

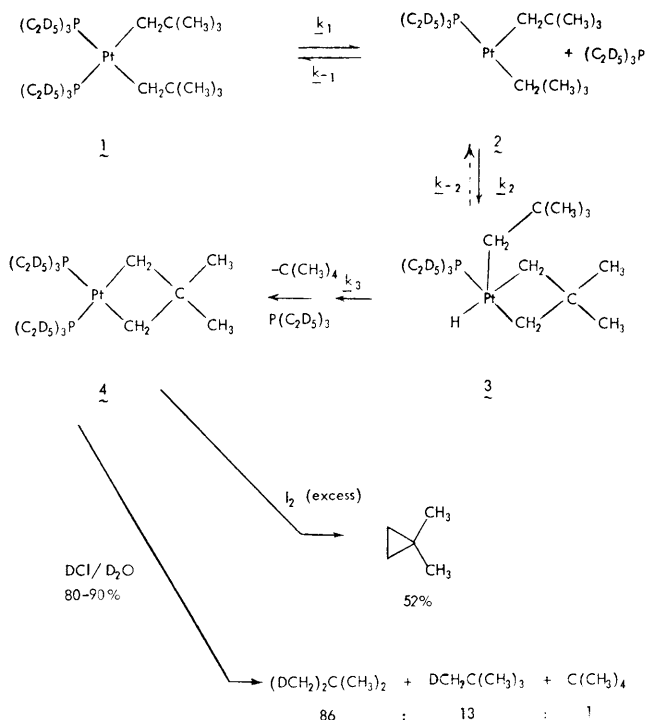
Thermal Generation of Bis(triethylphosphine)-3,3-dimethylplatinacyclobutane from Dineopentylbis(triethylphosphine)platinum(II)¹

Sir:

Reactions which cleave unactivated aliphatic carbon-hydrogen bonds are important in a range of heterogeneous platinum-catalyzed transformations of hydrocarbons, and a mechanistic understanding of these types of reactions is one objective of current research in catalysis.² The mechanisms of heterogeneous reactions are difficult to examine directly. Here we outline the mechanism of a tractable and well-defined solution reaction—the conversion of dineopentylbis(triethylphosphine)platinum(II) (**1**) to bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (**4**)—which involves cleavage of an unactivated C-H bond by intramolecular oxidative addition to a soluble platinum species. This mechanism establishes certain of the structural features which facilitate C-H bond activation in solution and suggests, by analogy, possible characteristics of the heterogeneous reactions.

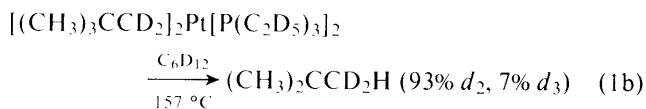
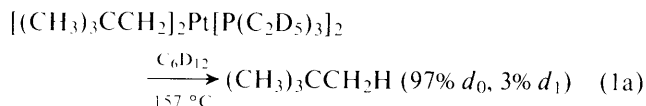
Heating a solution of **1** (0.08 M, 157 °C, 2.25 h, 0.02 M Et₃P)³ in cyclohexane results in the disappearance of **1** and the appearance of 1 equiv of neopentane, 0.8 equiv of **4**, and 0.1 equiv of 2,2,5,5-tetramethylhexane. The solution remains homogeneous throughout the decomposition. Compound **4** was

Scheme I. Mechanism of Conversion of **1** into **4**. No Stereochemistry Is Implied by **3**



isolated as a light yellow oil by removing cyclohexane and titrating with acetonitrile to remove unreacted **1**. **4** showed the following: ¹H NMR (C₆D₆) δ 0.73 (t of t, 4 H, 1:4:1, J_{Pt-H} = 74, J = 12 Hz, Pt-CH₂), 1.57 (t, 6 H, J = 3 Hz, C(CH₃)₃); ³¹P (C₆H₁₂, H₃PO₄ external reference) δ +9 ppm (t, 1:4:1, J_{Pt-P} = 1862 ± 8 Hz). Treatment of **4** with aqueous 38% DCl in D₂O yielded a mixture of deuterated neopentanes.⁴ Examination of the cracking pattern of this neopentane indicated that the deuterium was present in CH₂D rather than CHD₂ groups and is consistent with activation of a γ C-H bond and not an α C-H bond.⁵ Treatment of **4** with excess iodine generated 1,1-dimethylcyclopropane. The dimethylcyclopropane derived from thermolysis of [(CH₃)₃CCD₂]₂Pt(PEt₃)₂ followed by treatment with I₂ was *d*₂.

