

Homogeneous styrene hydrogenation catalyzed by the pyrophosphito-bridged $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ complex¹

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Abstract

The dinuclear complex $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ (**1**) catalyzed styrene, phenylacetylene, 1-octene, and 1-hexyne hydrogenation. Kinetic studies of styrene hydrogenation showed the rate was first order in both styrene and catalyst **1**. Below 400 lbf in^{−2} the rate exhibited a first-order dependence on hydrogen pressure. The rate equation was $r = kP_{\text{H}_2}$ [**1**] [styrene]. The rate was independent of stirring speed in the range 800–3200 rotations min^{−1} and therefore not mass transfer limited in this range. The addition of excess mercury did not lower the rate, demonstrating that hydrogenation was not catalyzed by metallic platinum formed from **1**. A very small amount of aniline was formed when nitrobenzene was added to styrene hydrogenations. The rate of nitrobenzene reduction was far less using **1** than when Pt–C was employed in an amount of 5% **1**. The activation parameters obtained were $E_a = 10.3$ kcal mol^{−1}, $\Delta H^\ddagger = 9.8$ kcal mol^{−1} and $\Delta S^\ddagger = -40.4$ cal mol^{−1} K^{−1}. The catalytic turn-over frequency remained constant with increasing catalyst concentration, indicating fragmentation equilibrium to an active lower nuclearity or higher nuclearity species was not occurring. The UV spectra of **1** in reaction solutions was unchanged after over 10³ turnovers at both 47 and 56°C. All evidence was consistent with catalysis by the dinuclear complex. A few allowed mechanisms are suggested for discussion.

Keywords: Platinum; Hydrogenation; Homogeneous catalysis; Pyrophosphito-bridging ligands; Dinuclear complex; Styrene

1. Introduction

Homogeneous catalysts have advantages including high activity (because all catalytical centers are identical), high selectivity and mild operating conditions. Homogeneous organometallic complexes are now used in many industrial catalytic processes [1,2]. One obstacle to the wider use of homogeneous catalysts is their inability to catalyze many types of reaction that are only catalyzed by heterogeneous catalysts. Many reactions require the cooperative assistance of several active sites on the metal surface, working together [3–5]. Soluble dinuclear complexes or metal clusters could, in principle, provide more than one metal site to promote reaction. The central hope of the cluster–surface analogy [6] has been that adjacent metal atoms in a cluster might act cooperatively like the surface of a small particle of bulk

metal, while simultaneously retaining the advantages of homogeneous catalysts. However, few examples exist. Instead, metal clusters often fragment into mononuclear complexes [7–9] or form larger clusters [10] which are active catalysts under the reaction conditions [11]. Thus, attempts have been made to build clusters that do not fragment during catalysis [11–18]. One example is $\text{Co}_2(\text{CO})_8(\mu_2\text{-CO})_2(\mu_4\text{-PPh})_2$ which catalyzes hydroformylation without fragmentation [5,17–18].

Dinuclear species offer two potential catalytic centers. Bimetallic cooperativity in dinuclear complexes during stoichiometric model reactions [19–22] and catalytic reactions [23] have been reported. Stanley and coworkers [24–27] have demonstrated that the bimetallic hydroformylation catalysts, racemic and *meso*- $[\text{Rh}_2(\text{nbd})_2(\text{et,ph-P4})]^2+$, give high regioselectivity via a mechanism involving bimetallic cooperation between the two rhodium centers during intramolecular hydride transfer. They achieved more than 12 000 turn-overs with no sign of catalyst fragmentation [24].

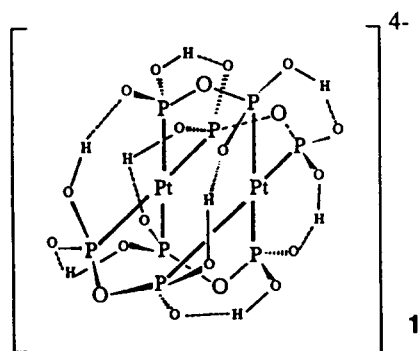
Richmond and Pittman [28] found that the fluorophosphine-bridged iron and cobalt dimers $[\text{CH}_3\text{-N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$, $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{PPh}_3)_2$ and

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¹ This paper is dedicated to Professor Marvin Rausch, a good friend, on the occasion of his 65th birthday. Extensive discussions of the uncertainties and surprises associated with both chemistry and women during the 1970s and early 1980s are fondly remembered.

$[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Fe}_2(\text{CO})_5$ withstood reaction conditions without fragmentation during photocatalytic hydrogenations, isomerizations and hydrosilations since too many metal–phosphine bonds would have had to rupture in order for fragmentation to occur.

More examples of multiply bridged dinuclear complexes which are catalytically active have been sought in our laboratory in the hope they might withstand fragmentation. We now report that the well-known [29,30] dinuclear complex $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ (**1**) catalyzed the thermal hydrogenation of styrene, phenylacetylene, 1-octene and 1-octyne. Styrene hydrogenation studies are reported here. The structure of **1** is shown below:



The two platinum atoms are linked together by four pyrophosphito bridging ligands, suggesting that this dimer would be very difficult to fragment during a catalytic reaction because so many platinum–phosphorus bonds would have to rupture to allow the complete separation of platinum atoms. The complex has two sets of paired electrons shared between the platinum: a $d\sigma$ pair and a $d\sigma^*$ pair which are formally

represented in valence bond notation as no Pt–Pt bonding.

