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The Mechanism of Hydrogenolysis of Dineopentylbis(triethylphosphine)platinum(II)[1]

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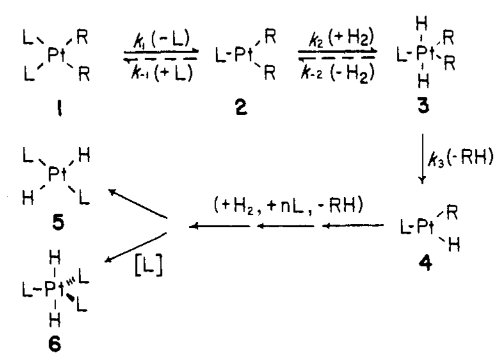
Abstract: Dineopentylbis(triethylphosphine)platinum(II) reacts with H_2 (34 psi) at 32 °C in hydrocarbon solvents and yields neopentane and *trans*-dihydridobis(triethylphosphine)platinum(II). The addition of triethylphosphine (L) changes the rate-limiting step of the reaction. When $[L] = 0$ M, the overall rate-limiting step is the dissociation of triethylphosphine from L_2PtR_2: no isotope effect is observed on substitution of D_2 for H_2, and the rate is independent of the pressure of H_2. When $[L] > 0.1$ M, phosphine loss is reversible, and a later step, either addition of H_2 to platinum or (more probably) elimination of neopentane from platinum, is rate limiting: the rate of reaction depends on the first order of the H_2 pressure, and an isotope effect of $k_H/k_D \simeq 1.9$ is observed on substitution of H_2 by D_2. Activation parameters obtained at 0.0, 0.1, and 0.5 M triethylphosphine are presented. These data are useful in understanding the differences in rates of inter- and intramolecular oxidative additions to platinum(II). The rate of reaction of H_2 with several structurally related bis(phosphine)dialkylplatinum(II) compounds was surveyed under similar reaction conditions. In general, bulky substituents on platinum accelerate the reaction. This observation suggests that phosphine dissociation is a general feature of reaction of bis(phosphine)dialkylplatinum(II) compounds with dihydrogen.

The formation and cleavage of bonds between carbon, hydrogen, and transition metals is important in many catalytic processes.[3-6] This paper describes a study of the mechanism of the homogeneous hydrogenolysis of dineopentylbis(triethylphosphine)platinum(II) (**1**).[7] The reaction proceeds under mild conditions (32 °C, 34 psi of H_2) and yields neopentane and *trans*-dihydridobis(triethylphosphine)platinum(II) (**5**) quantitatively (Scheme I). In Scheme I and throughout this paper L refers to triethylphosphine, R to $CH_2C(CH_3)_3$, and L^D to $P(CD_2CD_3)_3$. We use [L] to refer to the concentration of L resulting from *added* triethylphosphine (that is, triethylphosphine added to the solution rather than that present as a result of dissociation from L_2PtR_2). Thus, $[L] = 0.0$ M implies only that no phosphine has been added to the solution. We know from qualitative ^{31}P NMR studies that the equilibrium constant for phosphine loss from **1** is low, but we have not measured it quantitatively.

Mechanistic studies of thermal reactions of bisphosphinedialkylplatinum(II) compounds involving *intramolecular* addition of β-,[8,9] γ-,[10] δ-,[11] and ϵ-[11] C–H bonds to platinum(II) have established the high reactivity of coordinatively unsaturated intermediates of structure $LPtR_2$ in such reactions. This study indicates that this same intermediate is also the reactive species in the *intermolecular* addition of H_2 to platinum(II) under the conditions studied, and it suggests a broad mechanistic parallel between C–H and H–H addition to platinum(II).

In the absence of added triethylphosphine, the overall rate-limiting step in the hydrogenolysis of **1** was dissociation of phosphine. When L was present at concentrations greater than ~0.1 M, loss of phosphine was reversible and another step—either reductive elimination of a C–H bond from platinum or oxidative addition of an H–H bond to platinum—was rate limiting. We cannot presently distinguish between these alternatives.

Scheme I. Mechanism of Hydrogenolysis of 1 in Cyclohexane: $L = PEt_3$; $R = CH_2C(CH_3)_3$



Results

Products. In the absence of added L, the reaction of H_2 with **1** in cyclohexane yielded **5**[12] and 2,2-dimethylpropane (neopentane) quantitatively. No 2,2,5,5-tetramethylhexane (dineopentyl) was formed. The solution became slightly yellow as the reaction proceeded, but only **5** was observed by ^{31}P NMR spectroscopy.[13] When deuterium (D_2) gas was substituted for H_2, neopentane-d_1 was the sole product derived from the neopentyl moieties.[14] When the hydrogenolysis was run in the presence of added L (≥ 0.1 M), the products were neopentane and dihydridotris(triethylphosphine)platinum(II) (**6**) (Scheme I).[15] Compound **6** was not observed by ^{31}P NMR spectroscopy at room temperature because rapid phosphine exchange broadened the ^{31}P resonances. At −50 °C in toluene-d_8, compound **6** was visible by ^1H NMR spectroscopy, and the platinum hydride resonances (at −3 ppm)[16] were split into a quartet ($J_{PH} = 17$ Hz). This observation suggests that **6** has a trigonal-bipyramidal structure containing three equivalent phosphines (Scheme I). No *cis*-**5** was observed in this system. Panonessa and Trogler[17] have recently observed *cis*-**5** in acetone

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[2] NCI Predoctoral Trainee 1981–1982.

