

Apparent Fluxionality in Diethyl(triethylphosphine)platinum(II), a Coordinatively Unsaturated Intermediate in β -Hydride Elimination¹

Thomas J. McCarthy,² Ralph G. Nuzzo,³ and George M. Whitesides*⁴

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received August 15, 1980

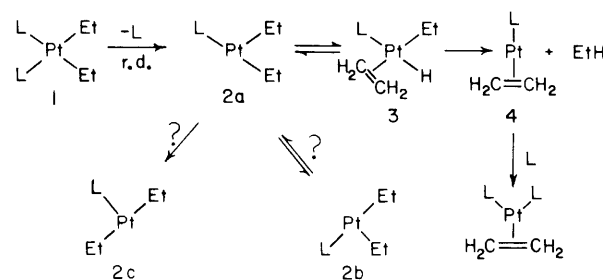
Abstract: The thermal decomposition of $(\text{Et}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_5)_2$ proceeds by rate-limiting dissociation of triethylphosphine, followed by β -hydride elimination from a PtC_2H_5 group (Scheme I, $2 \rightarrow 3$). Isotopic labeling and kinetics indicate that the two platinum-bound ethyl groups of the coordinatively unsaturated intermediate diethyl(triethylphosphine)platinum(II) lose hydrogen with approximately equal probability (Scheme I). Thus, either side-to-side motion of the triethylphosphine ligand within a "T"-shaped complex ($2a \rightleftharpoons 2b$, Scheme I) is fast relative to reductive elimination of ethane from 3 or some other process or geometry renders the ethyl groups roughly equivalent on this time scale.

The mechanism of thermal decomposition of diethylbis(triethylphosphine)platinum(II) (1) in cyclohexane solution is summarized in Scheme I.⁴ In the absence of added L, the initial loss of L ($1 \rightarrow 2$) is rate limiting. The coordinatively unsaturated, 14-electron species 2 appears to be highly reactive: the conversion $2 \rightarrow 3$ is faster than either $1 \rightarrow 2$ or $3 \rightarrow 4$.⁴ Species having the composition LMR_2 are important intermediates in other β -hydride eliminations involving platinum^{5,6} and nickel⁷ and in reactions in which unactivated γ , δ , and ϵ C-H bonds add oxidatively to platinum(II).^{8,9} Although there is no experimental information concerning the geometry of 2 , the related species $(\text{Ph}_3\text{P})_3\text{Rh}(\text{I})^+\text{ClO}_4^-$ is "T" shaped,¹⁰ and *cis*-(CH_3)₂Au(H_2O)Tf is square planar.¹¹ This paper provides evidence that the two ethyl groups bonded to platinum in the three-coordinate species 2 are equivalent in β -hydride elimination. This equivalence might reflect movements of triethylphosphine ($2a \rightleftharpoons 2b$) or ethyl groups ($2a \rightarrow 2c$) which are rapid relative to the subsequent conversion of 3 to 4 , a "Y"-shaped geometry for 2 , or other processes (outlined below). In what follows, we will discuss the interpretation of experimental results in terms of only one of these several possibilities: viz., "T"-shaped intermediates which equilibrate by a rapid, side-to-side "windshield wiper" movement of the remaining triethylphosphine ligand ($2a \rightleftharpoons 2b$). Analogous arguments apply to other structures in which the ethyl groups are effectively equivalent.

Results

The deuterated complex 5 was synthesized by using conventional techniques and decomposed in cyclohexane solution at 118 °C for 1 h (Scheme II). Under these conditions, dissociation of L is rate limiting, and no isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.0 \pm 0.1$) is observed on comparison of the rates of decomposition of L_2Pt -

Scheme I. Mechanism of Thermal Decomposition of L_2PtEt_2 in Cyclohexane Solution^a



^a L = Et_3P .⁴ No stereochemistry is implied by 3 .