Complex **1** is known to undergo thermal two-electron two-center oxidative addition of halogens or alkyl iodides to give substituted diplatinum(III) complexes $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4\text{X}_2]^{4-}$ ($\text{X} = \text{Cl}, \text{Br}$ or I) or $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4(\text{R})\text{I}]^{4-}$ [31,32]. Mixed-valence complexes from **1** have been made [33]. Both oxidation and reduction lead to enhanced platinum–platinum bonding [29]. The excited state of **1** can be formed by the $d\sigma^* \rightarrow p\sigma$ transition between metal-centered molecular orbitals [29] leading to increased metal–metal bonding. The singlet state rapidly converts to the triplet ($^3A_{2u}$) state with a high quantum yield (0.5). Triplet **1** has a 9 μs lifetime and is a one-electron reductant in water.

Alkenes and alkynes are activated by triplet **1**. Energy transfer to *cis*- or *trans*-stilbenes leads to photoisomerization [30,34,35]. The triplet state also abstracts allylic hydrogen atoms [34], hydrogen from typical hydrogen atom donors (isopropanol, Bu_3SnH , H_3PO_3 etc.) [34–37] and halogens [34,37]. Furthermore, it serves as a photochemical catalyst for converting ethanol to acetaldehyde and hydrogen [38] and the transfer hydrogenation of cycloalkenes with isopropyl alcohol [39]. Thermal catalysis by **1** was unknown until now.

2. Results and discussion

2.1. Synthesis of pyrophosphito-bridged diplatinum $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$

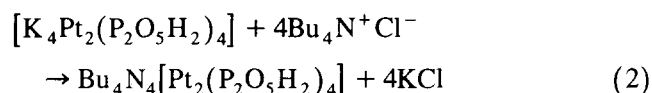
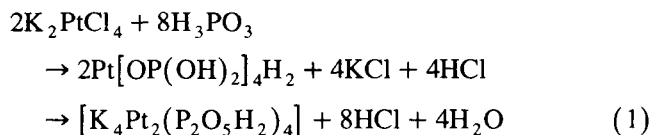
Pyrophosphito-bridged diplatinum $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$ was prepared with 75% isolated yield from K_2PtCl_4 in phosphorous acid to give $\text{K}_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$

Table 1
Attempts to hydrogenate different substrates using $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ as the catalyst at 60°C^a

Substrate	Reaction time (h)	Solvent	Product
Nitrobenzene	12	Isopropanol	None
1-Nitropropane	12	Isopropanol	None
Acetonitrile	12	Isopropanol	None
Benzaldehyde	12	Isopropanol	None
Butyraldehyde	12	Isopropanol	None
Phenylacetone	12	Isopropanol	None
Cyclohexanone	12	Isopropanol	None
Acetyl acetate	12	Isopropanol	None
Dimethylsulfoxide	12	Isopropanol	None
2-Butanone	12	Dimethylformamide	None
Ethyl acetate	12	Dimethylformamide	None
Phenyl isocyanate	12	Dimethylformamide	None
Styrene	10	Isopropanol	Ethylbenzene
Phenylacetylene	10	Isopropanol	Ethylbenzene
1-Octene	10	Isopropanol	Octane
1-Hexyne	10	Isopropanol	Hexane

^a Catalyst, $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$, employed at a concentration of 3.4×10^{-4} M; substrate concentration, 0.62 M; hydrogen pressure, 20.7 atm (300 lbf in⁻²).

followed by cation exchange with $\text{Bu}_4\text{N}^+\text{Cl}^-$, employing a slight modification of Roundhill's synthesis [39,40]. The synthesis proceeds according to



$(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$ decomposes at 268°C and exhibits an intense UV absorption at 365 nm.

2.2. Hydrogenation attempts with different substrates

Table 1 summarizes the attempted hydrogenation of various substrates at 60°C under 20.7 atm of hydrogen using $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$ as the catalyst. Complex 1 only catalyzed hydrogenation of alkenes and alkynes. Aliphatic and aromatic nitro, aldehyde, keto, sulfoxide, isocyanate and ester groups were not reduced.

2.3. Kinetic study of styrene hydrogenation

The kinetics of styrene hydrogenation, catalyzed by 1, were studied in isopropanol. Acetone was not observed in the products.

2.3.1. The effect of the temperature on the rate of styrene hydrogenation

The conversion to ethylbenzene vs. time at 26, 47, 56, and 67°C are summarized in Table 2. The rate of styrene hydrogenation increases with an increase in temperature. The Arrhenius activation energy $E_a = 10.3 \pm 0.8 \text{ kcal mol}^{-1}$ ($43 \pm 3.2 \text{ kJ mol}^{-1}$), was obtained from the following equation where the pre-exponential factor $A = 1 \times 10^{-8} \text{ atm}^{-1} \text{ mol}^{-1} \text{ h}^{-1}$:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

The enthalpy $\Delta H^\ddagger$ of activation and entropy $\Delta S^\ddagger$ of activation were obtained from the Eyring equation

$$\ln\left(\frac{k'}{T}\right) = \ln K \frac{k}{h} - \frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \quad (4)$$

where k' is the rate constant at different temperatures. From the plot of $\ln(k'/T)$ vs. $1/T$ (Fig. 1) the values of $\Delta H^\ddagger = 9.9 \pm 0.70 \text{ kcal mol}^{-1}$ (41 kJ mol^{-1}) and $\Delta S^\ddagger = -40.4 \pm 2.8 \text{ cal mol}^{-1} \text{ K}^{-1}$ ($-166 \text{ J mol}^{-1} \text{ K}^{-1}$) were obtained.