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[12] The ^{31}P and ^1H NMR spectra obtained for **5** are in agreement with those reported by Yoshida and Otsuka: Yoshida, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134–40.

[13] The color is probably due to $(Et_3P)_3Pt$ from a reaction of **5** with trace amounts of O_2.

[14] The GC-MS of the alkane is indistinguishable from that of alkane obtained from a DCl quench of $L_2Pt(CH_2C(CH_3)_3)_2$.

[15] Compound **6** has been prepared by reaction of $(Et_3P)_3Pt(O)$ and H_2: Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Meutterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543–44. We have shown that compound **6** is also formed from $(Et_3)_2PtH_2$ and Et_3P.

[16] Upfield from tetramethylsilane.

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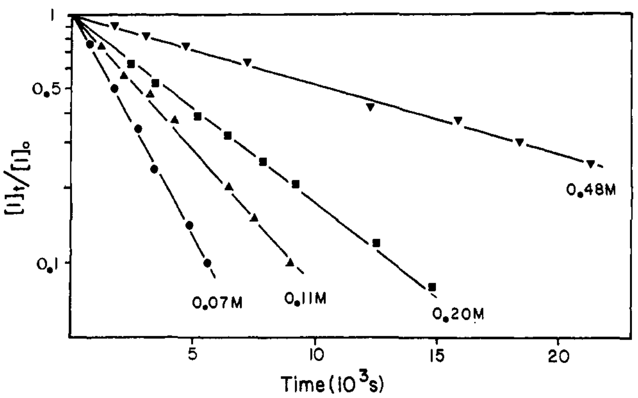

Figure 1. Hydrogenolysis of **1** in the presence of added triethylphosphine: $[\mathbf{1}]_0 \simeq 0.026$ M; H_2 pressure = 33.9 psi, $T = 50$ °C. [L] is indicated on the figure for each line.

and have noticed a decrease of the ratio of cis to trans isomers in less polar solvents. They report $[cis\text{-}\mathbf{5}]/[trans\text{-}\mathbf{5}] = 0.03$ in toluene. The absence of signals attributable to *cis*-**5** in our spectra is consistent with their observations. In solution, compound **5** decomposes quickly when exposed to air. No decomposition of **5** in cyclohexane solution was observed after several months at room temperature when the compound was kept in an atmosphere of H_2 or argon.

Kinetics. The disappearance of **1** (followed by ^{31}P NMR spectroscopy) was first order in **1** to greater than 3 half-lives. The observed pseudo-first-order rate constant (defined by eq 1) at 32 °C and 33.9 psi of H_2 in cyclohexane was $k^{obsd} = 3.0 \pm 0.03 \times 10^{-4}\ s^{-1}$. The rate constant was independent of the initial concentration of **1** from 0.017 to 0.044 M.[18]

$$d[\mathbf{1}]/dt = -k^{obsd}[\mathbf{1}] \qquad (1)$$

The observation of first-order kinetics indicates that a step involving two platinum centers is not important under the conditions studied. Bergman and Janowicz[19] have concluded that the methane-producing autocatalytic hydrogenolysis of (η^5-cyclopentadienyl)(triphenylphosphine)dimethylcobalt(III) goes through a binuclear intermediate formed by the reaction of product $Cp(Ph_3P)CoH_2$ with starting material. We have observed an analogous reaction in the present system when **1** and **5** are mixed in the absence of H_2 (eq 2). Although reaction 2 does occur,

$$\underset{\mathbf{1}}{L_2PtR_2} + \underset{\mathbf{5}}{L_2PtH_2} \xrightarrow[c\text{-}C_6H_{12}]{\sim 40h,\ 25\ °C} L_3Pt^0 + 2RH + (Pt^0) \qquad (2)$$

it is apparently not fast enough under the conditions studied here to be important in hydrogenolysis of **1**. The ^{31}P NMR spectra show that the concentration of **5** increases as the reaction proceeds. If the reaction of eq 2 were occurring, a deviation from first-order kinetics would be expected. We observe simple first-order kinetics, with no evidence of autocatalysis or of an induction period.