(CH_2CH_3)₂ and $\text{L}_2\text{Pt}(\text{CD}_2\text{CD}_3)_2$.⁴ Since 6 is formed irreversibly, if $6a$ and $6b$ are *not* in equilibrium, the isotopic composition of the ethane and ethylene produced should be determined by phosphine dissociation. Any isotope effect on this dissociation would be reflected in an isotope effect on the relative rates of decomposition of $\text{L}_2\text{Pt}(\text{C}_2\text{H}_5)_2$ and $\text{L}_2\text{Pt}(\text{C}_2\text{D}_5)_2$: since no isotope effect is, in fact, observed, we infer that $6a$ and $6b$ are generated from 5 at indistinguishable rates.

To establish whether the hydrocarbons obtained from 5 are derived from ethyl- d_5 or ethyl- d_0 groups, it is necessary to measure their isotopic compositions: we have used gas chromatography/mass spectroscopy (GC/MS). The analysis of isotopic compositions of hydrocarbons by GC/MS is not entirely straightforward: isotope effects on ionization cross sections and fragmentations, isotopic fractionation in the GC column or the separator, nonlinear response of the ion detector, and other experimental artifacts can all contribute significant errors.⁴ Here we have relied on a comparison which minimizes the importance of most of these effects: in parallel experiments, a sample of 5 and a separate sample containing a 1:1 mixture of $\text{L}_2\text{Pt}(\text{C}_2\text{H}_5)_2$ and $\text{L}_2\text{Pt}(\text{C}_2\text{D}_5)_2$ were treated with HCl. These experiments both test the isotopic purity of 5 and demonstrate that there is not a significant isotope effect on fragmentation of the parent ions. These data are needed to determine accurately the selectivity for C-H bond activation. Figure 1 shows the relative isotopic compositions inferred from GC/MS for ethane and ethylene produced by proteolysis of 5 and those obtained by proteolysis of a 1:1 mixture of $\text{L}_2\text{Pt}(\text{C}_2\text{H}_5)_2$ and $\text{L}_2\text{Pt}(\text{C}_2\text{D}_5)_2$. Inspection of the mass spectrum of the ethane and ethylene generated in the decomposition of 5 shows an experimentally significant preference for hydrogen transfer and formation of HC_2D_5 , relative to deuterium transfer and formation of DC_2H_5 . (We estimate $k_{\text{H}}/k_{\text{D}} = 2.3$ for formation of ethane). We infer from the observation of isotopic discrimination in decomposition of 5 that *both* ethyl groups can

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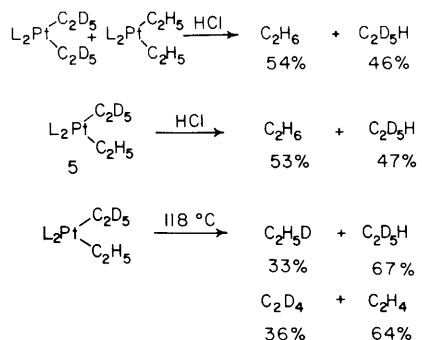
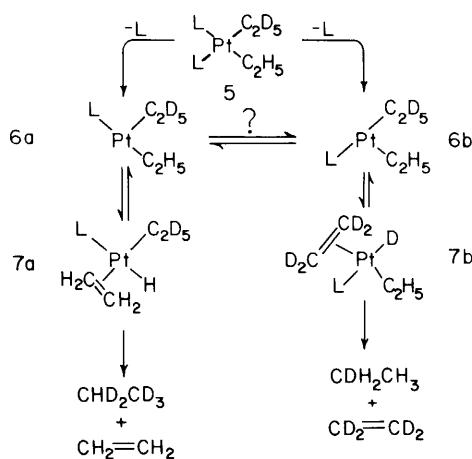


Figure 1. Relative amounts of ethanes generated by proteolysis of a 1:1 mixture of $L_2Pt(C_2D_5)_2$ and $L_2Pt(C_2H_5)_2$ (upper) and **5** (middle); relative amounts of ethanes and ethylenes generated by thermal decomposition of **5** (0.05 M, cyclohexane, 118 °C, 1 h) (lower). The percentages are based on the relative intensities of molecular ions. Corrections were made for the contribution of fragment ions to the observed molecular ion intensities of the lower molecular weight products.

Scheme II. Thermal Decomposition of $L_2Pt(C_2D_5)(C_2H_5)$



take part in β -hydride elimination. This observation seems incompatible with *nonequilibrating* structures **6a** and **6b**.