2.3.2. Determination of the rate equation.

Kinetic studies were conducted to determine the dependence of the rate on the hydrogen pressure and the

Table 2

The effect of temperature on the rate of styrene hydrogenation^a catalyzed by $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$

Reaction time (h)	Ethylbenzene yield (%) at the following temperatures			
	26°C	47°C	56°C	67°C
0.5	2.8	9.3	14.5	17.8
1	4.8	16.1	19.7	29.0
2	7.3	22.6	31.6	51.6
4	9.6	35.5	37.1	66.1
7	12.9	43.5	56.4	80.6
10	17.7	58.0	62.9	95.1

^a H_2 pressure, 41.4 atm; styrene concentration, 0.62 M; catalyst concentration, $38.7 \times 10^{-5} \text{ M}$; solvent, isopropanol.

concentrations of styrene and catalyst 1 (Table 3). The conversions of styrene to ethylbenzene vs. time were measured as a function of hydrogen pressures from 6.8 to 53.1 atm (100 to 780 lbf in⁻²) at 47°C. The concentrations of styrene and catalyst employed were 0.62 M and $3.87 \times 10^{-4} \text{ M}$ respectively. A log-log plot of rate vs. hydrogen pressure was linear up to 400 lbf in⁻² with a slope of 1.01. Thus the rate exhibits a first order dependence on hydrogen pressure below 400 lbf in⁻². At higher pressures (600–700 lbf in⁻²) a negative dependence (–0.91) was observed.

Ethylbenzene yields vs. time at 47°C were obtained at different styrene concentrations using a constant catalyst concentration ($3.87 \times 10^{-4} \text{ M}$) and hydrogen pressure (40.8 atm). These data are summarized in Table 4. A log-log plot of rate vs. concentration of styrene demonstrated the rate had a 0.994 order dependence on the styrene concentration.

The effect of catalyst concentration on rate at 47°C was determined at a constant styrene concentration (0.62 M) and a constant hydrogen pressure (40.8 atm). These data (Table 5) gave a log-log plot of rate vs. catalyst concentration corresponding to a 1.08 order dependence of rate on the concentration of catalyst 1. The overall

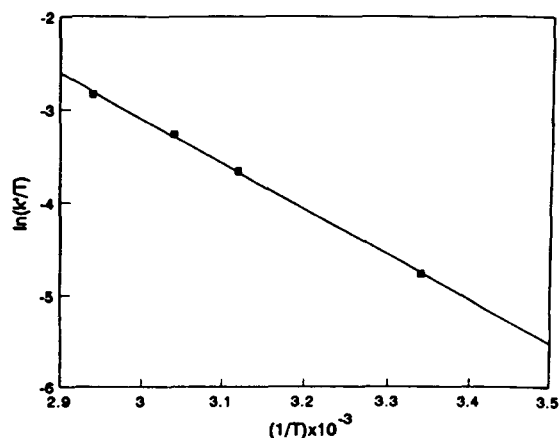


Fig. 1. The plot of $\ln(k'/T)$ vs. $1/T$ in styrene hydrogenations catalyzed by $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$.

kinetic equation was $r = kP_{H_2}^{1.01}[1]^{1.08}[\text{styrene}]^{0.994}$. Thus the styrene hydrogenation rate exhibited a first-order dependence on the styrene concentration catalyst concentration and hydrogen pressure.

2.4. The effect of stirring speed on the rate

The effect of stirring on the rate was studied at three stirrer speeds 800, 1600 and 3200 rev min⁻¹. The hydrogenation rate was constant over this range with values of 0.11, 0.09 and 0.10 mol l⁻¹ h⁻¹ respectively. This demonstrates that styrene hydrogenation was not mass transfer limited under the conditions employed through this entire study. Furthermore, this hydrogenation was not diffusion controlled. Usually diffusion

controlled reactions have Arrhenius E_a values in the range 2–3 kcal mol⁻¹ (8.2–12.6 kJ mol⁻¹). The value of $E_a = 10.3$ kcal mol⁻¹ (43 kJ mol⁻¹) obtained for this styrene hydrogenation is far too large for a diffusion-controlled reaction and strongly supports chemical control of the rate.