Dependence of Rate on Phosphine Concentration. Figure 1 shows first-order plots at various phosphine concentrations. All runs were conducted at 50 ± 0.3 °C and 33.9 ± 0.4 psi of H_2. Figure 2 plots pseudo-first-order rate constants at 50 and 56.5 °C (determined by eq 1) as a function of $[L]^{-1}$. The reactions were run at 56.5 °C so that reaction rates at higher phosphine concentrations could be measured in a convenient interval of time.

The straight lines observed in Figure 2 establish an inverse first-order dependence of rate on [L] for [L] < 1.0 M. This behavior is consistent with the mechanism outlined in Scheme I with either **2** → **3** or **3** → **4** as the rate-limiting step: both involve dissociation of L before the rate-limiting step, and are indistinguishable by this criterion. In principle, this kinetic dependence on $[L]^{-1}$ might also be rationalized by *association* of L with L_2PtR_2 before the rate-limiting step, but the absence of L_3PtR_2 species detectable in the ^{31}P NMR spectra in the presence of added L and the observation that the solubility of **1** is not increased in solutions containing added L indicate that association of L with **1** is not important.[20]

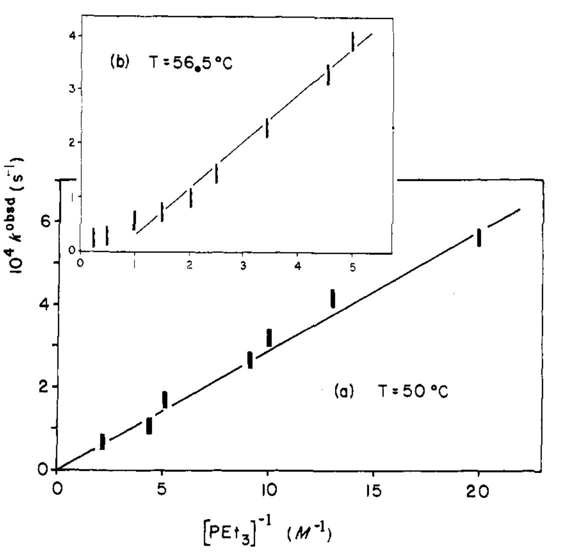

Figure 2. Observed first-order rate constants ($[\mathbf{1}]_0 = 0.026$ M, H_2 pressure = 33.9 psi) as a function of $[L]^{-1}$: (a) $T = 50$ °C; (b) $T = 56.5$ °C. The lines indicate a first-order dependence of k^{obsd} on $[L]^{-1}$.

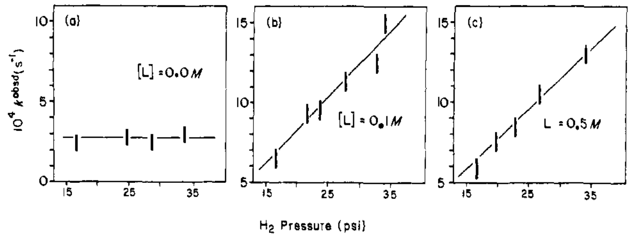

Figure 3. Observed rate constants as a function of H_2 pressure at three different phosphine concentrations: (a) [L] = 0.0 M, $T = 32$ °C; (b) [L] = 0.1 M, $T = 50$ °C; (c) [L] = 0.5 M, $T = 56.5$ °C. For a the line indicates a zero-order dependence on H_2. For b and c the line indicates a first-order dependence. $[\mathbf{1}]_0 \simeq 0.026$ M.

Table I. Characteristics of the Hydrogenolysis of 1 at Different Concentrations of L[a]

	[L], M		
	0.0	0.1	0.5
kinetic order in L		$[L]^{-1}$	$[L]^{-1}$
kinetic order in H_2	$[H_2]^0$	$[H_2]^1$	$[H_2]^1$
k_H/k_D[b]	1.0 ± 0.2	1.9 ± 0.2	1.9 ± 0.2
E_a, kcal/mol	29 ± 2	30 ± 2	29 ± 3
log A	18 ± 1	18 ± 2	17 ± 2
$\Delta G^{\ddagger}$(50 °C), kcal/mol	21 ± 4	22 ± 5	23 ± 6
$\Delta H^{\ddagger}$(50 °C), kcal/mol	28 ± 2	29 ± 2	28 ± 3
$\Delta S^{\ddagger}$(50 °C), eu	22 ± 5	22 ± 9	17 ± 9

[a] Kinetic parameters were determined from k^{obsd} for [L] = 0.0 M, and from k' (eq 6) for [L] = 0.1 and 0.5 M; H_2 pressure was 33.9 psi, $[H_2] \simeq 1.2 \times 10^{-2}$ M.[22] [b] The isotope effect at [L] = 1.0 M was 1.7 ± 0.2.

When [L] > 1.0 M the rate constants in Figure 2 deviate from linearity (Figure 2b). The deviations are not large and more probably due to solvent effects (at 2.0 M, the solution is 30% w:w triethylphosphine).