An independent verification of the conclusion that the ethyl groups in **2** are equivalent comes from examination of the mass spectrum of the ethane- d_n mixture produced by thermal decomposition of **8**, $L_2Pt(CH_2CD_3)_2$ (Scheme III). If the three-coordinate intermediates (**9**, **11**, ...) are stereochemically rigid and the ethyl groups are nonequivalent, the ethyl- d_3 group cis to the vacant coordination site will eventually transfer a hydrogen or deuterium to an *unscrambled* CH_2CD_3 group *trans* to the vacant coordination site: any sequence of this type can generate only two deuterium substitution patterns in the ethane: HCH_2CD_3 or DCH_2CD_3 . If, however, interconversion of three-coordinate species (e.g., **11** \rightleftharpoons **13**) is facile, then it is possible to transfer hydrogen to a *scrambled* ethyl group and produce HCD_2CH_2D and HCD_2CD_2H . Only one methyl substitution pattern is unique to paths requiring an interconversion of this type: viz., HCD_2 , from decomposition of a species such as **16** or **19**.

Figure 2 shows the region of the mass spectrum of ethane corresponding to methyl cation for a sample obtained by thermal decomposition of **8**. Reference spectra of a number of deuterated ethanes are included.¹² The peak at m/e 17 is clearly diagnostic of a CHD_2 group present in a mixture of deuterated ethanes. This peak is abundant in the spectrum of ethane derived from **8** and confirms that interconversions of the type **11** \rightleftharpoons **13** and **17** \rightleftharpoons **18** occur readily in this system. The quality of the analysis is not such that it justifies an effort to estimate the rate of this interconversion relative to the final reductive step, but the observed

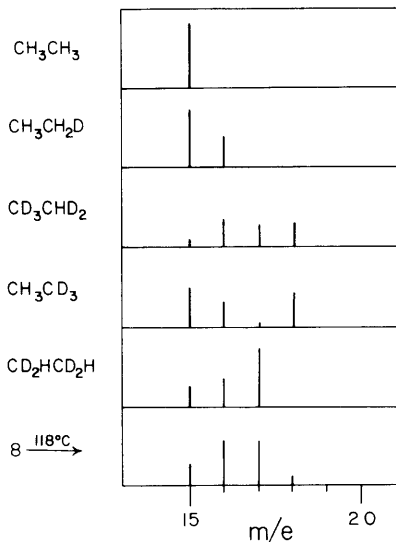
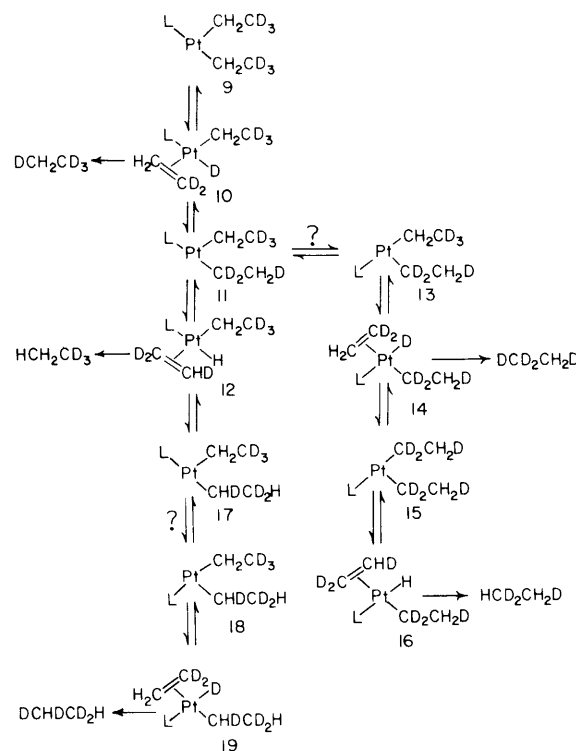


Figure 2. Mass spectra (70 eV, corrected for background) of the methyl cation region of authentic deuterated ethanes, and ethane from thermal decomposition of **8** (0.05 M, cyclohexane, 118 °C, 1 h). The spectrum of CD_2HCD_2H is taken from ref 12.