2.5. Studies of the turn-over frequency vs. catalyst concentration and the UV spectra of the catalyst in reaction solutions

The turn-over frequency (TF) was studied as a function of the initial catalyst concentration charged to the reaction (Fig. 2). This was done for both initial (time zero) TF values and TF values obtained after 2 h. Both

Table 3

The effect of hydrogen pressure on the rate of styrene hydrogenation catalyzed by $Pt_2(P_2O_5H_2)_4^{4-}$ at 47°C^a

Time (h)	Ethylbenzene yield (%) at the following P_{H_2}					
	100 lbf in ⁻²	200 lbf in ⁻²	300 lbf in ⁻²	400 lbf in ⁻²	600 lbf in ⁻²	780 lbf in ⁻²
0.5	2.4	4.9	7.6	9.8	11.3	6.4
1.0	3.2	9.7	12.1	17.7	16.1	11.3
2.0	9.7	16.1	24.2	30.6	22.6	14.5
4.0	17.7	30.6	32.2	51.6	35.5	20.9
log P_{H_2}	2.00	2.30	2.48	2.60	2.78	2.89
log r^b	-1.47	-1.21	-0.95	-0.89	-0.85	1.22

^a All reactions were conducted in isopropanol using a styrene concentration of 0.62 M and a catalyst concentration of 3.87×10^{-4} M.

^b r is the reaction rate in moles per litre per hour.

Table 4

The effect of styrene concentration on the rate of styrene hydrogenation catalyzed by $Pt_2(P_2O_5H_2)_4^{4-}$ at 47°C^a

Time (h)	Ethylbenzene yield (%) at the following styrene concentrations			
	0.15 M	0.31 M	0.62 M	0.93 M
0.5	2.4	5.3	11.3	14.5
1.0	4.0	8.0	16.1	20.9
2.0	4.8	11.3	22.6	33.9
4.0	8.0	17.7	35.5	54.6
log [styrene]	-0.82	-0.51	-0.21	-0.03
log r^b	-1.36	-1.12	-0.76	-0.60

^a All reactions were conducted in isopropanol using a catalyst concentration of 3.87×10^{-4} M and a hydrogen pressure of 41.4 atm.

^b r is the reaction rate in moles per litre per hour.

Table 5

The effect of $Pt_2(P_2O_5H_2)_4^{4-}$ on the rate of styrene hydrogenation catalyzed by $Pt_2(P_2O_5H_2)_4^{4-}$ at 47°C^a

Time (h)	Ethylbenzene yield (%) for the following $Pt_2(P_2O_5H_2)_4^{4-}$ concentrations			
	3.55×10^{-5}	6.45×10^{-5}	19.4×10^{-5}	38.7×10^{-5}
0.5	0.8	1.6	4.0	11.3
1.0	1.6	2.7	7.3	16.1
2.0	3.0	3.6	9.7	22.6
4.0	4.8	8.0	17.7	35.5
7.0	6.5	14.5	30.6	43.5
10.0	9.7	24.2	40.3	58.1
log $[Pt_2(P_2O_5H_2)_4^{4-}]$	-4.45	-4.19	-3.71	-3.41
log r^b	-2.00	-1.71	-1.31	-0.85

^a All reactions were conducted in isopropanol using a styrene concentration of 0.62 M and a hydrogen pressure of 41.4 atm.

^b r is the reaction rate in moles per litre per hour.

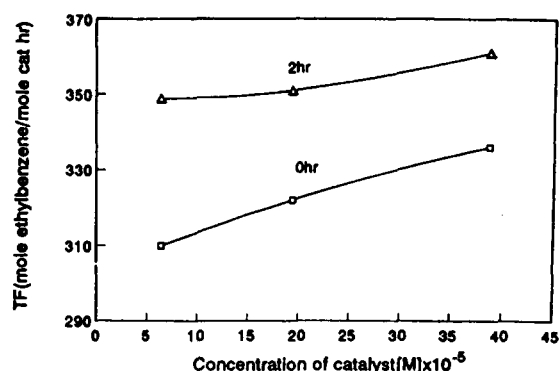


Fig. 2. Plot of TF vs. the concentration of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ in styrene hydrogenation at 47°C and a hydrogen pressure of 600 lbf in^{-2} .

plots (Fig. 2) show that the TF increased only slightly with an increase in catalyst concentration. This result is consistent with $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ acting as the active catalyst. According to Laine's [40] criteria this is not consistent with the fragmentation of **1** into catalytically important lower nuclearity species.

UV spectra of $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-}$ in reaction solutions were taken before and after the hydrogenation of styrene. No new bands appeared. The intense absorption band of **1** at 365 nm ($\epsilon = 3.7 \times 10^4$) was especially useful in monitoring any changes in the concentration of **1** from aliquots taken during the reaction. Within exper-

imental error no changes occurred at all in the spectra. Thus, according to the UV spectra, the concentration of **1** remained unchanged throughout the reaction. Even after 10^3 catalyst turn-overs had taken place, no changes in catalyst concentration occurred at either 47 or 56°C .

2.6. Nitrobenzene and metallic mercury tests to rule out catalysis by metallic platinum

The simultaneous hydrogenation of an equimolar solution of styrene and nitrobenzene, catalyzed by **1**, was conducted at 47°C . The hydrogenation of nitrobenzene alone was not catalyzed by **1** (Table 1). Platinum metal, however, catalyzes the rapid hydrogenation of nitrobenzene to aniline. Thus, since nitrobenzene was not rapidly reduced during styrene cohydrogenation, metallic platinum was probably not being formed in the styrene hydrogenation. Table 7 summarizes a styrene–nitrobenzene hydrogenation. During styrene hydrogenation, only a very slow hydrogenation of nitrobenzene to aniline was observed. An intermediate catalytic species, produced during styrene hydrogenation, might react with nitrobenzene. These results appear to rule out the formation of metallic platinum from **1** during styrene hydrogenation.