Dependence of Rate on the Pressure of H_2**.** Figure 3 plots the dependence of the pseudo-first-order rate constants on H_2 pressure at [L] = 0.0, 0.1, and 0.5 M. When [L] = 0.0 M, the reaction

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(17) Panonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 1138–40.

(18) The limit of solubility of **1** in cyclohexane at 32 °C is approximately 0.045 M.

(19) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2488–9.

(20) These tests for association are described fully in ref 10.

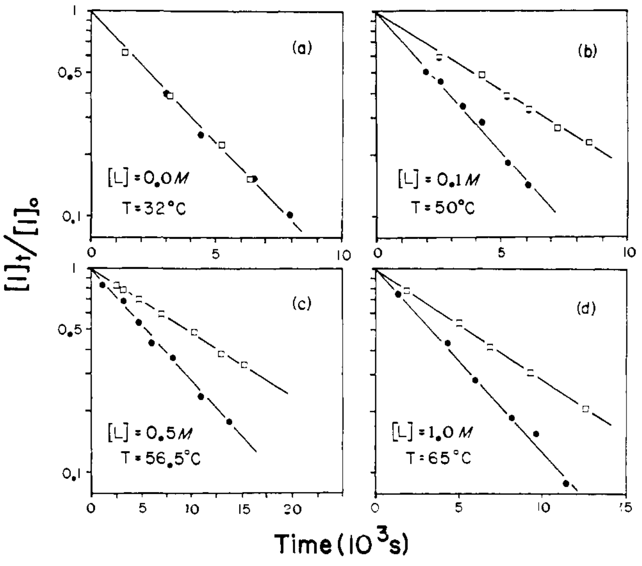

Figure 4. Hydrogenolysis of **1** with H_2 (●) and D_2 (□) at four values of [L]. Temperatures are indicated above plots. H_2 pressure = 33.9 psi, $[1]_0 = 0.026$ M.

is approximately zero order in H_2 pressure over the range of 15.7 to 33.9 psi (Figure 3a). When [L] = 0.1 or 0.5 M, the dependence on H_2 pressure is first order.

Deuterium kinetic isotope effects were determined by measuring the change in the rate of reaction on substitution of D_2 for H_2. The isotope effects (k_H/k_D) are listed in Table I. Figure 4 shows representative rate data. The slowing of the rate with increasing phosphine concentration made it necessary to measure the isotope effects at different temperatures for different values of [L]. We assume that the effect of temperature on the isotope effect is negligible. When [L] = 0.0, no isotope effect was observed (k_H/k_D = 1.0). This observation and the independence of the reaction rate on H_2 pressure are consistent with dissociation of phosphine (**1** → **2**) as rate determining.

In the presence of added phosphine ([L] ≥ 0.1 M) we observed both an isotope effect (k_H/k_D = 1.9) and a first-order dependence of rate on H_2 pressure. These data are consistent with either **2** → **3** or **3** → **4** as rate determining. The expression for the observed rate constant (k^{obsd}) that is predicted by the mechanism of Scheme I is given in eq 3. If k_3 is the rate-determining step, the expression simplifies to eq 4. If k_2 is rate determining, the expression is given by eq 5.

$$k^{obsd} = \frac{k_1k_2k_3[H_2]}{k_2k_3[H_2] + k_{-1}(k_{-2} + k_3)[L]} \qquad (3)$$

$$k^{obsd} = \left(\frac{k_1}{k_{-1}}\right)\left(\frac{k_2}{k_{-2}}\right)k_3\frac{[H_2]}{[L]} \qquad (4)$$

$$k^{obsd} = \left(\frac{k_1}{k_{-1}}\right)k_2\frac{[H_2]}{[L]} \qquad (5)$$

$$k' = k^{obsd}\frac{[L]}{[H_2]} \qquad (6)$$

The observed isotope effect of k_H/k_D = 1.9 is similar to that (k_H/k_D = 1.7 ± 0.3) observed for what is believed to be reductive elimination of a C–H bond from a 5-coordinate platinum species similar to **3** ($LPtRR'_2H$ rather than $LPtR_2H_2$).[21] The third step of Scheme I (**3** → **4**) is also reductive elimination from a 5-coordinate platinum species. An isotope effect of k_H/k_D = 1.22 (30 °C) has been measured by Chock and Halpern and that of k_H/k_D = 1.026 (30 °C) by Vitale and San Filippo for $H_2(D_2)$ addition to Vaska's complex ($IrCl(CO)(Ph_3P)_2$).[23] These values do not permit us to distinguish between reductive elimination (step 3) and $H_2(D_2)$ addition (step 2) as the rate-limiting step for conversion of **1** to **5**. Both these isotope effects for oxidative addition of H_2 to a metal center and the isotope effects we[8,10,24,32] and others[25] have measured previously for reductive elimination of a C–H from a metal center are sufficiently similar that criteria other than simple hydrogen kinetic isotope effects will be required to distinguish H–H bond breaking and C–H bond forming.