Scheme III. Thermal Decomposition of $L_2Pt(CH_2CD_3)_2$ (**8**)



distribution of ions is close to that which would be expected for a statistical distribution.¹³

Discussion

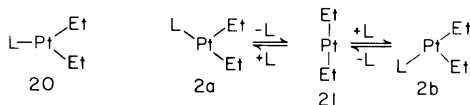
These studies establish that the two ethyl groups of $LPtEt_2$ are equivalent with respect to the combination of β -hydride elimination and reductive elimination which generates ethane and ethylene

(13) If there were no isotopic discrimination in selection of hydrogen or deuterium in forming ethane (i.e., if $C_2D_3H_3$ and $C_2D_4H_2$ were formed in equal amounts), if these atoms were distributed randomly between the two carbons, and if there were no isotope effects in fragmentation, the expected distribution of methyl cations would be as follows: CH_3 , 6%; CDH_2 , 31%; CD_2H , 44%; CD_3 , 19%. This distribution is not very sensitive to an isotope effect in the ethane-forming step: for $k_H/k_D = 2.3$, these numbers become 9%, 35%, 43%, and 13%. For comparison, the distribution of ions estimated from the mass spectrum of **8** is 19%, 36%, 36%, and 9%.

(12) Amenomiya, Y.; Pottie, R. F. *Can. J. Chem.* **1968**, *46*, 1735-1739.

on thermal decomposition of L_2PtEt_2 . That is, within the accuracy of our experiments, it is equally probable that either ethyl group of L_2PtEt_2 will be converted to ethane (or ethylene), regardless of its position in L_2PtEt_2 relative to the triethylphosphine group whose dissociation constitutes the rate-limiting step. This conclusion is also supported by independent data concerning product yields from decompositions of L_2PtRR' .¹⁴

There are several alternatives to a side-to-side movement of triethylphosphine within a "T"-shaped complex which would also render the ethyl groups equivalent: a "Y"-shaped ground-state geometry (**20**), dissociation-recombination of triethylphosphine



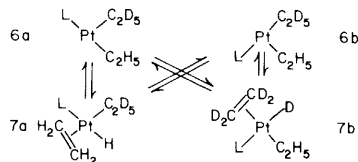
(**2** ⇌ **21** with no stereochemistry implied in the latter), and more complex movements of alkyl groups (**2a** ⇌ **2c** ⇌ **2b**).¹⁵ Thorn and Hoffmann¹⁶ have calculated that the barriers for processes analogous to **2a** ⇌ **2b** and **2a** ⇌ **2c** for $H_2Pt(PH_3)_2^+$ and Me_3Au are ~3 kcal/mol; our experiments are compatible with extension of this theoretical prediction to the related neutral system L_2PtEt_2 .^{17,18}

(14) Komiya, S.; Yamamoto, A.; Yamamoto, T. *Chem. Lett.* **1978**, 1273-1276. These workers report that unsymmetrical dialkylbis(triethylphosphine)platinum(II) compounds (L_2PtRR') produce RH and R'H in a ratio which correlates with the numbers of β -hydrogens in the alkyl groups.

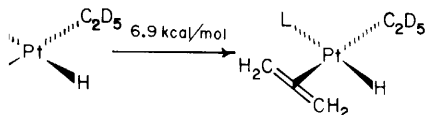
(15) Equilibration of *cis*-dicyclopropylbis(triethylphosphine)platinum(II) to a 28:72 mixture of *cis* and *trans* isomers occurs in 1 h at 139 °C.⁶ Although we have not observed conversion of the *cis* to the *trans* isomer of **1** or related compounds, we cannot exclude this reaction as one lying along the main path to decomposition or as a parasitic equilibrium: the *trans* isomer of **1** has not been prepared and its reactivity is unknown.

(16) Thorn, D. L.; Hoffman, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079-2090. See also: Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *Ibid.* **1976**, *98*, 7255-7265.

