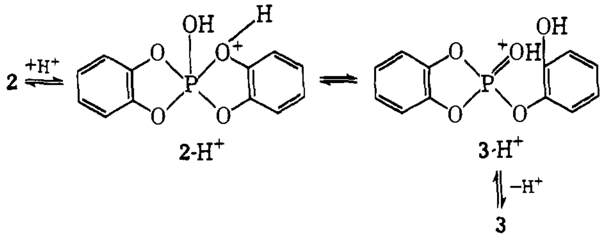
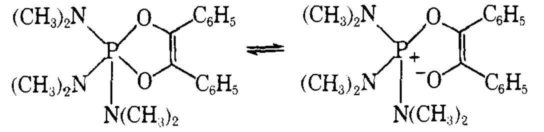
the structure of the solvent, suggests that the hydroxyl groups bonded to *pentavalent* phosphorus may be a relatively weak acid, weaker than the phenolic hydroxyl group.

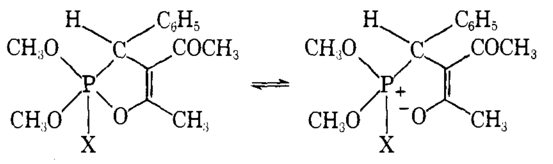


2-H$^+$ **3**-H$^+$ **3**

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



8 **9**



10, X = OCH$_3$ or C$_6$H$_5$ **11**, X = OCH$_3$ or C$_6$H$_5$

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(4) Elemental analyses of new compounds agree with expected values. $\delta_{^{31}P}$ values are given in parts per million vs. H_3PO_4 at 40.5 MHz (positive values correspond to signals at higher magnetic field); $\tau_{^1H}$ in parts per million vs. Me_4Si = 10; ^{1}H-decoupled $\delta_{^{13}C}$ in parts per million to low field of Me_4Si = 0. All spectra were taken in $CDCl_3$ at ~30 °C, except as noted.

(5) Anhydrous HCl was passed through a 0.1 M CH_2Cl_2 solution of spirodicatechol(trimethylsilyloxy)phosphorane[2] (**1**) at 0 °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 °C; τ 2.25, 2.85 (1:8 relative intensities) (CD_3CN).[4]

(6) Equimolar amounts of reactants and triethylamine in benzene at 20 °C (2 h). **4**: mp 72–74 °C (hexane); τ 6.33 (J = 14.0 Hz); $\delta_{^{13}C}$ 56.6 (J = 9.2), 110.7 (J = 16.8), 122.3, 143.2 (J = 6.9).

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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.[1] Since titanocene species undergo deactivation by polymerization processes,[2] 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,[3] 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.[1]

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 milliters/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[5] (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

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

where k = monomer rate constant

Table I. Hydrogenation of 1-Hexene by Polymer Supported Cp_2TiCl_2 at Room Temperature[a]

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

[a] 0.1 g of catalyst in 10 mL of cyclohexane.

Table II. Hydrogenation of 1-Hexene by Homogeneous Hexane Solution of Cp_2TiCl_2 at Room Temperature

$[Cp_2TiCl_2]$, $M \times 10^3$	No. of molecules/mL of solution $\times 10^{-18}$	Rate of hydrogenation: mL of H_2/min mL of solution	Rate of hydrogenation: mL of H_2/min mL of Ti
0.402	0.242	0.030	74.63
0.722	0.435	0.044	60.94
1.287	0.775	0.049	38.07
1.850	1.114	0.058	31.35
2.530	1.524	0.063	24.90