The origin of the hydrogen atom consumed in conversion of a neopentyl group of **1** to neopentane was established as a methyl group of a second neopentyl group by deuterium labeling experiments:



The decomposition of [(CH₃)₃CCH₂]₂Pt[P(C₂D₅)₃]₂ in solutions of C₆D₁₂ containing added P(C₂D₅)₃ (0.02–0.3 M) was followed by NMR spectroscopy. These decompositions obeyed the empirical rate equation

$$d[\mathbf{1}]/dt = k_{\text{obsd}}[\mathbf{1}][\text{P}(\text{C}_2\text{D}_5)_3]^{-1} \quad (2)$$

The observed rate equation is compatible with the formal rate expression

$$d[\mathbf{1}]/dt = k_1 k_2 [\mathbf{1}] / (k_2 + k_{-1} [\text{P}(\text{C}_2\text{D}_5)_3]) \quad (3)$$

derived for a pre-equilibrium dissociation of phosphine followed by rate-limiting C-H addition, and with an analogous expression for a scheme in which C-H reductive elimination (*k*₃) is rate limiting (Scheme I). Analysis of the temperature dependence for decomposition of **1** over the range 118–157 °C yielded these values for the Arrhenius activation parameters: *E*_a = 49 ± 4 kcal mol⁻¹, *A* = 10^{20±2} s⁻¹. The exchange of (CH₃CH₂)₃P into [(CD₃CD₂)₃P]₂Pt[CH₂C(CH₃)₃]₂ was followed by ³¹P NMR spectroscopy. This exchange was complete at 100 °C in 1.0 h with no detectable decomposition of **1**. The rate of this exchange was independent of added Et₃P concentration from 0.1 to 1.7 M and indicated that exchange occurred by an S_N1 process. This observation is consistent with the pre-equilibrium dissociation of Et₃P implied in Scheme I.⁶

The solubility of **1** in solutions of cyclohexane containing triethylphosphine established that the decrease in rate of decomposition of **1** observed on adding triethylphosphine could

not be rationalized by assuming an associative equilibrium forming $[(\text{CH}_3)_3\text{CCH}_2]_2\text{Pt}(\text{PEt}_3)_3$: a quantity of triethylphosphine which decreased the rate of decomposition of **1** by a factor of 15 increased its solubility by only 16%.⁷ Examination of the ³¹P NMR spectrum of **1** in the presence of triethylphosphine also showed no evidence of formation of a species containing three triethylphosphine moieties under conditions (0.08 M **1**, 0.3 M Et₃P,) in which 93% of **1** would have necessarily been converted into such a species to rationalize the observed decrease in k_{obsd} .

The observation of a significant kinetic isotope effect in the decomposition of **1** indicates that C–H bond breaking or bond forming occurs in or before the rate-limiting step. The rates of decomposition of **1**-*d*₀ and $[(\text{CD}_3)_3\text{CCD}_2]_2\text{Pt}[\text{P}(\text{C}_2\text{D}_5)_3]_2$ (**5**) were determined by comparing the yields of neopentane as a function of time. After correction for isotopic impurities, analysis of these data yielded $k_1/k_5 = k_{11}/k_{1D} = 3.0\text{--}3.5$.