(17) It is in principle conceivable that **6a** and **6b** interconvert via **7a** and



7b. Microscopic reversibility mandates that all of these processes be competitive if this mechanism is followed, and **6a** → **7b** (**6b** → **7a**) seems improbable, a priori. Moreover, Thorn and Hoffmann¹⁶ calculate that twisting ethylene from perpendicular to the square-planar plane requires 6.9 kcal/mol. This route is predicted theoretically to be much less favorable than **6a** → **6b**.



Experimental Section

General Procedures. General techniques were those described previously.^{4,6,7} Syntheses of $[(H_5C_2)_3P]_2Pt(CD_2CD_3)_2$ and $[(H_5C_2)_3P]_2Pt(C-H_2CD_3)_2$ have been reported.⁴ Mass spectra were obtained with the use of a Hewlett-Packard Model 5990A GC/MS, both with and without background subtraction; results were indistinguishable. So that the effects of isotopic fractionation could be minimized, each GLC peak was scanned repeatedly as it emerged: the spectra reported represent the weighted averages of ca. 50 spectra.

$[(H_5C_2)_3P]_2Pt(C_2D_5)(C_2H_5)$. Di(ethyl-*d*₃)bis(triethylphosphine)platinum(II) (400 mg, 0.84 mmol) was dissolved in 15 mL of 1:1 v/v methanol-ether and cooled to -20 °C. Acetyl chloride (59 μ L, 0.84 mmol) was added in one portion. After 30 min the solvent was removed at reduced pressure and the crystalline residue recrystallized from methanol-ether at -78 °C to yield 400 mg (95%) of chloro(ethyl-*d*₃)bis(triethylphosphine)platinum(II), mp 53-54 °C, showing only one spot on TLC. This complex (200 mg, 0.4 mmol) was dissolved in ether and cooled to -78 °C where 1.3 mL of 0.38 M ethyllithium (0.5 mmol) was added. The mixture was warmed to -20 °C and stirred for 1 h. Addition of wet methanol (1 mL) at -78 °C, warming to room temperature, filtration through a small portion of alumina, and removal of solvent yielded a slightly yellow oil that gave crystals of ethyl(ethyl-*d*₃)bis(triethylphosphine)platinum(II) (171 mg, 86%, mp 27-29 °C; for L_2PtEt_2 mp 35.5-36.0 °C⁴) from methanol-ether at -78 °C. The assumption that an exchange forming $L_2Pt(C_2H_5)_2$ and $L_2Pt(C_2D_5)_2$ does not occur is based on the facts that a mixture of $L_2Pt(C_2H_5)_2$ and $L_2Pt(C_2D_5)_2$ do not undergo a similar exchange at 157 °C⁴ and that unsymmetrical complexes of this type have been prepared.¹⁴

Thermal decompositions were carried out with the use of ca. 10-mg samples of platinum complexes dissolved in 0.4 mL of cyclohexane. The samples were sealed under vacuum in glass tubes and heated at 118 °C for 1 h. Tubes were opened inside collapsed, argon-flushed 2-mL pipet bulbs to prevent loss of gases. Samples for GC/MS analysis were taken from the gas above the samples. Ethylene samples were taken after adding triethylphosphine to the solution to release ethylene from ethylenebis(triethylphosphine)platinum(0).

Proteolysis. Release of ethane from diethylplatinum(II) moieties was accomplished by adding 50 μ L of concentrated HCl to ca. 3 mg of organoplatinum complex in 0.2 mL of cyclohexane at room temperature. Reaction appears to be complete on mixing. Samples of ethane were taken from the gas above the solution as described above.

Acknowledgment. We thank Mr. Robert DiCosimo for his assistance in obtaining GC/MS data.

(18) These calculated barriers predict very rapid interconversion of **2a**, **2b**, and **2c** ($k \approx 10^{11} s^{-1}$ at 100 °C, assuming a normal Arrhenius $A \approx 10^{13} s^{-1}$). We have no independent measure of these rates other than they are faster than reductive elimination of ethane. The mechanistically related reductive elimination of methane from *cis*-(Ph_3P)₂PtHCH₃ proceeds with a first-order rate constant of $k = 4.5 \times 10^{-4} s^{-1}$ at -25 °C (assuming $\log A = 16$, $k(100 \text{ °C}) = 1.4 \times 10^3 s^{-1}$): Abis, L.; Sen A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915-2916.