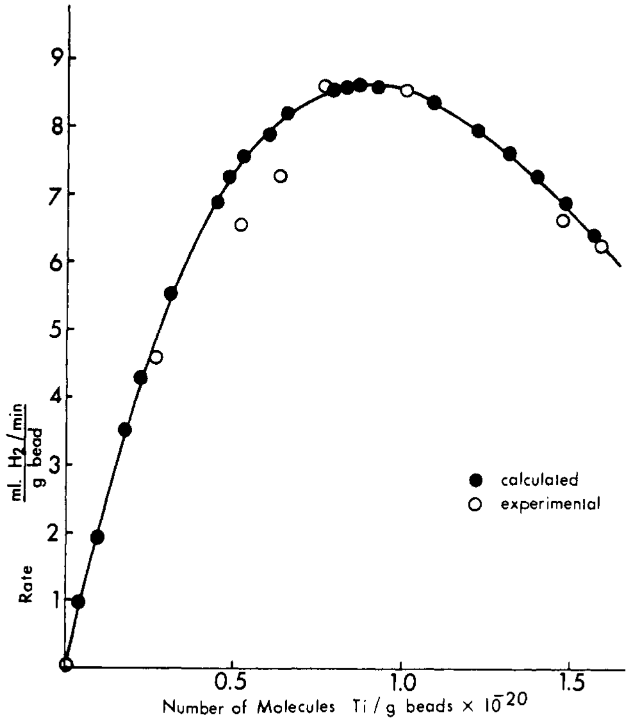

Figure 1. Rate of hydrogenation of 1-hexene as a function of the loading of Ti on the polymer beads.

$$\rho = \frac{\text{number of sites occupied}}{\text{maximum possible sites}}$$

$$= \frac{(\text{moles loaded})\,(6.023 \times 10^{23}) \times (\text{area of each complex})}{\text{total surface area of polymer}}$$

$$n = 4 \text{ or } 6 \text{ for square sites or circular sites}$$

This equation gives a maximum value for R/k at $\rho = 0.2$ for $n = 4$.[6] In Figure 1, this equation is plotted as a function of R/k vs. ρ. The shape of the curve is reasonable if it is considered that, without any site-site destruction, the rate should increase smoothly with increased loading. However, when sites do interact, the rate is decreased. Site interaction should increase with loading; so the rate-loading relationship should be a sum of two curves with opposite shapes. This result is a curve with a maximum as observed. Figure 1 shows the experimental data plotted on a best-fit calculated curve. The fit is amazingly good considering the sensitivity of the catalyst system to poisoning. From this curve it is easily determined that the maximum rate for hydrogenation is at a loading of 0.14 mmol of Ti/g of polymer. From the calculated ρ at the maximum rate (0.2), the loading of Ti at the maximum rate (0.14 mmol of Ti/g), and the surface area of the polymer used (90 m^2/g),[4] an area for each site can then be calculated. The value for this system is 22 $Å^2$. Although this value is smaller than expected, the difference could be accounted for by recognizing that the dimerization reaction requires a very specific relative orientation of the two adjacent molecules[2] and that the normal surface area measurements may not truly reflect the solution reaction area.

A series of parallel experiments with homogeneous hexane solutions of Cp_2TiCl_2 was carried out. Solutions of varying concentrations were reduced with BuLi and used to catalyze the hydrogenation of 1-hexene. The results (Table II) show an ever lessening increase in hydrogenation rate with increasing catalyst concentration, as one would expect if active catalyst monomer is in equilibrium with an inactive dimer. The data in Table II exhibit no maximum as those in Table I for the polymer-supported catalyst.

This work is most consistent with site isolation on highly cross-linked polystyrene and defines the parameters which can be used to design other experiments requiring site isolation.[6,7]

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Transition State Sensitivity in the Barton Reaction

Sir:

Irradiation of nitrite esters (Barton reaction) provides an elegant way to functionalize an unactivated site intramolecularly.[1] The reaction involves alkoxy radicals that strongly prefer to abstract a hydrogen via a six-membered transition state.[2] We discovered that apollan-11-ol nitrite (**1b**) gives the same oximino alcohol (**3a**) on irradiation as does apollan-*epi*-11-ol nitrite (**1d**).[3] This C-O epimerization in the **1b** → **3a** conversion likely involves a ring-opened radical, **2a** (Scheme I).[3,4] The plane of symmetry in substrates **1b** and **1d** makes C-3