The most important conclusion from this work is that the cleavage of an unactivated C–H bond which takes place during the conversion of **1** into **4** proceeds by an oxidative addition to the platinum atom of a reactive (trialkylphosphine)dialkylplatinum(II) moiety. We are currently studying a number of other examples of related, unactivated C–H bond cleavage reactions involving additions to platinum:⁸ most appear to involve a LPtR₂ moiety as the reactive intermediate, and thus to require a vacant coordination site on (formally) three-coordinate platinum(II). The available evidence is not sufficient to distinguish between oxidative addition of a C–H bond to platinum(II) (k_2) or reductive elimination of a C–H bond from platinum(IV) (k_3) as the overall rate-limiting step.⁹

Activation of C–H bonds by surface atoms of platinum metal occurs readily.¹⁰ We note that a prominent feature of a metal surface is the availability of vacant coordination sites and suggest that explicit comparisons of the reactivity of vacant sites on soluble complexes and on metal surfaces should be one of the most useful and direct methods of establishing parallels between homogeneous and heterogeneous catalysts. The activation energy determined for the transformation **1** → **4** described here ($E_a \approx 49 \text{ kcal mol}^{-1}$) cannot be directly compared with the lower values ($E_a \approx 10 \text{ kcal mol}^{-1}$) characterizing C–H bond cleavage during surface reactions,¹⁰ since the former is composed of contributions from the energy of dissociation of a phosphine ligand, the energy (or the energy of

activation) of addition of the C–H bond to platinum, the strain energy involved in forming the platina-cyclobutane ring, and (possibly) the energy of activation for reductive elimination of neopentane from **3**. Studies of other C–H oxidative additions to platinum and of systems designed to provide comparable thermodynamic parameters for homogeneous and heterogeneous activation of C–H bonds by platinum will be reported as they are completed.

References and Notes

- (1) Supported by the National Science Foundation (MPS 74-20956 and 7711282CHE).
- (2) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113–117. Clarke, J. K. A.; Rooney, J. J. *Adv. Catal.* **1976**, *25*, 125–183. Shilov, A. E.; Shteynman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97–143.
- (3) Compound **1** was prepared by reaction of 1,5-cyclooctadienedichloroplatinum(II) with neopentylmagnesium bromide, followed by treatment with triethylphosphine. See Young, G. B.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 5808–5815, for similar procedures.
- (4) All isotopic analyses were obtained using a Hewlett-Packard Model 5990 A GC/MS. The accuracy of these determinations varied with the sample, but should be considered to be precise to $\pm 2\%$ for neopentane. For example, treatment of **1** with aqueous DCl yields neopentane (99% *d*₁, 1% *d*₀). The 13% *d*₁ neopentane obtained on reaction of **4** with DCl is well outside experimental error and seems to represent a real (if presently unexplained) side reaction.
- (5) Schrock, R. R. *Acc. Chem. Res.*, in press.
- (6) In principle, a plot of $(k_{\text{obsd}})^{-1}$ vs. $[\text{P}(\text{C}_2\text{D}_5)_3]$ can be used to estimate values of k_1 and k_{-1}/k_2 . In practice, the uncertainty in these rate constants is so large that they are of only qualitative significance.
- (7) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258–5270, discuss the use of solubilities to differentiate between associative and dissociate equilibria.
- (8) For other examples of intramolecular C–H oxidative additions, cf. ref 2 and references cited in the following. Goel, R. G.; Montemayor, R. G. *Inorg. Chem.* **1977**, *16*, 2188–2196. Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147–188. Anderson, R. A.; Jones, R. A.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Chem. Commun.* **1977**, 283–285. Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1978**, *152*, 347–357.
- (9) The neopentyl methyl and methylene groups of $(\text{Et}_3\text{P})_2\text{Pt}[\text{CD}_2\text{C}(\text{CH}_3)_3]_2$ do not interchange. This observation does not guarantee the irreversibility of the step **2** → **3**, since we do not know that the methylene groups of **3** are equivalent.
- (10) Biloen, P.; Dautzenberg, F. M.; Sachtler, W. M. H. *J. Catal.* **1977**, *50*, 77–86. Gault, F. G.; Rooney, J. J.; Kamball, C. *ibid.* **1962**, *1*, 255–274. Karpinski, Z.; Guzzi, L. *J. Chem. Soc., Chem. Commun.* **1977**, 563–564.

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