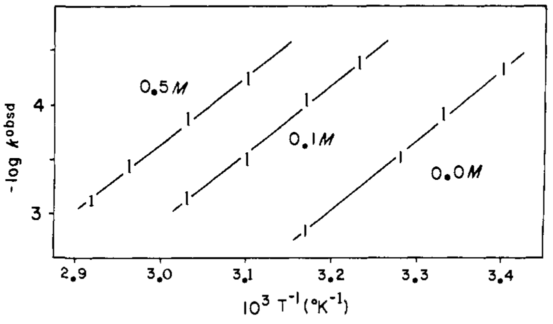

Figure 5. Arrhenius plots for hydrogenolysis of **1** at three values of [L] (indicated on the figure). H_2 pressure = 33.9 psi, [**1**] = 0.026 M.

We note that the reverse of step 3 (**4** → **5**) is the activation of a C–H bond of neopentane by addition to platinum(II). We conclude from previous experience that intermolecular C–H bond activation does not occur under the mild conditions used in this work. We therefore assume that **3** → **4** is irreversible, and we conclude that transformations between **4** and **5** (or **6**) do not influence the kinetics.

Arrhenius Parameters. Figure 5 shows Arrhenius plots (–log k^{obsd} vs. T^{-1}) for [L] = 0.0, 0.1, and 0.5 M. Table I lists Arrhenius and Eyring parameters calculated from k^{obsd} for [L] = 0.0 M and from k' (eq 6) for [L] = 0.1 and 0.5 M. Both k^{obsd} and k' have units of s^{-1}. When [L] = 0.0 M, E_a = 29 ± 2 kcal/mol. This value for the activation energy is consistent with rate-limiting loss of phosphine: an E_a of 29 ± 2 kcal/mol was obtained previously for rate-limiting dissociation of phosphine in the thermal decomposition of $(PEt_3)_2Pt(CH_2CH_3)_2$.[8] The observed value of log *A* is consistent with a reaction in which one particle goes to two in the transition state.[26]

Phosphine Exchange. Reaction of a 1:1 mixture of L_2PtR_2 and $L^D{}_2PtR_2$ with H_2 to 50% completion followed by ^{31}P NMR analysis of unreacted starting material showed no detectable exchange of L^D for L.[27] The absence of exchange under these conditions ([L] = 0.0 M) is a necessary consequence of rate-limiting dissociation of L.

Hydrogenolysis of Related Organoplatinum Compounds. The reactions of several compounds having the structure L_2PtR_2 with H_2 are summarized in Table II. When L was Me_3P or Ph_3P, hydrogenolysis did not yield a stable platinum(II) dihydride. The solution darkened and a black precipitate (apparently platinum metal) formed. The ^{31}P NMR spectra taken during and after the reaction showed $(Me_3P)_4Pt$[28] and $(Ph_3P)_3Pt$[29] respectively as

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[21] The authors could not rigorously rule out the possibility that the observed isotope effect was due to ethylene loss as the rate-determining step; see ref 8.

[22] $[H_2]$ was calculated from solubility data for H_2 in heptane and octane. Cook, M. W.; Hanson, D. N.; Alder, B. J. *J. Chem. Phys.* **1957**, *26*, 748–51. It was assumed that $[H_2]$ would not be significantly different in cyclohexane or dodecane.

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[25] Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332–8 for reductive elimination of $CH_3(H,D)$ from $(Ph_3P)_2Pt(H,D)CH_3$, k_H/k_D = 3.3 ± 0.3. Michelin, R. A.; Faglia, S.; Uguagliata, P. *Inorg. Chem.*, **1983**, *22*, 1831. Reductive elimination of *cis*-$PtH(D)(CH_2CF_3)(PPh_3)_2$, k_H/k_D = 2.2 (40 °C).

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[27] Due to the sensitivity of the instrument under the conditions of the experiment, <10% exchange could have gone undetected.

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Table II. Reactions of *cis*-L_2PtR_2 with H_2[a]

	L	R	solvent	conditions for complete reaction	products
	Me_3P	$-CH_2C(CH_3)_3$	C_6H_6	<6 h, 25 °C	$L_4Pt + Pt(O) + C(CH_3)_4$
(1)	Et_3P		C_6H_6, C_6H_{12}	<5 h, 25 °C	*trans*-$L_2PtH_2 + C(CH_3)_4$
	Ph_3P		C_6H_6	<2.5 h, 25 °C	$L_3Pt + Pt(O) + C(CH_3)_4$
	dmpe[b]			no reaction, 48 h, 140 °C	
	i-Pr_3P	$-CH_3$	C_6H_{12}	<2.5 h, 25 °C	*trans*-$L_2PtH_2 + CH_4$
	Ph_3P		C_6H_6	no reaction, 3 days, 25 °C	
	Et_3P	$-CH_2CH_3$	C_6H_{12}		
		$-CH_2Ph$			
		$-(CH_2)_2C(CH_3)_2$[c]			
(7)		-c-C_3H_5		<44 h, 100 °C	*trans*-L_2PtH_2 + c-C_3H_6

