1, at -48 °C in a 0.25 M solution. The two signals coalesce at ca. +10 °C and become sharper again as the temperature is increased to the limit allowed by the solvent. Some decomposition is observed at the higher temperatures; otherwise, the changes in the spectra are reversible. In the less polar (ε 21 at 25 °C) and basic solvent acetone-*d*<sub>6</sub>, the ratio of the P(5)/P(4) compounds is ~3/1, at -48 °C in a 1.0 M solution. In this solvent, the two signals coalesce at ca. +55 °C, but the low boiling point of the solvent prevents the observation of the sharpening of the signals above the coalescence temperature.

The addition of 1 mol equiv of diazomethane in ether to a suspension of **2** (or **3**) in dichloromethane at 0 °C results in the virtually *exclusive* formation of spirodicatcholmethoxyphosphorane (**4**). The same result is observed if **2** (or **3**) is suspended in ether, alone or in the presence of catalytic amounts of boron trifluoride-etherate complex, and is treated with diazomethane. An authentic sample of oxyphosphorane **4** was synthesized<sup>6</sup> from spirodicatcholchlorophosphorane and methanol. The phenoxy analogue (δ<sub>31P</sub> +30.2) of **4** has also been prepared<sup>7</sup> and has been submitted to x-ray diffraction analysis,<sup>8</sup> which shows that the skeletal geometry of this type of phosphorane departs significantly from those of the ideal trigonal bipyramid and tetragonal pyramid.

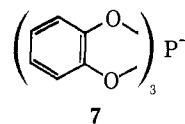
Treatment of **2** (or **3**) with an excess of acetyl chloride at 25



**Figure 1.** <sup>31</sup>P NMR signals of the hydroxyphosphorane **2** (+27 ppm to high field of H<sub>3</sub>PO<sub>4</sub> = 0), and the hydroxyphenylphosphate **3** (-7 ppm). Spectra 1-3 in 0.25 M, 4-6 in 0.5 M acetonitrile-*d*<sub>3</sub>; spectra 7-10 in 1.0 M acetone-*d*<sub>6</sub>. In acetonitrile-*d*<sub>3</sub> the signals coalesce at ca. +10 ± 5 °C and in acetone-*d*<sub>6</sub> at ca. +55 ± 5 °C.

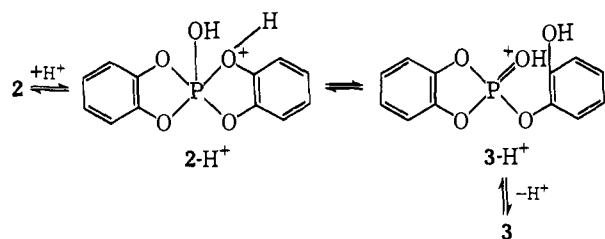
°C produces mostly (~80%) 2-acetoxyphenyl-*o*-phenylene phosphate (**6**)<sup>9</sup> and relatively small amounts (<20%) of what appears to be spirodicatcholacetoxyphosphorane (**5**), from the value of its <sup>31</sup>P NMR signal.

The introduction of basic substances, including dimethyl sulfoxide, into solutions of **2** (or **3**) causes the disappearance of the signals of these compounds, and the appearance of a sharp signal at +83.5 ppm, which is presumably due to the hexacoordinate phosphorus anion, **7**.<sup>10-12</sup>

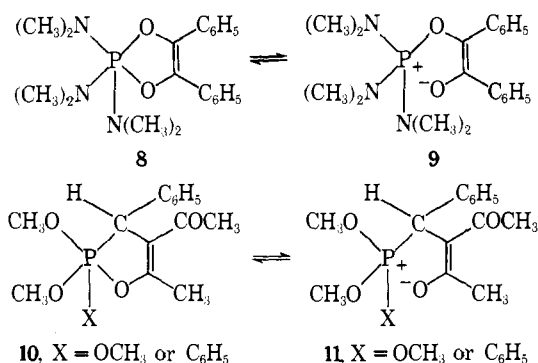


From these data we speculate that the equilibrium **2** ⇌ **3** is acid catalyzed, as indicated by structures **2**-H<sup>+</sup> and **3**-H<sup>+</sup>. The relationship between the ratio of P(5)/P(4) at equilibrium, and

the structure of the solvent, suggests that the hydroxyl groups bonded to pentavalent phosphorus may be a relatively weak acid, weaker than the phenolic hydroxyl group.