For comparison, experiments were conducted on 1-to-1 styrene–nitrobenzene solutions into which 1% Pt–C

Table 6
UV spectra of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ in reaction solutions before and after styrene hydrogenations ^a

Temperature ($^\circ\text{C}$)	Extinction coefficient ϵ ($\text{cm}^{-1} \text{ mol}^{-1}$) ^b		Catalytic turn-over ^c
	Before reaction	After reaction	
47	3.7×10^4	3.7×10^4	930
56	3.5×10^4	3.5×10^4	1008

^a Concentration of catalyst = $38.7 \times 10^{-5} \text{ M}$; H_2 pressure, 41.4 atm ; styrene concentration, 0.62 M ; solvent, isopropanol.

^b Absorptions measured at 365 nm .

^c The catalytic turn-over is the number of moles of product per mole of catalyst.

Table 7
The simultaneous hydrogenation of styrene and nitrobenzene: comparison of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ and 1% Pt–C as catalysts ^a

	Product composition (mol%) after the following times				
	0 min	5 min	10 min	20 min	40 min
<i>$\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ as catalyst ^b</i>					
Nitrobenzene	100	—	100	100	96
Aniline	0	—	0	0	4
Styrene	100	—	93	87	80
Ethylbenzene	0	—	7	13	20
<i>1% Pt–C as catalyst ^c</i>					
Nitrobenzene	100	90	84	76	56
Aniline	0	10	16	24	44
Styrene	100	60	38	7	0
Ethylbenzene	0	40	62	93	100

^a Reactions conducted at $P_{\text{H}_2} = 41.4 \text{ atm}$. in isopropanol (80 ml) at 47°C with styrene (50 mmol) and nitrobenzene (50 mmol).

^b The catalyst concentration was $3.87 \times 10^{-5} \text{ M}$.

^c 23 mg of 1% Pt–C (0.23 mg of Pt) were used.

was introduced as the catalyst. The amount of platinum introduced to these reactions was equal to only 5% of the platinum which would have been present if 60 mg of catalyst **1** had been added (the amount used in the first case). These results are also summarized in Table 7.

Using this small amount of 1% Pt–C, 93% of the styrene was converted into the ethylbenzene in 20 min at 47°C and a hydrogen pressure of 40.8 atm. Moreover, 24% of the nitrobenzene had converted into aniline in 20 min and 44% was converted in 40 min. Clearly, this small amount of 1% Pt–C reduced nitrobenzene 10–15 times more rapidly than the reaction employing 20 times more of the homogeneous complex **1**. Therefore, only about 0.33–0.5% of **1** present in the reaction could have decomposed to platinum metal based on a comparison with the Pt–C-catalyzed system. Any decomposition of **1** in such a dilute solution would have produced a highly dispersed metallic Pt. Certainly very little **1** could have decomposed to the platinum metal during the homogeneous hydrogenation.

In order to determine unequivocally whether styrene hydrogenation was the result of a homogeneous or a heterogeneous species, a reaction catalyzed by **1** was carried out in the presence of an excess of elemental mercury. Mercury will poison Pt metal surfaces and completely destroy their ability to function as hydrogenation catalysts. However, mercury will not interfere with a homogeneous-reaction-catalyzed complex **1**. The validity of this test has been demonstrated and discussed by Smith and Shuford [41] and Whitesides and coworkers [42]. Styrene hydrogenations catalyzed by **1**, both with and without mercury, are compared in Fig. 3. The rates obtained in the presence of mercury are almost identical with those in the absence of mercury. This conclusively demonstrated that a homogeneous species catalyzed the styrene hydrogenations. When considering all the evidence, this homogeneous catalytic species should be **1** or a dinuclear kinetically equivalent species.

2.7. Activation energy, activation enthalpy and the rate law

Styrene hydrogenation, catalyzed by **1**, exhibited the following activation parameters: $E_a = 10.3 \text{ kcal mol}^{-1}$, $\Delta H^\ddagger = 9.8 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -40.4 \text{ cal mol}^{-1} \text{ K}^{-1}$. The large negative entropy of activation is consis-

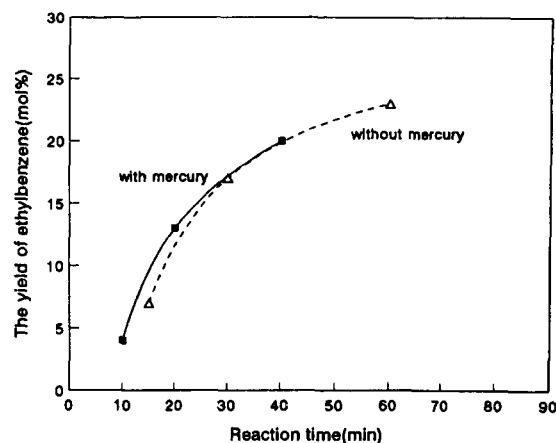


Fig. 3. Effect of added mercury on the conversion of styrene to ethylbenzene in hydrogenations catalyzed by $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^-$.