[a] Reactions were carried out in cyclohexane or benzene solutions with $[L_2PtR_2]_0 \simeq 0.03$ M, H_2 pressure = 2–4 atm. [b] dmpe = 1,2-bis(dimethylphosphino)ethane. [c] 3,3-Bis(dimethylplatina)cyclobutane.

the only soluble phosphorus-containing products.[30] This limited survey suggests that compounds containing bulky alkyl groups or bulky phosphines hydrogenolyze rapidly (<6 h) at room temperature but that compounds without bulky substituents do not react within several days at room temperature. The observation that bulky substituents speed the reaction is compatible with a mechanism involving dissociation of phosphine.[31] The low reactivity of dineopentyl(dmpe)platinum(II) is also compatible with this mechanism.[32]

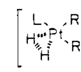
Discussion

Our evidence indicates that reaction of **1** with H_2 proceeds by the mechanism outlined in Scheme I. This mechanism parallels that observed previously for intramolecular C–H additions to platinum(II) in similar coordination environments.[8-11] The identity of the rate-limiting step in this mechanism depends on [L]. We discuss the mechanism at [L] = 0 M and in the presence of added L separately.

[L] = 0. The independence of rate on H_2 pressure, the absence of a deuterium kinetic isotope effect, and the lack of phosphine exchange in starting material recovered after partial reaction indicate that phosphine dissociation is overall rate limiting. The E_a of 29 kcal/mol is compatible with this assertion, and the log A is that expected for one particle going to two in the transition state.[26]

In the Presence of Added [L]. The inverse first-order dependence of rate on [L] establishes a reversible loss of phosphine before the rate-limiting step. It is not surprising that the creation of a vacant coordination site would increase the reactivity of platinum toward an H–H bond, since it strongly increases reactivity toward C–H bonds. The first-order dependence of the rate on H_2 pressure and the isotope effect of $k_H/k_D \simeq 1.9$ confirm that the loss of phosphine is no longer rate limiting in the presence of added L.

We cannot clearly distinguish between **2** → **3** and **3** → **4** as the rate-limiting step for [L] > 0.1 M. The transition states **8** and **9** for these steps are similar. We favor **9**, but only on the weak grounds that reductive elimination of C–H bonds seems to be slow in related systems.[8,10] A transition state such as **10**, in which cleavage of the H–H bond is concerted with cleavage of the Pt–C bond and formation of the C–H bond, also cannot be rigorously excluded by using the available data.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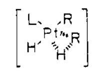
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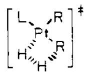
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The interest in this study lies in its demonstration that *intermolecular* reactions involving the intermediate $LPtR_2$ can be facile. Previous studies had indicated that intramolecular reactions involving unactivated C–H bonds were facile but had provided neither an example of an intermolecular reaction involving a C–H bond (i.e., hydrocarbon solvent activation) nor a clear rationale for the fact that intermolecular reactions do not seem to compete effectively with intramolecular ones. This work establishes that the intermolecular reaction of $LPtR_2$ with H_2 is facile and suggests that there is no inherent entropic barrier to intermolecular reactions with the C–H bonds of solvent. If we make the crude assumption that the E_a for solvent activation would be the same as that observed for *intra*molecular γ-C–H activation and that the log A would be the same as that for *inter*molecular H_2 activation, we estimate (clearly erroneously) that the relative rate of intermolecular C–H activation for cyclohexane should be 10 times greater than that of the intramolecular reaction (Figure 6)! The fact that this analysis predicts such a high rate for the intermolecular reaction indicates that the entropic disadvantage to intermolecular reactions attributable to the combination of two particles into one in the transition state is not solely responsible for the unobservably slow rate of solvent C–H activation. The reason why intermolecular C–H activation is slower than predicted by this crude analysis may be that the analysis neglects nonbonded steric interactions. The added strain should tend to increase E_a and to slow these reactions. Restrictions to vibrations in a sterically crowded transition state may also slow the intermolecular addition of molecules larger than H_2.