The experimental demonstration of the existence of a dynamic equilibrium involving the hydroxyphosphorane **2** and the hydroxyphosphate **3** supports the earlier,<sup>1,13</sup> and the most recent,<sup>3,12,14-16</sup> postulations of the occurrence of analogous equilibria in many reactions of phosphate and phosphonate esters. Related equilibria between pentacoordinate and tetracoordinate phosphorus compounds **8**  $\rightleftharpoons$  **9** and **10**  $\rightleftharpoons$  **11** have been detected<sup>17,18</sup> by means of <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy and, in one case,<sup>17</sup> **8**  $\rightleftharpoons$  **9**, by the actual isolation of both structures involved in the equilibrium.



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- (5) Anhydrous HCl was passed through a 0.1 M  $CH_2Cl_2$  solution of spirodicatechol(trimethylsilyloxy)phosphorane<sup>2</sup> (**1**) at  $0^\circ C$  (1 h). Ar was passed through the solution (20 min), the solvent was evaporated, and the residue was crystallized from  $CH_3CN$ . **2** (or **3**): mp  $120-121^\circ C$ ;  $\tau$  2.25, 2.85 (1:8 relative intensities) ( $CD_3CN$ ).<sup>4</sup>
- (6) Equimolar amounts of reactants and triethylamine in benzene at  $20^\circ C$  (2 h). **4**: mp  $72-74^\circ C$  (hexane);  $\tau$  6.33 ( $J = 14.0$  Hz);  $\delta_{13C}$  56.6 ( $J = 9.2$ ), 110.7 ( $J = 16.8$ ), 122.3, 143.2 ( $J = 6.9$ ).
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Received March 29, 1977

## Polymer Attached Metallocenes. Evidence for Site Isolation

Sir:

We recently reported that the attachment of titanocene species to a rigid polymer resulted in an increase in activity for olefin hydrogenation.<sup>1</sup> Since titanocene species undergo deactivation by polymerization processes,<sup>2</sup> it was proposed that this increase in activity resulted from site isolation on the polymer. Since this phenomenon has become a major concern with polymer attached reagents and catalysts,<sup>3</sup> we have studied site isolation as a function of loading of catalyst.

Titanocene dichloride was attached to 20% divinylbenzene-styrene copolymer by the method reported earlier.<sup>1</sup>

The loading was controlled to give values between 0.044 and 0.266 mmol of Ti/g of polymer as indicated in Table I. Each sample (1-hexene) was reduced with *n*-BuLi in hexane and then used for the catalytic hydrogenation for each sample. As can be seen, the rate as expressed in milliliters of  $H_2$ /minute mmol of Ti, increases as the loading decreases. Also, the rate in milliliters/minute gram of polymer reaches a maximum at a loading of 0.14 mmol of Ti/g of polymer. Both of these observations are consistent with site isolation at low loadings.

The rate expressed in milliliters/minute mmol of Ti gives a measure of the percentage of the titanium centers which are active. As the loading increases, the percentage of metal centers close enough to interact will increase. Consequently the rate per potential active sites will decrease.

A consideration of the data as expressed in terms of milliliters/minute gram of polymer is quite revealing. A model for this system can be considered that is made up of a near rigid surface<sup>5</sup> (the surface of the polymer) with the metal sites put on in a completely random fashion. The sites can be assumed not to overlap completely and, if two complexes touch, i.e., are within reaction distance, the center can be assumed to be inactive. If each complex is also assumed to occupy a constant surface area, then the equation for such a model is

$$\text{rate}_{\text{obsd}} = k\rho(1 - \rho)^n$$

where  $k$  = monomer rate constant

Table I. Hydrogenation of 1-Hexene by Polymer Supported  $Cp_2TiCl_2$  at Room Temperature<sup>a</sup>

Loading, mmol of Ti/g of beads	Rate of $H_2$ reduction	
	mL/min mmol of Ti	mL/min g of polymer
0.2655	23.49	6.24
0.2459	27.13	6.65
0.1746	49.00	8.55
0.1284	67.38	8.65
0.1055	68.90	7.25
0.0868	76.24	6.63
0.0443	103.46	4.6

<sup>a</sup> 0.1 g of catalyst in 10 mL of cyclohexane.