tent with a substantial increase in order occurring in the rate-determining step (RDS). For example, the addition of dihydrogen or styrene to **1** would be consistent with the observed entropy of activation. Activation enthalpy values from cyclohexene hydrogenations catalyzed by heterogeneous supported platinum metal [43] and palladium metal systems [44] are listed in Table 8. The value of $\Delta H^\ddagger$ for platinum metal is smaller ($6.4 \text{ kcal mol}^{-1}$) than that obtained in the homogeneous hydrogenation of styrene catalyzed by **1** ($9.8 \text{ kcal mol}^{-1}$). This is consistent with a homogeneous styrene hydrogenation [45]. Activation energy and activation enthalpy values for the hydrogenation of styrene catalyzed by **1** at $P_{\text{H}_2} = 41.4 \text{ atm}$ ($E_a = 10.3 \text{ kcal mol}^{-1}$ and $\Delta H^\ddagger = 9.8 \text{ kcal mol}^{-1}$) are not high. However, these values are far higher than those of a diffusion-controlled reaction (e.g., $2\text{--}4 \text{ kcal mol}^{-1}$). The E_a and $\Delta H^\ddagger$ values obtained in this work are compared with literature values for metal-surface-catalyzed olefin hydrogenations in Table 8.

The kinetic studies in this work demonstrate that the rate law for styrene hydrogenation, catalyzed by **1**, follows the equation $r = k[\text{styrene}][\textbf{1}]P_{\text{H}_2}$. This rate law is first order in olefin. This observation establishes the homogeneous nature of this catalytic reaction. In heterogeneous-platinum metal-catalyzed hydrogenations of olefins, the order in olefin concentration is zero or less than one. The observed kinetic order of one in styrene concentration indicates homogeneous catalysis. Such an order has not been encountered in heteroge-

Table 8

The activation energies and activation enthalpies of hydrogenations of cyclohexene and styrene catalyzed by metallic Pt and by **1**

Substrate	Catalyst	E_a (kcal mol^{-1})	$\Delta H^\ddagger$ (kcal mol^{-1})	Temperature (K)
Cyclohexene [43]	Supported Pt	7.0	6.4	320
Cyclohexene [44]	Supported Pt	9.4	8.8	320
Styrene [45]	Supported Pt	8.7	8.1	320
Styrene	1	10.3	9.8	320

neous catalysis, especially in the heterogeneously catalyzed reactions where the olefin is present in large excess over the number of available platinum surface sites [46]. The kinetic studies in this work used styrene-to-1 ratios of 1600 to 1. In Section 2.6 it was shown that only about 0.5–0.3% of the available homogeneous complex 1 present could have decomposed into platinum metal deposits. Therefore styrene would be present in a 3.8×10^5 -fold excess over metallic platinum. If every platinum atom present in that metallic deposit was an active hydrogenation site (an impossibility since only surface layers can participate) then the styrene-to-active heterogeneous site ratio would be 3.8×10^5 . Clearly, at such low levels of metallic platinum (high styrene-to-Pt ratios) one would expect a kinetic order of less than one in styrene concentration if the reaction had been heterogeneously catalyzed. Finally, a platinum-metal-catalyzed pathway was ruled out definitively by the mercury addition experiments.

2.8. Potential reaction mechanisms

The method of representing the structure of 1 (as shown in mechanistic cycle I) needs to be clarified before individual mechanistic cycles are discussed. Two sets of paired electrons are shared between the platinum atoms in 1. They occur in the $d\sigma$ and $d\sigma^*$ molecular orbitals. Both a bonding and an antibonding orbital are each doubly occupied. The $d\sigma$ bonding electrons are represented in 1 as a straight line between the two platinum atoms whereas the $d\sigma^*$ antibonding pair are represented by the curved line. This same convention is used in all the mechanistic cycles shown.

Each platinum is d^8 because each Pt atom has a charge of +2. In addition, the four phosphorus atoms which are coordinated to each Pt atom add an additional eight electrons to each platinum. Finally, the bonding and antibonding bonds (e.g. Pt—Pt) coordinate two more electrons with each platinum. Thus each platinum