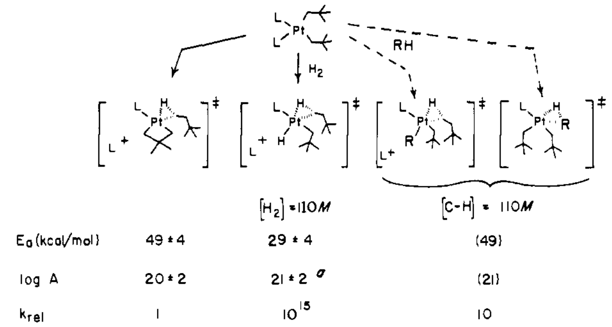

Figure 6. Comparison of kinetic parameters and an estimate of the rate of intermolecular carbon–hydrogen bond activation. In this estimate [L] = 0.1 M; $[H_2]$ and [C–H] are set to 110 M (the concentration of C–H bonds in pure cyclohexane) to facilitate comparison. The value of log A used here, marked with a superscript a, is higher than that given in Table I due to the high molarity of H_2 assumed in this analysis ($[H_2]$ is 10^4 greater).

Why do hydrocarbon solvents not react with $LPtR_2$? The facts that *intramolecular* C–H addition and *intermolecular* H–H addition both occur establish that there are not large intrinsic barriers to such reactions. The recent successful additions of alkanes to iridium and rhenium also establish that intermolecular C–H activation is not an intrinsically difficult reaction.[33] Instead, the

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[30] The platinum(II) dihydrides analogous to **5** may be unstable under the reaction conditions: the compound $(Ph_3P)_2PtH_2$ is unknown; $(Me_3P)_2PtH_2$ has only recently been characterized.[17]

[31] Tolman, C. A. *Chem. Rev.* **1977**, *77(3)*, 313–48.

[32] Additional evidence which supports phosphine loss as a prerequisite for hydrogenolysis is that compound *cis*-**7** hydrogenolyzes slowly at 100 °C. Under these conditions *cis*-**7** is known to isomerize to *trans*-**7** (presumably via phosphine dissociation). Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem.* Soc. **1981**, *103*, 3404–3410.

[33] Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352–354; *Ibid.* **1983**, *105*, 3929–39. Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *Ibid.* **1982**, *104*, 107–13. Hoyano, J. K.; Graham, W. A. G. *Ibid.* **1982**, *104*, 3723–5. Baudry, D.; Ephritikhine, M.; Felin, H. *Chem., Commun.* **1982**, 606–8.

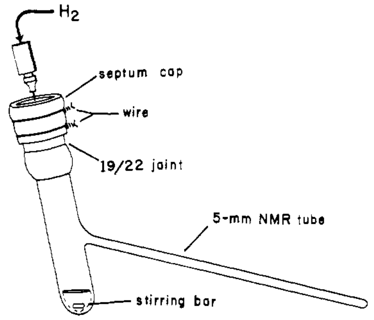

Figure 7. Reactors used for ^{31}P NMR kinetics.

best present rationalization for the apparent low reactivity of $LPtR_2$ toward unactivated C–H bonds in intermolecular reactions seems to be that other *intra*molecular reactions (cyclometallations involving C–H bonds to neopentyl and triethylphosphine moieties, reductive elimination of R–R from PtR_2 moieites, migration of alkyl groups from phosphorous to platinum) occur more rapidly.

Experimental Section

General. ^{31}P and ^{1}H NMR spectra were taken on a JEOL FX 90Q spectrometer. Mass spectra were obtained on a Hewlett-Packard 5590-A GC-MS with 70-eV ionization voltage. Olefins were removed from cyclohexane and dodecane by stirring over H_2SO_4 for 3 days. The hydrocarbons were washed with sodium bicarbonate solution and water, dried with phosphorous pentoxide, and distilled under argon. Benzene was purified by distillation from calcium hydride under argon. Dineopentylbis(triethylphosphine)platinum(II) (**1**)[10] and triethylphosphine-d_{15}[8] were prepared as described previously. H_2 (Airco Inc) and D_2 (Matheson) were used without further purification.

Kinetic studies by NMR were performed in septum-capped tubes with 5-mm NMR tubes attached (Figure 7). The reactors allowed the rate of the reaction to be measured without disturbing the system by transfer of the solution or removal of aliquots. The reactors also allowed the solution to be stirred under constant H_2 pressure between spectra. Stirring of the solution was necessary so that the rate of hydrogenolysis would not be limited by the rate of H_2 mass transport. The vessel need not spin in the spectrometer probe because the line width for ^{31}P in these samples is large enough that effects due to field inhomogeneity are negligible ($T_2 \simeq T^*_2$). On an average spectrum the line width at half height was $\nu_{1/2} \simeq 6$ Hz. The JEOL FX-90Q NMR spectrometer used in this work had an open-top electromagnet. This feature is necessary for the use of these reactors, as their size precludes their being lowered into a superconducting or closed-top electromagnet.