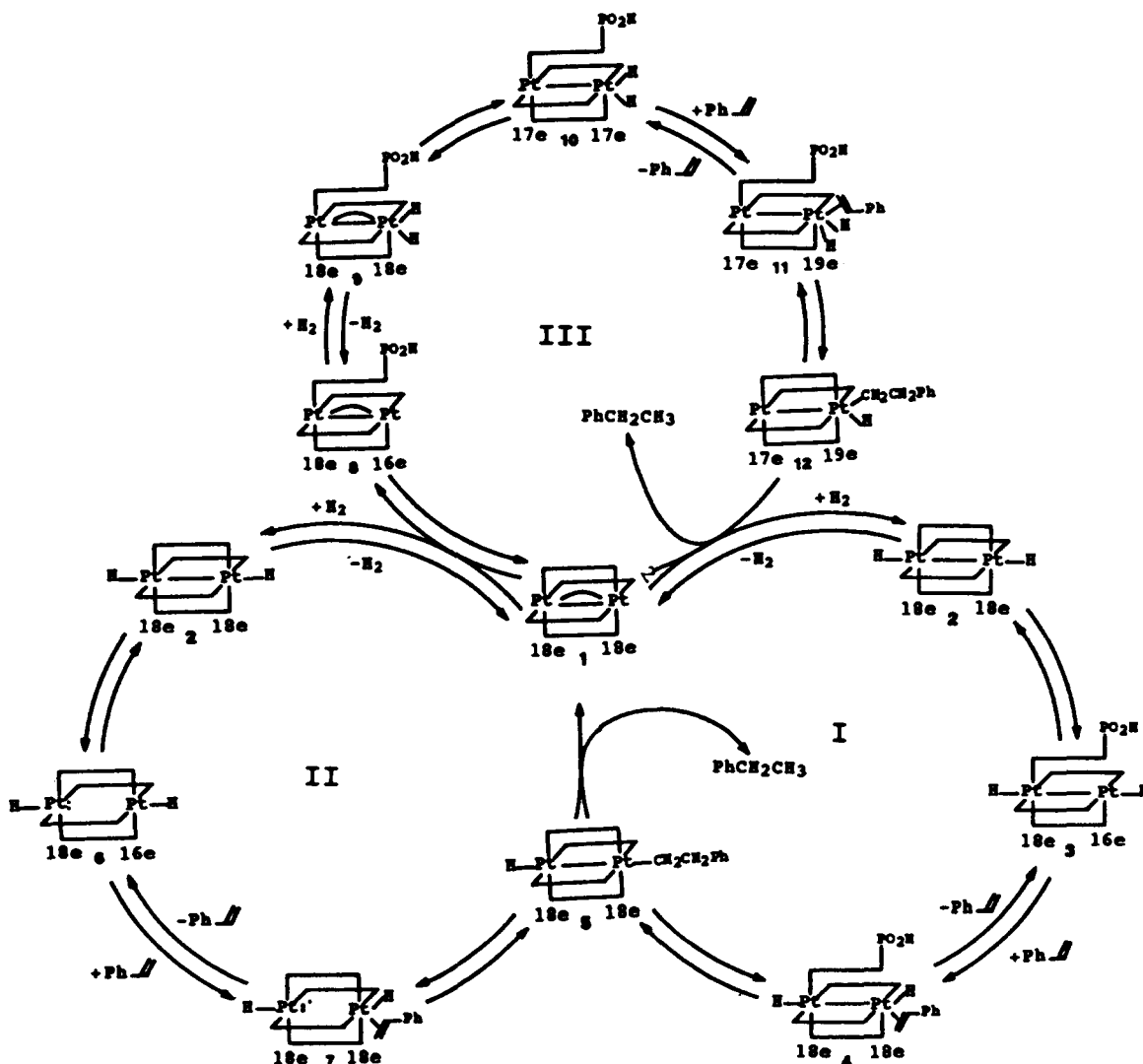


Fig. 4. Possible mechanisms for the catalysis of homogeneous styrene hydrogenation by $\text{Pt}_2(\text{P}_2\text{O}_3\text{H}_2)_4^{4-}$.

is considered an 18-electron species using this formalism. If one hydrogen coordinates to each Pt (as represented in species **2** in mechanistic cycle I) the antibonding $d\sigma^*$ pair is ruptured and each Pt now shares one of "its" electrons with an electron from the attached hydrogen. Hence, in **2**, each Pt is still an 18-electron species. The net result is tantamount to adding dihydrogen across the double (Pt—Pt) bond.

Many mechanisms fit the observed rate law. Three speculative cycles (related to the classic Rh(I)—Rh(III) hydrogenations) were conceived which involve both platinum atoms. These involve steps of considerable interest with respect to bimetallic cooperativity and are therefore shown in Fig. 4. They are speculative and only offered to illustrate the types of question which should be raised. In mechanistic cycle I (Fig. 4), binuclear oxidative addition of hydrogen breaks the platinum–platinum "antibond" to form **2**. Note that concerted binuclear oxidative additions appear to be unknown at adjacent metal sites. Direct coordination of **2** by styrene would give a 20-electron platinum atom. This would violate the EAN rule and require one Pt atom to have a coordination number of 7. To avoid this, dissociation of one phosphorus ligand is postulated to give **3** where one Pt atom is now a 16-electron species. Coordination of styrene to this 16-electron Pt atom gives **4**. Next, Pt–H addition to coordinated styrene followed by ligand recoordination gives alkyl metal species **5** followed by irreversible binuclear reductive elimination of ethylbenzene to regenerate the starting catalyst **1**.

Alternatively, formation of **2**, rupture of the Pt–Pt bond to form **6**, can be postulated (cycle II). Then styrene coordination to the 16-electron platinum atom of **6** would give **7**. Also, the reaction of styrene with **2** might directly give **7**. Pt–H addition to styrene with simultaneous Pt–Pt bond re-formation would give **5** followed by dinuclear reductive elimination of ethylbenzene.

In cycle III (Fig. 5), ligand dissociation from **1** to form **8**, and oxidative addition of hydrogen to give **9** (Fig. 5, cycle III) followed by antibond rupture in **9** would give **10**. Styrene coordination would generate **11** (alternatively **9** → **11** could be concerted). Pt–H addition to coordinated styrene with concomitant ligand recoordination forms **12**. Mononuclear alkane elimination with platinum–platinum antibond re-formation would generate **1**.

The rate equations for each of these cycles were derived where the RDS was systematically changed from one step to the next [47] using the steady-state approximation. Mechanisms represented in cycles I and II fit the observed rate law only when the RDS was step 3, 4 or 5. Cycle III fits the rate law if step 4, 5 or 6 were the RDS. A reviewer advocated consideration of one-electron transfer chemistry, similar to that observed for $\text{Co}(\text{ON})_5^{3-}$ catalysis. This suggestion may have merit.