Cyclohexane was used as a solvent when the reaction temperature was low (<50 °C). Dodecane was used at higher temperature to avoid solvent loss (through the septum) over the course of the kinetic run. This solvent change had no effect on the rate at 50 °C. In a typical run, 15 mg of **1** and 1.0 mL of cyclohexane or dodecane (containing 0.05 M triethylphosphate as internal standard) were added to reactors under argon. The reactors were flushed with H_2 at 0 °C and then put into a temperature-controlled (±0.3 °C) water bath. The reactors were kept under a static head of H_2 at the desired pressure (±0.4 psi). The reactors were removed at intervals and cooled to 0 °C. Spectra were taken (within 10 min) on external lock with the NMR probe at 12 ± 0.2 °C (the reaction rate was considered to be zero at this temperature). The loss of starting material was followed by measuring peak heights relative to an internal standard.

Table III. ^{31}P NMR Spectra of *cis*-L_2PtR_2

L	R	δ^a	*J*, Hz	solvent
Me_3P	$-CH_2C(CH_3)_3$	−29.9	1605	C_6H_6
Et_3P		−2.1	1638	C_6H_{12}
Ph_3P		21.0	1642	C_6H_6
dmpe		19.5	1533	
Ph_3P	$-CH_3$	27.8	1878	
$(i\text{-}Pr)_3P$		32	1833	C_6H_{12}
Et_3P	$-CH_2CH_3$	9.0	1674	
	$-CH_2Ph$	7.3	1902	
	$-(CH_2)_2C(CH_3)_2$	9.6	1860	
	$-c\text{-}C_3H_5$	8.0	1790	

[a] Relative to 85% phosphoric acid (downfield shifts positive).

Phosphine Exchange Experiment. L_2PtR_2 (13 mg) and $L^D{}_2PtR_2$ (13 mg) (R = $CH_2C(CH_3)_3$) and 0.75 mL of cyclohexane-d_{12} (a deuterated solvent used as internal lock for the spectrometer) were added to a reactor and hydrogenolyzed (31 psi of H_2, 32 °C, ~40 min) to ~50% completion. The solution was transferred by cannula into an NMR tube. The ^{31}P NMR spectrum showed only L_2PtR_2 and $L^D{}_2PtR_2$. No LL^DPtR_2 could be detected.[27] LL^DPtR_2 can be observed by equilibration of L_2PtR_2 and $L^D{}_2PtR_2$ as a doublet ($\delta = -1.1$, $J_{PP} = 8$ Hz).

Stability of 2 in Solution. To each of two reactors (similar to those in Figure 6, but having high vacuum Teflon stopcocks rather than septa) were added 15 mg of **1** and 1.0 mL of cyclohexane (with 0.05 M triethylphosphate as internal NMR standard). Each was hydrogenolyzed to completion. One was purged with, and left under, 25 psi of argon. The other was left under 25 psi of H_2. Both were heated for 24 h at 42 °C and then left for over 2 months at room temperature. ^{31}P NMR spectra taken throughout this time showed that little or no decomposition had taken place in either reactor.

Preparation of L_2PtR_2. The compound $(PEt_3)_2Pt(CH_2)_2C(CH_3)_2$ was prepared by thermolysis of **1** in cyclohexane.[10] All other compounds in Table II were prepared by the reaction of dichloro(1,5-cyclooctadiene)platinum(II) with the corresponding Grignard reagent (RMgX: X = Br, Cl) followed by displacement of the 1,5-cyclooctadiene with the desired phosphine to give *cis*-L_2PtR_2. This procedure is described in detail elsewhere.[8,10,32] The L_2PtR_2 compounds were recrystallized from ether/methanol at −78 °C. Their ^{31}P NMR spectra are summarized in Table III.

Reaction of H_2 with L_2PtR_2. Reactions were run in pressure tubes with crown cap and septa (Lab Glass Inc.) or in the reactors shown in Figure 7. A magnetic stirring bar and the platinum compound were added to the tube, which was sealed, evacuated, and refilled with argon (three times); 1–2 mL of cyclohexane or benzene was transferred into the tube by cannula under argon ($[L_2PtR_2] \simeq 0.03$ M). The tube was flushed with H_2 and pressurized to 2–4 atm. The reactions were followed by ^{31}P NMR spectroscopy and gas chromatography.

Registry No. 1, 75110-84-8; **7**, 77965-24-3; *cis*-$(Me_3P)_2Pt(CH_2C(CH_3)_3)_2$, 87681-52-5; *cis*-$(Ph_3P)_2Pt(CH_2C(CH_3)_3)_2$, 87681-53-6; *cis*-$(dmpe)Pt(CH_2C(CH_3)_3)_2$, 87681-54-7; *cis*-$(i\text{-}Pr_3P)_2Pt(CH_3)_2$, 87681-55-8; *cis*-$(Ph_3P)_2Pt(CH_3)_2$, 17567-35-0; *cis*-$(Et_3P)_2Pt(CH_2CH_3)_2$, 75847-39-1; *cis*-$(Et_3P)_2Pt(CH_2Ph)_2$, 42167-76-0; *cis*-$(Et_3P)_2Pt((CH_2)_2C(CH_3)_2)_2$, 70620-74-5.