3. Conclusions

$\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$, known for its rich photochemical reactivity, has now been shown to catalyze the thermal hydrogenation of alkenes and alkynes as a homogeneous dinuclear species. It was not destroyed during the process nor did it fragment to mononuclear species or generate metallic platinum. The overall kinetic equation for styrene hydrogenation was $r = k\text{P}_{\text{H}_2}^{1.01}[\textbf{1}]^{1.08} - [\text{styrene}]^{0.994}$ (below 400 lbf in⁻²).

Analysis of the relative merits of mechanistic cycles I–III (or others) is highly speculative. The addition of dihydrogen to **1** to give **2** (although not necessarily concerted) seems reasonable based on the known existence of **2** [48]. Furthermore, evolution of dihydrogen from **2** by heating, photolysis or reaction with HCl occurs [48]. The latter supports a $(\text{Pt}^{3+})_2(\text{H}^-)_2$ formalism for **2**. The μ -pyrophosphito ligands present a bulky hydrophilic axial-site interaction surface to an incoming substrate. Thus direct reaction of styrene with **2** or **6** to give **7** (cycle II) would not be favorable. This suggests that cycle II (or other related styrene coordination to platinum with all four P atoms coordinated) is less likely. The breaking of the $d\sigma^*$ bond should be favorable. This has been previously indicated by (a) an increase in the $J_{\text{Pt-Pt}}$ and decrease in $J_{\text{Pt-P}}$ values (NMR) upon oxidative addition to **1** to give Pt_2X_2 , (b) Raman force field analysis of Raman frequency shifts and (c) a decrease in the Pt–Pt bond distance [29,49]. This tempts one to speculate that conversions such as **2** to **6** (or **2** to **7**; cycle II) would be unfavorable. We suggest that these considerations might favor cycles I, III, relative to cycle II.

The reversible dissociation of the μ -pyrophosphito ligand from a Pt atom would be a crucial step in cycles I and III. Quantitative descriptions of this phenomena were not found. However, once the $d\sigma^*$ bond is broken, the decrease in $J_{\text{Pt-P}}$ values suggests that ligand dissociation would be more facile than in **1**, favoring cycle I relative to cycle III. While the kinetics rule out a large number of mechanistic possibilities, no direct experimental evidence exists to rule out specifically, or to favor strongly, the kinetically possible mechanisms.

4. Experimental details

All the chemicals used were purchased from Aldrich Chemical Company and the hydrogen gas was purchased from Capitol Welding Supply Company (99% purity). All the reactions were carried out in stainless steel autoclaves (300 ml; T316, Parr Instrument Company). UV–visible spectra were recorded on a Perkin–Elmer model 555 spectrophotometer. The mass spectra were recorded on a Finnigan model 4500 gas chromatograph–mass spectrometer. Reaction products were ana-

lyzed by gas chromatography (GC) (a Perkin–Elmer model Sigma 3 equipped with 30 m DB-5 capillary column).

4.1. Synthesis of $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$

K_2PtCl_4 (1 g, 2.4 mmol) and H_3PO_3 (3 g, 36.6 mmol) were dissolved into about 20 ml of distilled water and heated at 100°C for 2 h. During this period the deep-reddish-orange solution turned straw colored. Water was then removed at 100°C for 10 h. The resulting green–yellow residue was slurried in methanol. Methanol was removed by filtration. Then the solid was rinsed repeatedly with excess methanol. The resulting fine green–gray solid was dissolved in pure water (10 ml) to give a brilliant-yellow solution. Addition of 50–60 ml of methanol into this solution caused $[\text{K}_4\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$ to precipitate as a fine yellow–green solid.

$[\text{K}_4\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$ (0.7 g, 3.5 mmol) was dissolved into distilled water (60 ml). $\text{Bu}_4\text{N}^+\text{Cl}^-$ (3.5 g, 12.6 mmol) was dissolved into CH_2Cl_2 (120 ml). The two solutions then were thoroughly mixed in the dark in a separatory funnel and left undisturbed for 10 min. All the glassware was covered with aluminum foil. The lower layer was drained into 300 ml of anhydrous diethyl ether and 0.9 g (75% yield) of bright-green fluffy crystals of $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$ precipitated. It decomposed at 268°C .

4.2. General procedures for the hydrogenation reactions

Complex **1** was first charged to a 300 cm^3 autoclave followed by solvent. The complex completely dissolved. Then the substrate was charged and more solvent was added to keep the total reactant volume constant (80 ml). The autoclave was purged with hydrogen and stirred slowly; next the temperature was increased to the reaction temperature under hydrogen (1 atm). Then the stirring speed was increased ($1600\text{ rotations min}^{-1}$) followed by raising the hydrogen pressure to the desired level. Products were analyzed by GC on a 30 m DB-5 capillary column. The injector and detector temperatures were 200°C ; the initial column temperature of 75°C was held constant for 3 min and then raised to 90°C at a rate of 5°C min^{-1} . Styrene and ethylbenzene were confirmed by GC retention time vs. standards and by GC–mass spectroscopy analysis.

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